Scuola di Scienze Matematiche, Fisiche e Naturali



Ph.D THESIS

# "Functional oxides for optoelectronics"

CHEMICAL SCIENCES AND TECHNOLOGIES, XXXV cycle

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"Anyone who has never made a mistake has never tried anything new" Albert Einstein

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# Abstract

Nowadays, global warming is among the most urgent challenges that we have to meet. Decrease the energy consumption and enhance the amount of energy produced trough renewable sources rather than fossil fuels are imperative actions to deal with climate change.

Since lighting is responsible of about 20 % of the total energy consumption and since photovoltaics is among the renewable energy source that grew more in the last decades, optoelectronics is a central field in such a challenge. Many of the crucial improvements that have been reached in the last decades in this field were made possible thanks to the development and optimization of the materials involved.

In this study, oxides were investigated at the nanoscale and in the form of thin films as valuable solutions to current issues in modern optoelectronics. In particular, CsPbBr<sub>3</sub> nanocrystals are interesting materials for light emission applications, but they suffer from poor stability against moisture, polar solvents etc. As a consequence, the reaction between maleic anhydride and the oleylamine capping ligand was exploited to encapsulate CsPbBr<sub>3</sub> nanocrystals in SiO<sub>2</sub> shells (CsPbBr<sub>3</sub>@SiO<sub>2</sub>). Maleic anhydride converted the starting Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals into CsPbBr<sub>3</sub> ones, and the addition of silica precursor promoted the shell growth. Further experiments revealed the crucial role played by Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals as a starting material and of the reaction environment in order to successfully grow CsPbBr<sub>3</sub>@SiO<sub>2</sub>. This study paves the way for the exploitation of the reactivity of surface capping ligands for the encapsulation of nanocrystals, and potentially also for ligand exchange or stripping, a new chemistry route for more stable nanomaterials.

Functional oxides were also investigated in the form of thin films for solar cell applications. Cu(In,Ga)Se<sub>2</sub> and Sb<sub>2</sub>Se<sub>3</sub> are emerging photovoltaic technologies whose market availability is limited by the presence of a toxic CdS buffer layer.  $Zn_{(1-x)}Mg_xO$  was identified as a potential alternative oxide for the deposition of buffer layers for Cu(In,Ga)Se<sub>2</sub> solar cells, whereas titania was investigated for cells based on Sb<sub>2</sub>Se<sub>3</sub>. In view of their application as buffer layers in Cu(In,Ga)Se<sub>2</sub> solar cells, Zn<sub>(1-x)</sub>Mg<sub>x</sub>O thin films were grown trough chemical bath deposition onto soda lime glass, in order to optimize the extent of Mg incorporation and the morphology of the film, the role of the complexing agent citric acid together with the nominal Mg amount was investigated.

Likewise, titania thin films were prepared trough spin coating onto fluorine-doped thin oxide substrates. Several attempts were devoted to control and measure the n-type doping of the titania layers trough an acidic treatment with the final goal of improving the solar

cell performance. Lastly, thermodynamic calculations allowed a stability comparison among  $Ti_xO_y$  species.

# **Abstract (Italian version)**

Il riscaldamento globale è tra le problematiche più urgenti che dobbiamo affrontare. Diminuire il consumo energetico e incrementare l'energia prodotta da fonti rinnovabili piuttosto che dai combustibili fossili sono azioni fondamentali per affrontare il cambiamento climatico.

Dato che l'illuminazione è responsabile del 20% del consumo totale di energia e che il fotovoltaico è tra le fonti di energia rinnovabile che è cresciuta di più negli ultimi decenni, l'optoelettronica riveste un ruolo centrale in questa sfida. Molti degli impressionanti miglioramenti raggiunti negli ultimi decenni in questo campo sono stati resi possibili dallo sviluppo e dall'ottimizzazione dei materiali impiegati.

Film sottili e nanostrutture di ossidi sono stati studiati in questo lavoro come una possibile soluzione a problematiche nel settore dell'optoelettronica. In particolare, nanocristalli di CsPbBr<sub>3</sub> sono di largo interesse come emettitori di luce, ma risultano poco stabili quando esposti a umidità, solventi polari, ecc. Di conseguenza, nanocristalli di CsPbBr<sub>3</sub> sono stati incapsulati in un guscio di silica (CsPbBr<sub>3</sub>@SiO<sub>2</sub>) sfruttando una reazione tra l'anidride maleica e il legante oleilammina sulla superficie del CsPbBr<sub>3</sub>. In particolare, nanocristalli di Cs<sub>4</sub>PbBr<sub>6</sub> vengono convertiti dall'anidride maleica in nanocristalli di CsPbBr<sub>3</sub> e l'aggiunta di un precursore della silica permette l'incapsulamento. Ulteriori esperimenti hanno rivelato il ruolo cruciale dei nanocristalli di Cs<sub>4</sub>PbBr<sub>6</sub> e dell'ambiente di reazione ottenuto dopo la loro conversione per garantire la formazione di CsPbBr<sub>3</sub>@SiO<sub>2</sub>. Questo lavoro apre la strada allo studio della reattività dei leganti superficiali per l'incapsulazione dei liganti, una nuova chimica per nanomateriali più stabili.

Gli ossidi funzionali sono stati investigati anche in forma di film sottili per applicazioni fotovoltaiche. In dettaglio, la commercializzazione di celle solari a base di materiali emergenti come Cu(In,Ga)Se<sub>2</sub> e Sb<sub>2</sub>Se<sub>3</sub> contengono un buffer layer a base di CdS, un composto altamente tossico che ostacola la loro commercializzazione. Zn<sub>(1-x)</sub>Mg<sub>x</sub>O è stato identificato come un potenziale materiale alternativo per celle solari a base di Cu(In,Ga)Se<sub>2</sub> mentre la titania per Sb<sub>2</sub>Se<sub>3</sub>. Film sottili di Zn<sub>(1-x)</sub>Mg<sub>x</sub>O sono stati preparati mediante deposizione da bagno chimico su substrati di vetro. E' stato studiato il ruolo dell'etanolammina e dell'acido citrico insieme al contenuto di Mg sulle proprietà del film con lo scopo di impiegare questi film come buffer layer in celle solari al Cu(In,Ga)Se<sub>2</sub>

anche mediate calcoli degli equilibri in soluzione per comprendere il meccanismo di formazione del film.

Analogamente, film sottili di titania sono stati preparati mediante spin coating su ossido di stagno drogato fluoro. Un trattamento acido è stato investigato per controllare il drogaggio nel film sottile di titania al fine di ottimizzare le performance della cella solare. Alcuni calcoli termodinamici sono stati eseguiti per confrontare la stabilità di fasi a diverso contenuto di titanio e di ossigeno.

# **General overview**

This thesis presents the work of the author during his Ph.D. Initially, a general introduction about the technological role of oxides and the main deposition techniques to prepare them is provided. A special focus on chemical bath deposition, sol-gel and spin coating techniques is dedicated since they were involved by the author. Thereafter, the three projects are presented independently, they start with a specific introduction including the motivation and the state of the art followed by a focus on the structure and the properties of the studied material. Subsequently, a detailed description of the experimental methods involved by the author followed by the discussion of the results are provided. Lastly, a unique conclusion recaps the three projects, highlights the main results and the future perspectives.

As a general objective, the thesis is a piece of evidence concerning the importance of oxides in modern optoelectronics and more in general in the global technological effort that humanity is making to fight climate change. In fact, thanks to their intriguing and various physical and chemical properties together with their easy fabrication and many years of research and development, oxides cover a crucial role in modern technology. They are employed in light emission, light harvesting, superconductors, antibacterial coatings, fuel cells, catalysis, etc. More specifically, in view of improving smarter lighting solutions and energy provision from photovoltaics, it is proposed to enhance the stability of CsPbBr<sub>3</sub> nanocrystals trough their encapsulation in a silica shell and to provide alternative buffer layers for emerging photovoltaic technologies, specifically,  $Zn_{(1-x)}Mg_xO$  for Cu(In,Ga)Se<sub>2</sub> and TiO<sub>2</sub> for Sb<sub>2</sub>Se<sub>3</sub> solar cells.

# **1. Introduction**

Nowadays, climate change and the closely related green energy provision are among the most urgent challenges that we have to address, given the worrying rise of global surface temperature (*Figure 1a*)<sup>1</sup>. In fact, climate action, together with affordable and clean energy, were included by United Nations among the 17 global goals<sup>2</sup> to reverse the tide by 2030. There are 2 possible approaches to slow down climate change: (i) increase the green energy provision by replacing fossil fuels, and (ii) decrease the energy consumption. (i) The development of clean energy sources can significantly influence the carbon footprint. In fact, renewable energies have been showing an impressive growth in the last decades (Figure 1b), and in particular photovoltaics (PV) is among the ones that grew the most in recent years.<sup>3</sup> It follows that the development of new approaches to photovoltaics and the improvements of existing technologies assume crucial roles in the fight against climate change. As for the energy consumption (ii), there are fields, such as lighting, which are responsible for a huge energy cost (about 19% of the global electricity demand).<sup>4</sup> Improving the performance and decreasing the carbon footprint of light emitting devices, such as light emitting diodes (LEDs), is of primary importance to lower the global energy consumption.



*Figure 1: Global trends. (a)* Surface temperature variation on Earth from 1850 to 2022 and (b) World electricity production by source from 1985 to 2021, reworked from Our World in Data.<sup>1,3</sup>

#### 1.1. Functional oxides: technological role and synthetic procedures

Oxides have been among the most investigated materials in the last decades. They are widely involved in many fields of technology such as energy, photonics, health, electronics, magnetism, superconductivity, catalysis, etc. (*Figure 2a*). For instance, solid oxide fuel cells (SOFC) are made of an oxide-based cathode like Sr doped LaMnO<sub>3</sub> or La<sub>0.8</sub>Sr<sub>0.2</sub>Mn<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub>, generally with a Y stabilized ZrO<sub>2</sub> electrolyte and an anode of the same material but with Ni doping.<sup>5–7</sup> In superconductivity, one of the most studied family

of superconductors are cuprates since they show superconductivity behavior at temperature higher than most of the other families.<sup>8,9</sup> In the therapeutics field, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> are among the most promising candidates for magnetic hyperthermia.<sup>10</sup> In microelectronics, SiO<sub>2</sub> is the most involved dielectric material above all in transistors thanks to its extraordinary dielectric properties such as its impressive dielectric strength ( $\sim 10^7$ V/cm) and extraordinary resistivity ( $\sim 10^{15}$  ohm) related to its large bandgap ( $\sim 9 \text{ eV}$ ).<sup>11,12</sup> Oxides have been widely studied also in optoelectronics, for instance, as electrodes and electron or hole transporting layers in solar cells and LEDs. One of the most common example of the utility of oxides is in silicon solar cells where an SiO<sub>2</sub> passivation layer was able to improve the performance of the device by reducing the charges lost by undesired recombination mechanisms.<sup>13</sup> While in Cu(Ga,In)Se<sub>2</sub> (CIGSe) solar cells up to three layers are made of oxides: undoped and Al doped ZnO thin films as the top electrode and Zn(O,S) or a Sn doped ZnO layer are often exploited as buffer layers to form the p-n junction with the p-type CIGSe.<sup>14,15</sup> In perovskite photovoltaics one of the electrodes is generally fluorine or indium doped SnO<sub>2</sub> and the electron transporting layers are generally SnO<sub>2</sub>, TiO<sub>2</sub>, etc.<sup>16,17</sup> Notably, all oxide-based PV are emerging in recent years thanks to their chemical stability, easy preparation in air atmosphere, abundance and low/nontoxicity of many of them.<sup>18</sup> Concerning LEDs, materials such as ZnO and Ga<sub>2</sub>O<sub>3</sub> doped with rare earths have been investigated as emitting materials in ultraviolet (UV)-blue and white LEDs, respectively, in addition oxides like fluorine doped SnO<sub>2</sub> have been also involved as electrodes in LEDs.<sup>19,20</sup>

Concerning the preparation of such oxides, both chemical and physical methods have been involved, as depicted in *Figure 2b*. The first ones exploit reactions starting from selected precursors whereas the second ones take advantage of physical phenomena such as evaporation, sputtering, ablation, etc. In this work, only chemical methods were investigated, hence a brief overview of this group of techniques is provided.

Sol-gel processing is among the most common techniques to prepare oxides even of complex stoichiometry, generally in bulk form but also as thin films when coupled with spin coating or dip coating techniques (*Scheme 1*). Sol-gel prepared materials find application in membranes for fuel cells, water purification, structural composite materials, nanomaterials encapsulation, optoelectronics, etc.<sup>19,21–23</sup> Another technique is the reverse microemulsion that is widely exploited to encapsulate nanomaterials with an oxide shell, generally made of SiO<sub>2</sub>.<sup>21</sup> Chemical bath deposition (CBD) is largely involved in the fabrication of high-quality thin films of chalcogenide materials; it is cheap, scalable, requires low temperature and does not need for expensive equipment, but it produces much chemical waste. CBD is widely exploited in electronics for conformal film preparation, nanostructure growth, and photovoltaics where it is used to prepare CdS

and alternative buffer layers for CIGSe solar cells.<sup>24</sup> Electrodeposition is a widely known technique usually exploited to prepare metal, metal oxides, metal chalcogenides or biominerals. It is a cheap technique with a great control over the deposition rate since it can be performed with varying applied current, voltage or both, even as a function of time.<sup>24</sup> The hydrothermal method exploits an aqueous solution system in a special closed vessel at high temperature and pressure by solubilizing and recrystallizing a material that is poorly soluble or insoluble at ambient conditions.<sup>25</sup> The hydrothermal synthesis enables the preparation of many oxides in the form of thin films such as: TiO<sub>2</sub>, ZnO, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>.<sup>25–29</sup> The co-precipitation involves soluble salts that release anions and cations in solution whose interaction causes the formation of a precipitate. Lastly, the precipitate is thermally treated to achieve the desired properties. This methodology is widely involved in the field of magnetic nanoparticles to prepare for instance  $Fe_3O_4$ ,  $Fe_2O_3$ , etc.<sup>30</sup> Lastly, chemical vapor deposition (CVD) relies on the formation of a precursor gas which contains the desired element(s) to be deposited, then the gaseous precursor is allowed to get in touch with the substrate where it will react forming the final product.<sup>31</sup> CVD was successfully employed to grow SiO<sub>2</sub>, Si, SiN, graphene and many other materials.<sup>32–34</sup>



PV = photovoltaics; TE = thermoelectric; SOFC = solid oxide fuel cell; LED = light-emitting diode; MRI = magnetic resonance imaging; CBD = chemical bath deposition; CVD = chemical vapour deposition; PLD = pulsed laser deposition.

**Figure 2: Functional oxides overview. (a)** Overview of the main application fields for functional oxides (yellow), most common devices/applications in those fields (green) and some examples of materials exploited to fabricate corresponding devices/applications (blue). (b) Schematic of the most common synthetic techniques to prepare oxide materials.<sup>35,36</sup>

#### 1.1.1. Sol-gel synthetic procedure

In this research, the sol gel technique, also coupled with spin coating process, and CBD were employed to grow oxide materials. The sol-gel technique ensures a precise control over the composition of the final product and requires low temperature.<sup>37</sup> Sol-gel prepared materials find application in membranes for fuel cells, in water purification, in nanomaterials encapsulation, in optoelectronics, etc.<sup>17,21,23,38,39</sup>

The sol-gel reaction method consists of the following steps (*Scheme 1*)<sup>37</sup>:

a) Preparation of alkoxides (monomers) precursor solution.

b) Hydrolysis and partial condensation forming a "sol".

c) Gelation: polycondensation of hydrolyzed precursors often accompanied by an abrupt enhancement of the viscosity.

*d)* Drying: solvent evaporation shrinks the gel into a dense structure with pores filled with liquid (xerogel) or, in case of supercritical drying, filled with air (aerogel).

e) Calcination: heat treatment to improve the mechanical properties of the material by removing volatile components.

Starting from an alkoxy solution (M(OR)<sub>4</sub> where M is an element and R an alkyl group), the two main reactions that drive the sol-gel process are hydrolysis and condensation. During the hydrolysis, the alkoxide undergoes a nucleophilic addition of a water molecule followed by the transfer of a proton which releases an alcohol (Eq. 1, Scheme 1). Then, the hydroxyl group undergoes a condensation reaction releasing water (Eq. 2, Scheme 1a), or alternatively, an hydrolyzed species may react with an un-hydrolyzed alkoxy group releasing an alcohol (*Eq. 3, Scheme 1a*).<sup>37</sup> The hydrolysis and the first part of the condensation lead to the formation of a colloidal suspension called sol (Scheme 1b). Upon the completion of the condensation reaction, clusters are formed which bind to each other forming a continuous three-dimensional polymeric network called gel, whose formation is accompanied by a strong enhancement of the viscosity (Scheme 1c).<sup>37</sup> The wet gel obtained after hydrolysis and condensation is typically dried at a temperature around 100 °C to desorb water and alcohol remained inside the pores. This shrinking process is mainly driven by the condensation reaction and capillary forces and may cause the formation of cracks originated by the difference in the contraction rates of inner and outer portions of the gel, which may negatively affect the material performance. This drying process causes a strong decrease of the porosity, which may be limited by performing supercritical drying leading to an aerogel (Scheme 1d).<sup>37</sup>

 $M(OR)_4 + H_2O \leftrightarrows M(OR)_3(OH) + ROH$ (1)



#### $M(OR)_3(OH) + M(OR)_4 \subseteq (OR)_3MOM(OR)_3 + ROH$



From the thermodynamic viewpoint, the hydrolysis step is dominated by the nucleophilicity of the incoming group and by the charge of M, which is related to the donating capacities of the OR group, the electronegativity of M and the stability of the leaving group. From the kinetic viewpoint, the reaction rate increases enhancing the difference between the coordination of M and its charge and is related with the steric hindrance of the alkoxy chain.<sup>37</sup> Since metals present higher electronegativities compared to non-metals (e.g. Si), the behavior of metallic (Ti, Zn, Al, etc.) and non-metallic (e.g. Si, Ge, P, etc.) alkoxides is strongly different. Metals display higher coordination number than their valency since they act as Lewis acids i.e. accepting lone electron pairs from coordination moieties and hence being susceptible to nucleophilic attack.<sup>42</sup> Non-metallic

15

(3)

alkoxides undergo a faster hydrolysis hence the condensation reaction happens in parallel with the hydrolysis reaction making the entire process harder to control.<sup>37,42,43</sup> On the contrary, such reactions occur slower and with less overlap in silicon alkoxides making them easier to investigate. Indeed, the reactivity of silicon alkoxides is often enhanced by catalysts (acids or bases), while the one of metal alkoxides is sometimes moderated by the addition of selected molecules in the system like competitive bidentate complexing ligands as acetic acid and acetylacetone.<sup>42</sup>

Regarding the sol-gel preparation of silica, the most involved alkoxy silanes are tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). These are generally dispersed in ethanol and treated with H<sub>2</sub>O in acidic, basic or neutral conditions.<sup>44</sup> Hydrolysis reaction in acidic conditions entails the protonation of alkoxy silicon (faster reaction step) (*Eq. 4*) followed by the reaction with H<sub>2</sub>O and the formation of an unstable penta-coordinated intermediate that evolves into a silanol species releasing an alcohol and a proton (slower reaction step) (*Eq. 5*).<sup>44</sup> Then, during the condensation reaction, a silanol species gets protonated (faster reaction step) (*Eq. 6*) and reacts with another silanol molecule forming a siloxane species and releasing H<sub>3</sub>O<sup>+</sup> (slower reaction step) (*Eq. 7*).<sup>44</sup>

In base catalyzed conditions, hydroxyl group attaches the silicon alkoxy forming silanols via an unstable penta-coordinated intermediate (*Eq. 8*) that turns into a silanol molecule (*Eq. 9*). Later, during the condensation step, a silanol species reacts with an hydroxyl group forming a silanolate anion and water (faster reaction step) (*Eq. 10*), the silanolate reacts with a silanol molecule forming a siloxane with its characteristic Si-O-Si bond (slower reaction step) (*Eq. 11*).<sup>44</sup>

#### Acidic catalysis

Hydrolysis reaction:

$$Si(OR)_4 + H_3O^+ \leftrightarrows Si(OR)_3(O^+RH) + H_2O$$
(4)

 $Si(OR)_{3}(O^{+}RH) + 2H_{2}O \rightarrow [Si(OR)_{3}(ORH)(OH_{2})]^{+} \rightarrow Si(OR)_{3}(OH) + ROH + H_{3}O^{+}(5)$ 

Condensation reaction:

$$\operatorname{Si}(\operatorname{OR})_3(\operatorname{OH}) + \operatorname{H}_3\operatorname{O}^+ \leftrightarrows [\operatorname{Si}(\operatorname{OR})_3(\operatorname{OH}_2)]^+ + \operatorname{H}_2\operatorname{O}$$
(6)

$$Si(OR)_{3}(O^{\delta^{+}}H_{2}) + Si(OR)_{3}(OH) \leftrightarrows (OR)_{3}Si-O-Si(OR)_{3} + H_{2}O$$

$$\tag{7}$$

**Basic catalysis** 

Hydrolysis reaction:

$$Si(OR)_4 + OH^- \leftrightarrows [Si(OR)_4(OH)]^-$$
(8)

$$[Si(OR)_4(OH)]^- \leftrightarrows Si(OR)_3(OH) + OR^-$$
(9)

Condensation reaction:

$$Si(OR)_{3}(OH) + OH^{-} \leftrightarrows Si(OR)_{3}O^{-} + H_{2}O$$
(10)

$$Si(OR)_{3}O^{-} + Si(OR)_{3}(OH) \leftrightarrows (OR)_{3}Si - O - Si(OR)_{3} + OH^{-}$$
(11)

Hydrolysis rate is slower at acidic rather than basic pH, as a result, the growth is governed by the nucleation of new particles, while in alkaline conditions the silica particles have more time to aggregate. This different kinetics yields alternative morphologies of the resulting silica network. In fact, under acidic conditions, SiO<sub>2</sub> is organized in linear chains connected by a low number of bonds, whereas under alkaline conditions yield branched clusters. Also the mechanism of gel formation is different: in acidic pH it consists of entangling linear chains, while in basic conditions, it occurs by bonding the clusters together.<sup>44</sup>

The condensation rate increases with higher negative surface charges that favor the nucleophilic attack (*Figure 3*). The condensation rate levels off at around pH 7.5, because of the instability of silicates at higher pH. However, a pH higher than 7.5 is generally involved thanks to the addition of surfactants that stabilize silica particles.<sup>45</sup>



Figure 3: How the pH affects the kinetics of SiO<sub>2</sub> growth. How pH influences silica condensation rate, and charge density of SiO<sub>2</sub> surface. Reproduced from Ref.<sup>45</sup> with permission from the Royal Society of Chemistry. <u>Copyright © 2000-2022</u> by John Wiley <u>& Sons, Inc.</u>, or related companies. All rights reserved.<sup>46</sup>

Recently, sol-gel synthesis has been developed in nonhydrolytic systems. Water is not deliberately added but comes from the adventitious water in the solvent of from the organic precursor decomposition, etc. The low amount of water results in a slower reaction rate compared to the traditional synthesis where water is deliberately added, allowing an easier control over the process.<sup>47,37,48</sup>

## 1.1.2. Sol-gel processes for thin film preparation: spin coating & dip coating

Sol-gel synthetic methods are exploited not only to prepare bulk ceramic materials, but also to fabricate thin films as depicted in *Scheme 1*. The most common techniques to deposit the sol onto the substrates are dip coating and spin coating. The first one consists of the immersion of a substrate inside a precursor solution containing the sol to be deposited, then a compact film is formed upon heating. The second one exploits the rotation of the substrate to spread the sol all over it and to favor the solvent evaporation, also in this case the compact film is obtained after a thermal treatment. In this research spin coating was employed.

Spin coating exploits the effect of the centripetal force combined with the surface tensions in the system to cover the substrate with a thin layer of the dispensed solution. Films from few tens of nanometers up to several micrometers can be prepared with this method.<sup>49</sup> There are several main advantages of spin coating: it is an easy and quick process, it requires low cost instruments, it yields high-quality thin films, and it is versatile given that it enables to grow oxides, nanomaterials, polymers, organic semiconductors, etc. The main disadvantages consist in the poor scalability and in the waste of most of the disposed material (~ 90 %).<sup>49</sup>

The spin coating process can be divided into 4 main steps: (a) deposition, (b) spin on, (c) spin off and (d) evaporation (Figure 4). (a) The deposition step can be performed by casting the solution onto a substrate before it starts to spin (static-dispensing) or once it is already rotating (dynamic-dispensing), in both cases the centrifugal force will spread the solution all over the substrate. (b) The rotation removes most of the solution, (c) airflow evaporates most of the solvent from the layer, lastly, (d) the film fully dries leaving the final material.<sup>49</sup>



*Figure 4: Spin coating schematic.* Description of the 4 main steps in spin coating process by static-dispensing: (a) deposition, (b) spin up, (c) spin off and (d) evaporation.<sup>49</sup>

The thickness of the film is one of the most important parameters to monitor. The final thickness of a spin coated film (t) is proportional to the angular velocity or rotation speed (w) as described in Eq. 12:

$$t \propto \frac{1}{\sqrt{\omega}} \tag{12}$$

This means that the rotation speed enables a fine control of the film thickness. However, many other parameters come into play to control the thickness of the film, e.g. the precursor solution concentration and the solvent evaporation rate.

#### 1.1.3. Chemical bath deposition (CBD): an introduction.

CBD is a widely known technique to prepare thin films, it is mainly involved in the fields of photovoltaics, optical imaging, solar window coating etc. generally to grow metal chalcogenides (selenides, sulfides and oxides).<sup>50</sup> The assets of CBD are its low cost (no need for expensive equipment), its suitability for large scale production, the low deposition temperature at which it operates, and the resulting film homogeneity over large areas.

CBD is a widespread technique to prepare thin films from an aqueous solution of the desired ions. An alkaline pH is generally exploited to precipitate oxides or hydroxides of the target composition. As a general rule, the precipitation can occur if the ionic product overcomes the solubility constant (Kps) where the ionic product is defined as the product of the molar concentrations of the ions formed after the dissociation reaction of a compound (AB  $\leftrightarrows$  A<sup>+</sup> + B<sup>-</sup>, ionic product = [A<sup>+</sup>]·[B<sup>-</sup>]). However, undesired precipitates often form in the solution resulting in a large amount of waste hence in a low yield of the process. Indeed, there are two main mechanisms of nuclei formation which are in competition: homogeneous and heterogeneous nucleation. Homogeneous nucleation consists in the formation of clusters and the resulting large amount of undesired precipitate in the solution that does not usually bond to the substrate strongly. Heterogeneous nucleation entails the deposition of the material onto a surface i.e. the substrate and the wall of the deposition container. The latter is the mechanism that is

exploited in CBD to prepare thin films. The heterogeneous nucleation is thermodynamically favored compared to homogeneous nucleation due to the presence of additional interfaces that decrease the Gibbs free energy of the system as shown in section  $4.2.^{51,52}$  However, homo-nucleation is generally kinetically favored. As a consequence, complexing agents are introduced in the solution in order to slow down the precipitation in solution and favor the heterogeneous nucleation. Those chemicals directly bind the metallic species forming a complex, if the metal-complex bond is sufficiently strong to bind the metal but weak enough to avoid the formation of a stable complex, the metal will be slowly released and the hetero-nucleation is favored.<sup>50,53</sup> Despite the discovery of many complexing agents, preventing homo-nucleation is extremely difficult, resulting generally in low yield and large amounts of chemical wastes.

To go deeper in the deposition mechanism, it is preferable to divide the materials prepared trough CBD into 2 groups: *sulfide-selenides* and *oxides*. Concerning the first one, the most investigated material is CdS, hence it was selected as an example. Several different reaction mechanisms are reported for CdS deposition (a, b, c), which generally involve an aqueous solution of a sulfide precursor like thiourea that is able to provide S<sup>2-</sup> slowly, and a Cd precursor like Cd acetate in the presence of a complexing agent such as thiourea itself.

(a) First of all, thiourea undergoes hydrolysis forming sulfide anions (*Eq. 13*) followed by their reaction with Cd cations (*Eq. 14*). This reaction allows an ion by ion deposition that occurs when the ionic product ( $[Cd^{2+}] \cdot [S^{2-}]$ ) overcomes the solubility product of CdS (Kps~10<sup>-28</sup>).<sup>54</sup>

$$SC(NH_2)_{2(aq)} + 2OH^{-}_{(aq)} \leftrightarrows S^{2-}_{(aq)} + CN_2H_{2(aq)} + 2H_2O_{(l)}$$
(13)

$$Cd^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow CdS_{(s)}$$
(14)

(b) Another reaction path entails the formation of Cd(OH)<sub>2</sub>, hence the hydroxide species reacts with sulfide anions forming CdS (*Eq. 15*).<sup>54</sup>

$$Cd(OH)_{2(s)} + S^{2-}_{(aq)} \rightarrow CdS_{(s)} + 2OH^{-}_{(aq)}$$
(15)

(c) A third reaction path may occur when Cd complexes form, e.g. by the reaction of  $Cd^{2+}$  with thiourea (*Eq. 16*). The breaking of the S-C bond allows the formation of CdS which deposits on the substrate following a cluster by cluster process which generally results in the formation of crystals of smaller size.<sup>54</sup>

$$Cd^{2+}(aq) + SC(NH_2)_{2(aq)} \leftrightarrows CdSC(NH_2)_2^{2+}(aq)$$
(16)

In the case of oxide films by CBD, several reaction paths are possible. However, they all generally entail the hydrolysis of the metal. The most common oxide deposited by CBD is ZnO which was chosen as an example. First,  $Zn^{2+}$  forms a complex with e.g. NH<sub>3</sub>, then once  $Zn^{2+}$  is released in the solution forms the corresponding hydroxide. Successively, Zn(OH)<sub>2</sub> dehydrates forming ZnO. More in details, it is described the ZnO deposition from solution of zinc nitrate hexahydrate starting an aqueous and hexamethylenetetramine (HMTA). Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolves releasing Zn<sup>2+</sup> (Eq. 17), while HMTA reacts with water producing formaldehyde, ammonia and hydroxyl ions (Eq. 18, 19). The latter reacts with  $Zn^{2+}$  forming  $Zn(OH)_2$  (Eq. 20) which decomposes into ZnO and water through a dehydration reaction favored by high temperature (typically 60 – 90 °C) (*Eq. 21*).<sup>55</sup>

$$Zn(NO_3)_2 \cdot 6H_2O_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2NO^{3-}_{(aq)} + 6H_2O_{(l)}$$
 (17)

$$(CH_2)_6N_{4(aq)} + 6H_2O_{(l)} \rightarrow 6HCHO_{(g)} + 4NH_{3(aq)}$$
 (18)

$$NH_{3(aq)} + H_2O_{(l)} \rightarrow NH_4^+_{(aq)} + OH^-_{(aq)}$$

$$\tag{19}$$

$$Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \rightarrow Zn(OH)_{2(s)}$$
<sup>(20)</sup>

$$Zn(OH)_{2(s)} \rightarrow ZnO_{(s)} + H_2O_{(l)}$$
<sup>(21)</sup>

Higher temperature and pH enhance the hydrolysis rate that has to be sufficiently low to promote the heterogeneous nucleation (thermodynamically favored) and inhibit the homogeneous nucleation.<sup>54</sup>

# 2. This study

The three projects described in this study focused onto SiO<sub>2</sub>, ZnO, and TiO<sub>2</sub> for optoelectronic applications. In particular, CsPbBr<sub>3</sub> nanocrystals (NCs) were encapsulated in SiO<sub>2</sub> shells (CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs) at the *Italian Institute of Technology* (IIT) of Genova, this study improved the knowledge about the shelling procedures to form LHP@SiO<sub>2</sub> a material mainly oriented to the fabrication of novel white LEDs (WLEDs). Zn<sub>(1-x)</sub>Mg<sub>x</sub>O<sub>y</sub> thin films were fabricated trough CBD at the *International Iberian Nanotechnology Laboratory* (INL) in Braga (PT) and at the *Department of Chemistry and Industrial Chemistry* of the University of Genova (DCCI) as a buffer layer for CIGSe-based solar cells. Similarly, TiO<sub>2</sub> thin films were prepared through spin coating and were post treated at DCCI in collaboration with the *Institute of materials for electronics and magnetism* (IMEM) of the CNR of Parma as a buffer layer for Sb<sub>2</sub>Se<sub>3</sub>-based solar cells.

## 2.1. CsPbBr<sub>3</sub>@SiO<sub>2</sub> maleic anhydride mediated synthesis for LEDs

## 2.1.1. Project overview

Light emitting technology has been widely developed in recent years, the first reported electrical lighting system is known as Edison's bulb at the end of the XIX century which exploiting a carbon filament was able to provide about 1.2-2 lm/W, then at the beginning of the XX century incandescent halogen lamps with a tungsten filament were developed and the luminous efficacy grew up to 16-24 lm/W. Few decades later linear fluorescent lamps reached 55-90 lm/W. The next milestone in lighting happens with the fabrication of the first light emitting diode (LED) which reached a record luminous efficacy of about 303 lm/W in 2014. In the 1990s high-efficient pure color LEDs covering the whole visible spectrum were prepared.<sup>56</sup>

The LED was invented based on a III-V semiconductor, GaAsP by *Holonyak and Bevacqua* in 1962 with a very low luminescence efficacy 0.1 lm/W.<sup>57,58</sup> Then, many others composition of III-V and II-VI semiconductors have been studied showing the high performance obtainable from III-V. For instance, AlGaAs is able to emit light from red to the IR portion of the spectrum by tuning the Al-Ga ratio, while AlInGaP emits light from amber to red-orange. AlGaInN shows a broader bandgap that allows it to cover the green, blue and UV spectral regions. Hence, combining the aforementioned three materials the spectral regions from UV to IR (hence also the whole visible) are accessible.<sup>56</sup>

Later in the 1980s, another electroluminescent technology made of organic material has been developed. Organic LEDs (OLEDs) consist of stacked organic thin films between 2 electrodes. When a potential difference is applied the organic films experience electroluminescence. The emission comes from  $\pi$ -conjugated molecules and its energy

can be controlled by tuning the conjugation length. Compared with inorganics, OLEDs experience lower reabsorption losses, flexibility, low cost, lighter, processable from solution, better view angle but worst color contrast. Also, OLED were quickly able to cover the whole visible spectrum.<sup>59,60</sup>

The possibility to emit all the visible light with LEDs paved the way for the fabrication of WLED. Three main strategies have been proposed for WLED preparation:

1) The electroluminescence from three different LEDs emitting red, blue and green is exploited to obtain a white LED emission.<sup>56</sup>

2) The light emitted by a violet LED is absorbed by an emissive material (phosphor) on its top and converted into white light.<sup>56</sup>

3) The blue light emitted by a LED is partially absorbed by phosphors able to reemit red and green light. Hence, the remained blue light together with the green and red light result in a white emission.<sup>56</sup>

The third approach is the most successful one and has been more exploited also for lead halide perovskite WLED.<sup>61</sup> The harsh working conditions for the phosphors in the third approach requires a very stable phosphors, organics were not able to reliably operate in such conditions while inorganic like rare earth phosphors became very attractive. Nowadays, the most common technology for white LED fabrication entails InGaN/GaN blue LED coupled with cerium-doped yttrium-aluminum garnet phosphors (YAG:Ce).<sup>56</sup> YAG:Ce which absorbs a portion of the blue light of InGaN/GaN and reemits yellow light that, together with the remaining blue light, results into white light. Rare earth phosphors consist of a host matrix which embeds rare earth or transition metal elements. Those materials are able to convert high frequency radiation into lower and reemit it thanks to their electronic structure. Rare earth phosphors emit light mainly trough f-f electronic transition of ions and f-d field-dependent broad emission band where in the f-d transitions also the host matrix plays a role. Such a matrix has to meet particular requirements, since the rare earth is introduced as a substitutional dopant (about 10 %) the host cations need to have a comparable radius to the rare earth to allow the substitution. In addition, the host matrix requires a broad transparency, an high refractivity, a tunable crystal phase, high photochemical and thermal resistance, etc.<sup>62</sup> The most common method to prepare YAG:Ce phosphors is high-temperature solid-state reaction, a long procedure that requires high temperature. Novel materials for WLED with easier synthetic procedures and higher color rendering index (CRI) and performance have been widely investigated.<sup>63</sup> In 1994 an LED made of CdSe quantum dots was fabricated. This zero dimensional structure favors the radiative recombination towards the non-radiative one enhancing the quantum efficiency of the device.<sup>64</sup> In addition the bandgap of a quantum dot can be tuned by modifying the particle size, in particular larger particle size results in a smaller bandgap.65 II-VI (e.g. CdSe), III-V (e.g. InP) and III-VI (e.g.CuInS) QDs have been investigated for light emission in LEDs. QDs can be exploited both as a phosphors as YAG:Ce and as electroluminescent emitter like InGaN. Compared to rare earth phosphors QDs can overcome their CRI thanks to their high color purity owed to narrow photoluminescence (PL) maintaining high efficiency comparable to inorganic white LEDs (~65 lm/W). In addition, quantum dots can be prepared from solution allowing a cheap fabrication trough e.g. inkjet printing.<sup>66</sup>

Among novel QDs technologies, lead halide perovskite (LHP) NCs have been emerging as a novel semiconductor nanomaterial with impressive optoelectronic properties. LED out of LHP NCs showed impressive performance both as an electroluminescent device or as a phosphor in WLED. In a typical LHP NCs based LED the active layer is sandwiched between an n-type electron transporting layer and a p-type one. The last and the first layer are typically electrodes like Al<sup>67</sup> or Ag<sup>68</sup> and a transparent one such as ITO that let light go trough, often further interfacial layers are introduced.<sup>69</sup> Remarkably, EQE of LED of LHP NCs grew from less than 1 % in 2014<sup>68</sup> to more than 20 % in 2018<sup>70</sup> with an LED based on CsPbBr<sub>3</sub> NCs.

In particular, LHP NCs display PL quantum yield (PLQY) that can reach almost 100%<sup>71</sup>. LHP NCs also show broad absorption, narrow PL spectra and large carrier diffusion lengths (about 9.2  $\mu$ m, close to GaAs that shows values of about 10-15  $\mu$ m<sup>72</sup>, whereas silicon has higher performance, 100-300  $\mu$ m<sup>73</sup>)<sup>74,75</sup>. Moreover, the system possesses a direct bandgap that is typically tuned trough halide exchange reactions and, in case of Cs based perovskite, spans from about 3.18 eV for CsPbCl<sub>3</sub> to about 1.87 eV for CsPbI<sub>3</sub><sup>76</sup>. The aforementioned impressive properties, combined with their solution processability at "low" temperature (from room temperarature<sup>77</sup> up to several hundreds Celsius degrees<sup>78</sup> with consequent properties modification) make LHP NCs very attractive for optoelectronics application and in particular for LEDs.<sup>79</sup> The properties of this novel material are closely linked to their stoichiometry and crystal structure. LHPs present an APbX<sub>3</sub> stoichiometry where A is a cation such as  $Cs^+$ , MA<sup>+</sup> and FA<sup>+</sup>, while X is an anion like Br, I<sup>-</sup> and Cl<sup>-</sup>. LHP NCs present ideally a cubic structure where the A cation occupies the corners, the B cation the center and the X anions the center of the facets of the cube (*Figure 5*). The structure can also be described as  $[BX_6]^{4-}$  corner sharing octahedra that form a 3D network. Generally, the octahedra are tilted resulting in an orthorhombic structure (Figure 5).<sup>80,81</sup> However, LHP NCs have several drawbacks that hinder their commercialization. They contain lead which is toxic and their non-polar nature requires dangerous solvents such as toluene or hexane.<sup>75,82</sup> They possess low stability against polar solvents, moisture, UV light and high temperature, all of which quickly lower their PL.83-<sup>85</sup> As a consequence, many efforts are required in order to solve the aforementioned issues. Many lead-free perovskite materials have been studied, nevertheless it is very

difficult to find materials with performance comparable to the lead-based ones. Sn, Ge, Bi, Sb, Cu and other elements have been tested in place of Pb.<sup>86,87</sup> Despite many combinations were tried, the PLOY of lead-free perovskites hardly exceed 80%<sup>86</sup> and many of them present similar stability issues of LHP. In other words, a lead free alternative with comparable optoelectronic properties is still to be found.<sup>86</sup> Regarding the stability issue, the most common strategy to deal with it entails the encapsulation of the CsPbBr<sub>3</sub> NCs within a matrix. Several materials have been exploited as matrix such as metal organic frameworks<sup>88</sup>, oxides<sup>83,89,90</sup>, polymers<sup>91</sup>, etc. Since many technologies require colloidal stability, the encapsulation strategy should not entail the formation of a bulky matrix but should be able to protect the NC at the nanoscale; as a consequence, a core@shell morphology would be ideal. Lead-free NCs solution-processable at low temperature, encapsulated into a SiO<sub>2</sub> shell, and possessing a near 100% PLQY would be very good candidates for WLED fabrication. In this study, a novel procedure to prepare CsPbBr<sub>3</sub>@SiO<sub>2</sub> is reported. The final performance of the encapsulated material is not interesting for practical applications, but the chemistry into play reveals interesting insights regarding the reaction mechanism which may help to better understand the shelling process and find the best procedure to protect perovskite (or chemically similar) NCs.



Figure 5: Representation of the crystal structures of the materials involved in this study. On the left CsPbBr<sub>3</sub> orthorhombic crystal structure, on the right  $\alpha$ -quarts SiO<sub>2</sub>.

In this study, CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs were prepared starting from Cs<sub>4</sub>PbBr<sub>6</sub> NCs which were synthesized following the hot injection method as similarly to *Baranov et al.*<sup>92</sup> (*Figure 6, step 1*)<sup>84</sup>, then upon the addition of maleic anhydride (MANH) they were converted into CsPbBr<sub>3</sub> NCs (*step 2*), the addition of TMOS or TEOS allowed the formation of low emissive CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs with penetrable shell (*step 3*), their PL was improved trough a PbBr<sub>2</sub> treatment and the shell was grown thicker by further addition of TEOS or TMOS (*step 4*).



**Figure 6:**  $CsPbBr_3@SiO_2@SiO_2$  **4** steps synthesis.  $Cs_4PbBr_6$  NCs were converted into  $CsPbBr_3$  NCs trough the reaction with MANH (step 1); the addition of TMOS or TEOS allowed the formation of  $CsPbBr_3@SiO_2$  (step 2) whose PL was enhanced exploiting a passivation treatment with PbBr\_2 solution (step 3); lastly, a thicker silica shell was grown adding TEOS/TMOS (step 4). Reproduced with the permission of Chemistry of Materials.<sup>84</sup>

Such a procedure was not discovered by the author, researchers (including Dr. Dmitry Baranov and Dr. Gianvito Caputo) of the Nanochemistry group of IIT (Genova) headed by Prof. Liberato Manna discovered the conversion of Cs<sub>4</sub>PbBr<sub>6</sub> into CsPbBr<sub>3</sub> NCs exploiting MANH. Then, in the same laboratory, Dr. Riccardo Scarfiello introduced TEOS as a silica precursor and successfully obtained CsPbBr<sub>3</sub>@SiO<sub>2</sub>, in fact some of the images presented in this study come from his work. The author developed such a procedure investigating the reaction mechanism, its optimization and post-synthesis treatments to improve the material properties. All the experiments and characterization shown were developed in IIT under the supervision of Prof. Liberato Manna and Nanochemistry researchers. Regarding the annular dark-field imaging in scanning transmission electron microscope (HAADF-STEM) images at low and high magnification and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental maps in Figure 13a, c, and all the images in Figure A1 (section 4.1.) were acquired by Dr. Rosaria Brescia, PhD. Photostability experiments and data analysis (Figure 14c) were performed by Dr. Dmitry Baranov, PhD. The Images in Figure 8c, d, e and Figure A4 come from samples prepared by Dr. Riccardo Scarfiello, PhD and were

acquired and analyzed by Dr. Rosaria Brescia, PhD trough microscopy techniques. This work has been recently published in Chemistry of Materials.<sup>84</sup>

## 2.1.2. Bulk and nano- silica: structural, morphological and physical properties

Nanomaterials have been widely studied in the last decades. They present peculiar behaviors and the most diverse properties in all the fields of science. In addition, different nanomaterials can be grown together in more complicated structures to modify the properties of the starting material, for example, a second nanomaterial can be grown all over the first one in structures called core@shell<sup>21,93,94</sup>, or they can share a facet forming the so-called Janus particles<sup>95</sup> and so on.

Despite their poor stability, scientists were able to coat LHP NCs with many different materials as reported by *Ahmed et al.*<sup>94</sup> Here several examples of heterostructure made out of CsPbBr<sub>3</sub> and inorganic materials are briefly discussed.<sup>94</sup> In particular, the synthesis, the stability and the optoelectronic properties of several shell materials families will be presented (in the order selenides and sulfides, perovskites, metal oxides and silica).

Shi et al.<sup>96</sup> reported the preparation of CsPbBr<sub>3</sub>@CdS trough wet chemistry methods. Assynthesized CsPbBr<sub>3</sub> NCs were treated with a mixture of Cd-oleate solution and sulfur/OA solution at 150 °C for 20 min under N<sub>2</sub> flow. The same heterostructure was then prepared also following an epitaxial growth by mixing CdO, ODE and OLAM at 280 °C. Later, the ODE and sulfur in an OLAM solution were added to Cd-oleate solution to fabricate the shell. Individual CsPbBr<sub>3</sub>/CdS heterostructure showed excellent thermal, chemical, and light excitation stability compared to unencapsulated CsPbBr<sub>3</sub> NCs. Later, Liu et al.<sup>97</sup> inserted Al ions in the heterostructure forming CsPbBr<sub>3</sub>@nCdS:Al. Al ions inhibited the photodegradation and preserved the optical properties of the NCs. Particularly, the growth of the aluminum layer maintained the morphology and the emission properties of the starting NCs. The preparation consists of the synthesis of CsPbBr<sub>3</sub> NCs followed by the injection of Cd and S at different times to form the first shell layer (n = 1, CsPbBr<sub>3</sub>@CdS), for the second formation Cd and S were added again forming CsPbBr<sub>3</sub>@2CdS. Once the third layer was grown, the Al precursor was injected in the dispersion of CsPbBr<sub>3</sub>@3CdS in ODE at 150 °C under Ar and retained for 5 min. The treatment accelerated the formation of Al(OH)<sub>3</sub> which protects the heterostructure. A continuous injection method was exploited by *Fan et al.*<sup>97</sup> to prepare CsPbBr<sub>3</sub>@PbSe core@shell heterostructure. PbI2 and ODE were first degassed under vacuum, then, OA and OLAM were slowly added in the reaction mixture at 70 °C followed by trioctylphospine oxide (TOP) and Se anions which enabled the nucleation of PbSe onto the CsPbBr3 surface. At this point, the temperature was raised to 180 °C and a small amount of Cs-oleate solution was inserted. The presence of both materials was certified

by HRTEM. CsPbBr<sub>3</sub>@PbSe showed an important storage stability against moisture. Similarly, *Fan et al.*<sup>98</sup> prepared an heterostructure out of 1D PbSe and CsPbBr<sub>3</sub> trough CVD. *Gong et al.*<sup>99</sup> synthesized a nano-heterostructure of PbS and CsPbBr<sub>3</sub> adding Csoleate, Γ, Pb<sup>2+</sup> to a solution of PbS clusters, which yielded PbS/CsPbBr<sub>3</sub> NCs. *Ravi et al.*<sup>100</sup> stabilized CsPbBr<sub>3</sub> NCs adding oleylammonium bromide and heating up to 180 °C for 1 h. Then, CsPbBr<sub>3</sub> NCs were treated with zinc diethyldithiocarbamate and oleylammonium bromide at 120 °C forming CsPbBr<sub>3</sub>@ZnS NCs.

Notably, CsPbBr<sub>3</sub>/CdS improved the thermal, moisture and water stability of the core. While the Al addition strongly improved the photostability. Since the PbSe shell is hydrophobic because of its ligands, the shell strongly improved the core stability against water. Also, CsPbBr<sub>3</sub>@ZnS showed impressive resistance towards water remaining emissive after 48 h of exposure. Concerning optical and electronical properties, after the CdS shell growth the bandgap of the material grew from  $\sim 2.4$  eV to  $\sim 2.6$  eV<sup>101</sup>. The narrow PL spectra was maintained with a slightly decreasing in PLQY from ~90 to ~88 %, a blue shift of both PL and ABS spectra, and a remarkable growth of the charge carrier lifetime due to the CdS coating. The multiple CdS shell grown by Liu et al.<sup>97</sup> showed an enhanced PL lifetime increasing the CdS layer thickness because of a reduction in the overlapping of electrons and holes wave functions. When CsPbI<sub>3</sub> was coated with PbSe its Stoke shift decreased, time-resolved PL (TRPL) measurements reveled that CsPbI<sub>3</sub>-PbSe exhibited an improved PL lifetime (42.6 ns towards 33.4 ns) suggesting an enhanced surface passivation after the coating.<sup>102</sup> While, the capping with PbS caused an optimal surface defect passivation with the consequent PL intensity improvement, narrow emission spectrum and lower Stoke shift together with improved stability.

The interest in perovskite based shell has several motivations, one of the most important is the near perfect crystallographic match among the two materials.<sup>103</sup> In case of  $Cs_2PbBr_6$  NCs an additional motivation is present, since this material experiences a wide bandgap (~4.0 eV), electrons in the core experience a strong confinement.<sup>103</sup>

*Jia et al.*<sup>104</sup> coated CsPbX<sub>3</sub> NCs with Cs<sub>4</sub>PbX<sub>6</sub> trough a modified hot-injection method. The core was prepared trough hot-injection method, then ZnBr<sub>2</sub> and Cs-oleate were added causing the formation of the heterostructure, but epitaxial growth was not yet shown. *Qiao et al.*<sup>105</sup> coated CsPb<sub>2</sub>Br<sub>5</sub> onto CsPbBr<sub>3</sub> NCs core trough a solution phase method. In brief, the Cs-oleate and PbBr<sub>2</sub> solution were heated up to 190 °C and quickly injected into the reaction mixture, the temperature and the excess of Pb were proved to be crucial parameters to successfully obtain the core@shell architecture. The PL of the core was strongly improved after the shell growth. *Wang et al.*<sup>105</sup> coated the CsPbBr<sub>3</sub> NCs with an amorphous CsPbBr<sub>x</sub> shell trough hot-injection method. Then, they exchange the cations

of the shell obtaining a CsPbBr<sub>3</sub>/Rb<sub>4</sub>PbBr<sub>6</sub> core/shell structure.<sup>106</sup> *Jiang et al.*<sup>107</sup> synthesized CsPbBr<sub>3</sub> covered by a shell of CsPb<sub>2</sub>Br<sub>5</sub> exploiting polymeric ligands as poly(methyl methacrylate) and poly(ethylenimine) to stabilize NCs during the mechanochemical synthesis. Such ligands induced a surface phase transformation of CsPbBr<sub>3</sub> into CsPb<sub>2</sub>Br<sub>5</sub> NCs with the formation of core@shell nanocrystal. Lastly, *Zhang et al.*<sup>108</sup> exploiting a wet chemical approach in order to epitaxially grow FAPbBr<sub>3</sub> shell onto a core of CsPbBr<sub>3</sub>. Pre-synthesized FAPbBr<sub>3</sub> NCs were treated with PbBr<sub>2</sub>, Cs<sub>2</sub>CO<sub>3</sub>, OLAM, ODE and OA at 80 °C in a N<sub>2</sub> atmosphere, after 20 min the reaction was quenched in a water-ice bath.

From the stability view-point, CsPbBr<sub>3</sub>/Rb<sub>4</sub>PbBr<sub>6</sub> core/shell NCs solution and in form of thin film experience only a decreasing of 10 % of the initial PLQY after 42 h of LED illumination. While, the ligand poly(methyl methacrylate) is hydrophobic and when exploited as a ligand it strongly improved the water resistance of the material. CsPbBr<sub>3</sub>@FAPbBr<sub>3</sub> core@shell showed high PLQY (93 %) and impressive stability after 70 days of exposure in ambient conditions and under an UV light radiation (50 h) preserving over 80 % of the initial PLQY. The CsPb<sub>2</sub>Br<sub>5</sub> shell strongly improved the stability of the core towards polar solvents. Regarding the optoelectronic properties, the coating of Cs<sub>2</sub>PbBr<sub>6</sub> onto CsPbBr<sub>3</sub> NCs improved the PLQY of the core material from ~84 % to ~96 % while the absorption spectrum resulted basically unchanged. Regarding CsPbBr<sub>3</sub> coated with Cs<sub>4</sub>PbBr<sub>6</sub>, the shell improved the NCs stability, their charge carrier lifetime (from 12 to 8 ns) and their PLQY from 74 to 82 % thanks to an optimized surface passivation of the core.<sup>109</sup> In case of CsPbBr<sub>3</sub>/CsPb<sub>2</sub>Br<sub>5</sub> the carrier lifetime remained almost unchanged<sup>104</sup>, while when a shell of amorphous CsPbBr<sub>x</sub> was grown onto CsPbBr<sub>3</sub> NCs the PLQY was boost from 54 to 84 %105, after the shell formation, a broader absorption spectrum was observed while the Stoke shift decreased from 0.16 eV before the shell growth to 0.1 eV after. Similarly, TRPL revealed a decrease in the average lifetime from 16 to 9 ns after the shelling process, the PL spectrum showed an asymmetric shape, no important differences were observed in terms of lifetimes while an higher PLQY was measured.<sup>105</sup> Regarding FAPbBr<sub>3</sub>/CsPbBr<sub>3</sub>, a notable stability improvement of the PLQY (93 %) was recorded.<sup>108</sup>

*Li et al.* prepared<sup>110</sup> CsPbBr<sub>3</sub>/TiO<sub>2</sub> trough a wet chemical approach. In particular, the asprepared CsPbBr<sub>3</sub> NCs were treated with titanium butoxide giving a CsPbBr<sub>3</sub>/TiO<sub>2</sub> composite. Then, the reaction mixture was stirred for 3 h during which hydrolysis and condensation reactions allowed the formation of titania. Subsequently, a calcination removed the residual water. Similarly, *Loiudice et al.*<sup>111</sup> grew an alumina coating onto CsPbBr<sub>3</sub> trough colloidal atomic layer deposition. In particular, trimethylaluminum and pure oxygen were injected in a solution of CsPbBr<sub>3</sub> NCs. The TiO<sub>2</sub> shell remarkably enhanced the stability of the CsPbBr<sub>3</sub> NCs core towards polar solvents and UV light exposure. The heterostructure showed a decreased PLQY compared to the starting material and the lifetime of CsPbBr<sub>3</sub>/TiO<sub>2</sub> core/shell was shortened from 14.8 to almost 2 ns after TiO<sub>2</sub> shelling. Concerning the AlO<sub>x</sub> shell effect, it enhanced the PLQY and the charge carrier lifetime of the core compared to the shell free material due to successful defect passivation on the surface of the core.<sup>111</sup>

The encapsulation of CsPbBr<sub>3</sub> cores in SiO<sub>2</sub> shell is among the most exploited method to stabilize CsPbBr<sub>3</sub> NCs. 2 main synthetic approaches have been developed to obtain CsPbBr<sub>3</sub>@SiO<sub>2</sub>. The first one entails the encapsulation of the NCs in a silica matrix, while the second one grows a small shell around each core avoiding shell aggregation providing colloidal stability of the NCs. Both strategies were able to achieve high PLQY while the highest stability performance have been reached encapsulating the NCs with a silica matrix, although this kind of material cannot be exploited for techniques like inkjet printing where colloidal stability is required. Hence, a colloidally stable material is preferred but it is not easy to obtain in such a configuration a bright and stable material. In particular, it is not easy to grow thick shells without their coalescence into a matrix, further efforts are required in this direction. Zhang et al.<sup>104</sup> successfully obtained encapsulated CsPbBr<sub>3</sub> NCs in a SiO<sub>2</sub> network exploiting a template assisted strategy. They selected all-silicon molecular sieves which were soaked in a solution of PbBr<sub>2</sub> and CsBr and then dried at 80 °C. Then, the mixture was placed into a furnace at 600-900 °C where the collapse of the sieves determined the formation of the CsPbBr<sub>3</sub>-SiO<sub>2</sub>. Mai and co-workers<sup>105</sup> successfully incorporated CsPbBr<sub>3</sub> into a silica matrix exploiting molten salts. A mixture of KNO<sub>3</sub>, KBr and NaNO<sub>3</sub> was used as the molten salts medium where PbBr<sub>2</sub> and CsBr salts were inserted. Then, the mixture was heated up to 350 °C for 60 min. Concerning colloidally stable core@shell materials, Zhong et al.<sup>90</sup> exploited a ligand assisted reprecipitation method to prepare colloidally stable CsPbBr<sub>3</sub>@SiO<sub>2</sub> with a onepot synthesis. In brief, they prepared a precursor solution containing PbBr<sub>2</sub>, CsBr, OLAM and OA in DMF, then they injected it into toluene containing TMOS, after 2 hours under stirring the core@shell material were successfully prepared. Meng and co-workers<sup>93</sup> also involved a one-pot procedure where PbBr<sub>2</sub> was mixed with ODE and OA at 120 °C, then (3-aminopropyl)triethoxysilane (APTES) was slowly inserted. At 140 °C and in argon atmosphere, 2 mL of Cs-oleate were injected in the reaction mixture, such a reaction was quenched in a water-ice bath after 5 s. Lastly, an hot injection synthetic procedure with APTES was exploited by Song et al.<sup>114</sup> to prepare colloidally stable CsPbBr<sub>3</sub>@SiO<sub>2</sub>. Cs<sub>2</sub>CO<sub>3</sub>, OA and ODE were heated up to 120 °C in a N<sub>2</sub> atmosphere, then PbBr<sub>2</sub> and ODE were stirred in presence of OA, OLAM and APTES the solution was heated up to 170 °C in N<sub>2</sub> atmosphere. Cs-oleate was injected into the second precursor solution, this reaction was quenched in a water-ice bath after 5s. The CsPbBr<sub>3</sub>-SiO<sub>2</sub> prepared by Zhang et al.<sup>104</sup>

showed a PLQY of 63 % with almost no PL intensity change after 50 days of water exposure, while *Mai et al.*<sup>105</sup> measured an higher PLQY (90 %) and about 95 % PL retention after 30 days of immersion in water. The colloidal CsPbBr<sub>3</sub>@SiO<sub>2</sub> of *Zhong et al.*<sup>90</sup> showed a PLQY of 90 %, their stability was tested after only 40 minutes of ultrasonication in water, initially the PLQY grew and then decreased reaching basically the same value of the untreated CsPbBr<sub>3</sub>@SiO<sub>2</sub> after the 40 min of water exposure. The heterostructure of *Meng et al.*<sup>93</sup>, showed a PLQY of about 82 % and their PL intensity lost only 10 % after 6 h of storage in high humidity environment. Lastly, when *Song et al.*<sup>114</sup> dipped their core@shell in water, after 48 h CsPbBr<sub>3</sub>@SiO<sub>2</sub> still showed a bright luminescence undistinguishable from the pristine material by eyes.

In this study, two nanomaterials were combined together in a core@shell structure in order to improve the stability of the core. In the first case, the bright emissive lead halide perovskite (LHP) nanocrystals (NCs), were encapsulated into silica (SiO<sub>2</sub>) shells to improve their stability against heat, moisture, polar solvents, etc. Silica was identified as the ideal candidate because it is chemically inert, mechanically robust and its chemistry is widely known. Silica possesses a huge bandgap of  $\sim 8.5 \text{ eV}^{115}$  which makes it an electronic insulator, nevertheless, this is not a problem in down-converting LEDs since the CsPbBr<sub>3</sub>@SiO<sub>2</sub> material will absorb the blue light from the underlying blue LED and will emit green light. As a consequence, transparency in the blue and green ranges is required, silica meet this requirement since is transparent in the whole visible and in the low-energy part of the UV portion of the spectrum. The aforementioned properties are closely related to silica crystal structure that is based on tetrahedra of SiO4<sup>4-</sup>. Such tetrahedra can be connected in many different ways resulting in 11 crystalline and 2 amorphous polymorphs.<sup>116,117</sup> Despite the impressive number of possible organizations, only  $\alpha$ -quartz (the common quartz) is stable at ambient conditions, the other polymorphs require high temperature and/or pressure conditions.  $\alpha$ -quartz possesses a trigonal crystal structure where SiO<sub>4</sub><sup>4-</sup> tetrahedra are connected sharing corners as represented in *Figure* 5. Once crystalline silica is melted and then quickly cooled down it preserves its disordered organization also in the solid state, forming amorphous silica where tetrahedra are randomly connected. Such an amorphous organization can be easily obtained at the nanoscale without the need for high temperature. Indeed, already in 1967 Stöber et al.<sup>118</sup> developed a methodology to finely control the size of amorphous silica nanoparticles in the nano-micron range (0.05 to 2  $\mu$ m). This synthetic procedure exploited the sol-gel process starting from alkoxy silanes in the presence of basic catalysis. Such a synthetic approach remains the most common way to prepare silica NPs. However, many improvements have been discovered in the recent past and novel procedures introduced. For instance, the Stöber method exploits ethanol as a solvent, but exposure to polar solvents quickly destroys LHP NCs due to their strong ionic character; hence this approach cannot be undertaken, and a peculiar synthetic recipe is required.<sup>118</sup> As widely reported, silica can be grown in a non-polar medium such as toluene, whose moisture content is often sufficient to allow the hydrolysis of silica, an approach exploited in this study.<sup>119</sup>

#### 2.1.3. Experimental part

**Materials.** Cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, 99 %), lead bromide (PbBr<sub>2</sub>,  $\ge$  98 %), oleic acid (OA, 90 %), oleylamine (OLAM, 70 %), 1-octadecene (ODE, 90 %), ethyl acetate ( $\ge$  99.5 %), toluene ( $\ge$  99.7 %), anhydrous toluene (99.8 %), deuterated toluene, maleic anhydride (MANH, 99 %), tetraethyl orthosilicate (TEOS > 99.5 % and the 99.999 % for the airfree experiment), and tetramethyl orthosilicate (TMOS,  $\ge$  99 %) were purchased from Sigma Aldrich and used without any further purification, except for OA and OLAM, which were degassed prior to use in the air-free experiment. Milli-Q water was obtained from the Millipore purification station installed in the laboratory. The MANH stock solution (0.34 M) was prepared by dissolving 500 mg of MANH in 15 mL of toluene. The oleylammonium-iodide (OLAM-I) for anion exchange stability test was prepared according to *Akkerman et al.*<sup>120</sup>

**Preliminary experiments.** 400  $\mu$ L of a CsPbBr<sub>3</sub> solution in toluene (10 mg/mL) were treated every 10 minutes with different volumes of a solution prepared dissolving 11 mg of MANH in 8 mL of ethyl acetate. The global amounts of MANH solution added after every addition are the following: 10, 20, 40, 80, 160, 320, 1280  $\mu$ L. In a 1 mL cuvette, 5  $\mu$ L of the resulting solution was diluted in 1 mL of toluene for PL and absorption measurement (10 mm optical path). In order to remove the effect of the dilution onto the absorbance spectra they were rescaled multiplying each spectrum for (V<sub>0</sub> + V<sub>MANH</sub>)/V<sub>0</sub>, where V<sub>0</sub> is the volume of the pristine sample (400  $\mu$ L) and V<sub>MANH</sub> is the volume of MANH solution added.

**Experimental procedures for the CsPbBr**<sub>3</sub>@SiO<sub>2</sub> preparation. The synthetic protocols for the preparation of Cs<sub>4</sub>PbBr<sub>6</sub>, CsPbBr<sub>3</sub>, CsPbBr<sub>3</sub>@SiO<sub>2</sub> and CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs are reported in the following sections.<sup>84</sup> The reported procedures are for the optimized synthesis, hence there might be some possible variations among different samples. Unless otherwise stated, all procedures, except Cs<sub>4</sub>PbBr<sub>6</sub> NCs preparation and the air-free experiment, were carried out in air atmosphere, at room temperature (~21 °C) and the isolation of the synthesis product consisted in the addition of about 500 µL of ethyl acetate followed by centrifugation at 4000 rpm for 10 min, by the removal of the supernatant, by the drying of the inner walls of the vial from the remaining liquid with a piece of paper tissue and by the redispersion of the precipitate in 500 µL of toluene. The reaction time began when the MANH solution was added.

Cs4PbBr6 NC Synthesis. The Cs4PbBr6 NCs were prepared via the hot-injection method similarly to Akkerman et al.<sup>121</sup> In particular, 2 precursor solutions, one as a source of cesium and the other one for lead and bromine, were involved. The Cs solution was prepared by dissolving 400 mg of Cs<sub>2</sub>CO<sub>3</sub> in 8 mL of OA (25.2 mmol) at 100 °C in a 20 mL vial under stirring and N<sub>2</sub> flow forming a Cs-oleate solution. The Pb and Br solution was prepared in a pre-weight 20 mL vial by mixing 72 mg (0.2 mmol) of PbBr<sub>2</sub>, 5 mL (15.6 mmol) of ODE, 1.5 mL (4.5 mmol) of OLAM, and 0.2 mL (0.63 mmol) of OA. The vial was located into a machined aluminum block preheated to about 150 °C on top of a hot plate and kept under stirring for the whole synthesis. The PbBr<sub>2</sub> precursor solution was left under stirring for about 15 min at ~100-120 °C under vacuum for a few minutes until the solution stopped bubbling. At that point, the vacuum was replaced with nitrogen flux. When PbBr<sub>2</sub> was not visually observed anymore, the vial was transferred into a second hot plate, and the temperature of the reaction mixture was let to stabilize at 80 °C. At that point, 0.8 mL of the Cs-oleate precursor solution was quickly injected in the PbBr<sub>2</sub> mixture with a 1 mL syringe equipped with a 16G needle. An initially clear reaction mixture acquired a cloudy-white appearance over the course of  $\sim 30$  s. After an additional 30 s, the vial was moved into a water-ice bath to quench the reaction. The resultant turbidwhite solution was centrifuged at 4000 rpm for 10 min, the supernatant was discarded and the inner walls of the vial were dried from the remaining liquid with a piece of paper tissue. The dried sample was weighed again and redispersed in the amount of nonanhydrous toluene required to obtain a NCs concentration of 30 mg/mL (called NC stock solution).

**CsPbBr**<sub>3</sub>@**SiO**<sub>2</sub> **NC one-step and two-steps preparation.** The reagents involved in the two procedures are the same but added in a different order. In both cases in a magnetically stirred (~500 rpm) 4 mL vial, 100  $\mu$ L of Cs<sub>4</sub>PbBr<sub>6</sub> NC stock solution, 100  $\mu$ L of toluene and 20  $\mu$ L of OLAM were mixed together in this order. Then, for the one-step procedure alkoxysilane (30  $\mu$ L of TMOS or 100  $\mu$ L of TEOS), 1 mL of MANH solution, and, after a brief period of time (9 min for TMOS or 3 min for TEOS), 500  $\mu$ L of OA were further added. Unless differently specified, after a reaction time of 16 h for TMOS and of 3 h for TEOS the samples were centrifugated and redispersed. Whereas, for the two steps procedure and the conversion of Cs<sub>4</sub>PbBr<sub>6</sub> into CsPbBr<sub>3</sub> NC the MANH solution was added before than the silica precursor. Hence, after OLAM 1 mL of MANH solution was added and the dispersion was let react for 15 min to allow the conversion of Cs<sub>4</sub>PbBr<sub>6</sub> NCs into CsPbBr<sub>3</sub> NCs. The 2-steps procedure requires 100  $\mu$ L of TEOS and 500  $\mu$ L of OA which were left to react for about 16 h followed by centrifugation and redispersion.

Surface Passivation with PbBr<sub>2</sub> and second silica coating post-synthesis treatments onto CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs. A sample of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs prepared following the one-step procedure and another one with its crude reaction mixture were split equally into two 4 mL vials and centrifuged at 4000 rpm for 10 min. The supernatant was discarded, and the precipitate was redispersed in 250  $\mu$ L of toluene. Each vial was treated with 37.5  $\mu$ L of PbBr<sub>2</sub> solution (prepared dissolving 18 mg of PbBr<sub>2</sub> in 850  $\mu$ L of OA and 850  $\mu$ L of OLAM) and kept under stirring for the entire process. After 10 min, each sample was treated with 250  $\mu$ L of toluene and 50  $\mu$ L of TEOS (or 32.5  $\mu$ L of TMOS). The silica overgrowth was tested twice daily by withdrawing an aliquot of the sample and mixing it with OLAM-I under UV light. If the green-emissive sample turned orange-/red-emissive (substitution of Br<sup>-</sup> with  $\Gamma$ ),<sup>76</sup> the second shell growth was considered incomplete, hence 1  $\mu$ L of water was added to the reaction mixture to further hydrolyze the unreacted TEOS.<sup>120</sup> Once the halide exchange in the aliquot was suppressed (after 24–48 h for TEOS or 12–24 h for TMOS, depending on the batch), the CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs were collected by precipitation with ethyl acetate (250  $\mu$ L, followed by centrifugation at 4000 rpm for 5 min) and redispersion of the precipitate in 250  $\mu$ L of toluene.

#### 2.1.4. Results & discussion

#### 2.1.4.1. CsPbBr<sub>3</sub> – MANH preliminary experiments

CsPbBr<sub>3</sub> NCs solution in toluene (6.9·10<sup>-3</sup> mmol of CsPbBr<sub>3</sub> NCs) were treated with different amount of a solution of MANH in ethyl acetate (0.14 M). The MANH solution was added every 10 min to the same starting material and the sample was characterized collecting the PL and the absorption spectra after each addition, while TEM images were acquired only after the last additions. The ratio between MANH and CsPbBr<sub>3</sub> moles (r) was gradually increased from 0.01 to 6.50 turning the solution from transparent and strongly green emissive to turbid yellow and weak green emissive. In details, the absorption and the PL spectra do not show clear modifications in their position (Figure 7a, b, c), PL spectra undergo a global reduction of intensity (Figure 7c, d) when the MANH amount is increased. This behavior can be explained considering two effects. Firstly, the NCs lose their optical properties by adding MANH solution, in fact, the sample is less emissive when is seen by eyes under the UV lamp (Figure 7e, f) and when measured with the spectrophotometer. Secondly, the solution is more diluted because of the volume of MANH solution added and, since the volume of the sample in the cuvette is the same for all the measurements, the dilution affects the spectra. In order to clarify the effect of MANH and avoid the dilution contribution, the absorption spectra were rescaled considering the solubility effect, in this way each aliquot has the same concentration of the pristine material. The corrected absorption spectra (Figure 7b) show that increasing the MANH solution the absorption is basically unchanged. However, since the sample presents NCs with different sizes (Figure 7g, h, i, l), the spectra are affected by an error making less effective whatever conclusion about spectra intensities. TEM 34

images show that the NCs whose lateral size initially was 8-10 nm (*Figure 7g*) aggregate forming bigger crystals with a lateral size of ~100 nm after reaction with MANH. The 100 nm crystals basically do not grow more upon further MANH solution additions (*Figure 7h, i, l*).



Figure 7: The effect of MANH solution in ethyl acetate onto CsPbBr<sub>3</sub> NCs. (a) Absorption spectra as measured and (b) corrected taking into account the dilution effect (in the legend in brackets it is indicated the MANH solution volume added). (c) PL spectra and (d) PL peak intensity as a function of MANH-CsPbBr<sub>3</sub> moles ratio r. Pictures of the CsPbBr<sub>3</sub> NCs solution before (e) and after (f) MANH treatment, as seen without illumination (top) and under UV light (bottom), respectively. (g) TEM image of a typical pristine CsPbBr<sub>3</sub> sample (a different batch from the one involved for the described experiment), and (h, i, l) MANH treated samples with r 2.60, 3.25, and 6.50, respectively.

## 2.1.4.2. CsPbBr<sub>3</sub>@SiO<sub>2</sub> synthetic mechanism and further improvements

CsPbBr<sub>3</sub>@SiO<sub>2</sub> were prepared following 2 similar procedures from Cs<sub>4</sub>PbBr<sub>6</sub>NCs. The latter were synthesized trough the hot-injection method following the procedure reported in the experimental part (2.1.3.). They display a roughly spherical shape with a diameter of 11.7  $\pm$  1.3 nm (*Figure 8a*), a rhombohedral crystal structure (*Figure 8g*), the typical absorption peak at 314 nm (*Figure 8h*), and no PL emission.

In the first procedure, MANH and alkoxysilane were added consecutively to  $Cs_4PbBr_6$  NCs (*one-step procedure*) (*Figure 6, step 1* and 2 together) forming CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs. *Figure 8b* shows a bright field TEM (BF-TEM) image of one of the best CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs samples showing a clear core–shell morphology of the NC product where each shell has a core and conversely (additional image of other samples are reported in *Figure A1*, section 4.1.). The best core–shell morphology (called "best sample") was obtained with TEOS, while TMOS gave more reproducible results, since the latter was one of the most

important issues in CsPbBr<sub>3</sub>@SiO<sub>2</sub> synthesis, TMOS was selected in the optimized procedure. However, both precursors do not prevent the aggregation of the shells. HR-TEM imaging and elemental analysis with STEM-EDS on the best sample (prepared by *Dr. Riccardo Scarfiello*) revealed NCs composed of ~10 nm diameter single-crystal CsPbBr<sub>3</sub> cores coated by ~5–7 nm thick SiO<sub>2</sub> shells (*Figure 8c–e*). The CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs demonstrated green emission, with a PL peak centered at 507 nm and a full width at half maximum of ~20 nm (*Figure 8h*) and a low PLQY (~1–4 %). Its absorption spectrum showed one peak at lower (497 nm) and one at higher (314 nm) energies ascribable to the band edge absorption of CsPbBr<sub>3</sub> NCs and Cs<sub>4</sub>PbBr<sub>6</sub> NCs, respectively (*Figure 8h*). These results agree with X-ray diffraction (XRD) patterns (*Figure 8f*) where both CsPbBr<sub>3</sub> and Cs<sub>4</sub>PbBr<sub>6</sub> reflections are observed suggesting a partial conversion of Cs<sub>4</sub>PbBr<sub>6</sub> into CsPbBr<sub>3</sub>. The absence of other phases in the XRD pattern suggests the amorphous nature of the silica shell.


Figure 8: Morphological, structural and optical characterization of the best sample of starting Cs<sub>4</sub>PbBr<sub>6</sub> NCs and CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs prepared via the one-step procedure. (a) BF-TEM image of starting Cs<sub>4</sub>PbBr<sub>6</sub> NCs; dark spots are Pb<sup>0</sup> domains likely formed under the electron beam;<sup>122</sup> (b) BF-TEM image of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs; (c) HR-TEM image of a CsPbBr<sub>3</sub>@SiO<sub>2</sub> NC with an inset showing a fast Fourier transform of the CsPbBr<sub>3</sub> core, matching with the cubic CsPbBr<sub>3</sub> phase (ICSD code 97852);<sup>123</sup> (d) HAADF-STEM image of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs with (e) the corresponding color maps of the distribution of elements obtained with EDS from the sample area indicated by a white dashed box in (d); (f, g) XRD patterns of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs and pristine Cs<sub>4</sub>PbBr<sub>6</sub> NCs, respectively with powder diffraction reference for rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> (black bars, ICSD code 162158) and orthorhombic CsPbBr<sub>3</sub> (red bars, COD code 4510745); (h) PL and absorption spectra of starting Cs<sub>4</sub>PbBr<sub>6</sub> NCs and CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs.<sup>84</sup> Modified with the permission of Chemistry of Materials.<sup>84</sup>

In order to investigate the formation mechanism of the one-step  $CsPbBr_3@SiO_2$  NCs several aliquots of the reaction mixture were observed at TEM at different reaction times (*Figure 9*). TEM images suggested that the conversion of  $Cs_4PbBr_6$  into  $CsPbBr_3$  NCs happened before than the silica shell formation proving the non-contemporaneity of the 2 processes. In particular,  $CsPbBr_3$  NCs were clearly distinguished thanks to their cubic

shape already after about 2 minutes of reaction time (*Figure 9b*), while silica was only observed after 4 minutes (*Figure 9c*). After longer reaction times (2 h, 3 h and 16 h, *Figure 9d, e, f*, respectively), a more defined core@shell morphology was observed.



Figure 9: BF-TEM images of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs synthesized following the one-step procedure as a function of the reaction time. (a) Pseudo spherical Cs<sub>4</sub>PbBr<sub>6</sub> NCs were converted into (b) cubic-shaped CsPbBr<sub>3</sub> NCs after 2 min of reaction, (c) while silica was observed after 4 minutes together with CsPbBr<sub>3</sub> NCs, whose shape evolved to a rounded one; (d) after 16 h (end of the reaction), the CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs were observed. Scale bars are 100 nm. Modified with the permission of Chemistry of Materials.<sup>84</sup>

This result suggested the independency of the CsPbBr<sub>3</sub> NCs formation and of the SiO<sub>2</sub> growth, hence, the two processes were separated in the so-called *two-step procedure* (*Figure 6, steps 1* then 2). In particular, the MANH and the TEOS treatment of Cs<sub>4</sub>PbBr<sub>6</sub> NCs (*Figure 10a, f, g*) are separated by a time interval of 15 min during which the CsPbBr<sub>3</sub> NCs form. The latter showed an orthorhombic CsPbBr<sub>3</sub> phase together with Cs<sub>4</sub>PbBr<sub>6</sub> one as before. CsPbBr<sub>3</sub> NCs showed a lateral size of  $7.9 \pm 1.4$  nm (*Figure 10b, e*), a PL peak centered at 501 nm (*Figure 10g*), and a PLQY of ~15%. The addition of TEOS successfully prepared CsPbBr<sub>3</sub> NCs where silica shells touch together (*Figure 10c*), XRD pattern shows the presence of both CsPbBr<sub>3</sub> and Cs<sub>4</sub>PbBr<sub>6</sub> (*Figure 10d*) confirmed by absorption spectra, whereas the PL slightly red shifted (*Figure 10g*).



Figure 10: Morphological, structural and optical characterization of pristine  $Cs_4PbBr_6$ NCs,  $CsPbBr_3$  NCs obtained after the reaction with MANH, and  $CsPbBr_3@SiO_2$  NCs synthesized via the two-step procedure. (a–c) BF-TEM images of  $Cs_4PbBr_6$ , converted  $CsPbBr_3$ , and  $CsPbBr_3@SiO_2$  NCs, respectively. (d–f) XRD patterns of  $CsPbBr_3@SiO_2$ ,  $CsPbBr_3$ , and  $Cs_4PbBr_6$  NCs, respectively, together with the powder diffraction references of rhombohedral  $Cs_4PbBr_6$  (black bars, ICSD code 162158) and orthorhombic  $CsPbBr_3$  (red bars, COD code 4510745). (g) Optical absorption and PL spectra of pristine  $Cs_4PbBr_6$ ,  $CsPbBr_3$  as reacted with MANH, and  $CsPbBr_3@SiO_2$  NCs.<sup>84</sup> Modified with the permission of Chemistry of Materials.<sup>84</sup>

In analogy with earlier work of the Nanochemistry group,<sup>124</sup> in order to study the reaction mechanism ongoing, IIT researchers, before the work of the PhD candidate, analyzed at 1H and 13C NMR the reaction between MANH and OLAM in different molar ratios (*Figure A2*) the reaction between MANH and OLAM was corroborated by the formation of maleamic acid (pKa ~ 3.5–4.0).<sup>125,126</sup>

The 2-step procedure proved that it is possible to obtain CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs starting directly from CsPbBr<sub>3</sub> NCs, questioning the need of Cs<sub>4</sub>PbBr<sub>6</sub> NCs as a starting material. CsPbBr<sub>3</sub> NCs prepared trough the hot-injection method were exposed directly to TEOS and, in another experiment, to free OLAM, MANH and TEOS (*Figure 11a, b*), but in both cases no CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs were observed. It results that MANH-converted CsPbBr<sub>3</sub> NCs have a peculiar surface chemistry able to promote silica shell growth, hence Cs<sub>4</sub>PbBr<sub>6</sub> NCs are a required starting material. In addition, the 2-steps procedure was modified including a centrifugation and a redispersion in toluene of the as formed CsPbBr<sub>3</sub> NCs, then they were exposed to TEOS but no CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs were

detected (Figure 11c). This evidence proves that the core@shells form in the environment produced by the reaction of MANH with Cs<sub>4</sub>PbBr<sub>6</sub> NCs and free OLAM. Lastly, the onestep procedure was repeated in a nitrogen filled glove box involving anhydrous solvents, and no silica growth was seen also in this case (Figure 11d, further details in Figure A3). In agreements with the *Huang et al.*<sup>127</sup>, this finding suggests that TEOS is hydrolyzed by the water present in the regular toluene. In conclusion, there are crucial aspects for the formation of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs: Cs<sub>4</sub>PbBr<sub>6</sub> NCs, the reaction environment obtained after MANH reaction, and the presence of moisture. This experimental evidence leads to the formulation of a hypothesis about the reaction mechanism. It is widely accepted<sup>45</sup> that silica precursors, e.g. TEOS or TMOS, get protonated in acidic environment converting the -OH termination into  $-H_3O^+$  (*Figure 3*). The hydronium cation has a similar cationic radius (141 pm<sup>128</sup>, 115 pm<sup>129</sup>) compared to Cs<sup>+</sup> (186 pm<sup>129</sup>) and -NH<sub>4</sub><sup>+</sup> (148 pm<sup>129</sup>) present in the perovskite crystal structure. In fact, several studies hypothesized that the incorporation of hydronium cation inside the perovskite crystal lattice is theoretically possible.<sup>130,131</sup> Hence, it is possible to hypothesize that the hydronium cations could replace oleylammonium (or  $Cs^+$ ) at the crystal's surface removed by MANH reaction. This mechanism would explain the need for acidic environment and for peculiar CsPbBr<sub>3</sub> NCs surface chemistry obtained after MANH reaction for the core@shell formation.



Figure 11: Control experiments aimed to understand the conditions required for CsPbBr<sub>3</sub>@SiO<sub>2</sub> formation. (a) CsPbBr<sub>3</sub> NCs (synthesized via hot injection) dispersed in toluene after the reaction with TEOS. (b) CsPbBr<sub>3</sub> NCs (synthesized via hot injection) dispersed in toluene were exposed to MANH and TEOS in the presence of free OLAM. (c) CsPbBr<sub>3</sub> NCs (obtained from the reaction of Cs<sub>4</sub>PbBr<sub>6</sub> NCs with MANH) centrifuged, redispersed in toluene and treated with TEOS. (d) MANH converted CsPbBr<sub>3</sub> NCs still in their reaction environment were treated with TEOS in air-free conditions using anhydrous toluene. All the BF-TEM images were acquired after 16 h of reaction time.<sup>84</sup>

Both CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs prepared following the one and the two-step procedures showed two shortcomings: a low PLQY and a quick PL intensity quenching upon exposure to ethanol (*Figure 14a*). Since OLAM occupies some crystallographic positions.

In addition, the PL of another sample showed negligible variation within ~19 days (*Figure 12a*) after the exposure to the PbBr<sub>2</sub> solution showing that the PL enhancement is stable in time. There are 2 main possible reasons for the PL enhancement, the passivation of the NC surface or the conversion of the remaining  $Cs_4PbBr_6$  NCs into the bright CsPbBr<sub>3</sub> NCs. The boost of optical property was attributed to the surface passivation since the absorbance of CsPbBr<sub>3</sub> NCs did not increase after the treatment with PbBr<sub>2</sub> solution suggesting any further conversion of Cs<sub>4</sub>PbBr<sub>6</sub> NCs into CsPbBr<sub>3</sub> NCs (*Figure 12c*) while their PL was boosted by a factor of three (*Figure 12d*). The possibility to passivate the CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs surface strengthens the hypothesis of the presence of pores in silica.



Figure 12: PL intensity variation of CsPbBr<sub>3</sub>@SiO<sub>2</sub> after passivation treatments. (a) PL intensity enhancement of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs upon treatment with PbBr<sub>2</sub>/OA/OLAM solution. 100  $\mu$ L of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs, prepared following the 2-step procedure, were loaded into a cuvette filled with 1 mL of toluene and were treated with 15  $\mu$ L of a solution containing PbBr<sub>2</sub> (18 mg PbBr<sub>2</sub>, 850  $\mu$ l OA, 850  $\mu$ L OLAM). The black solid line shows the PL spectrum of PbBr<sub>2</sub>/OA/OLAM solution that contributes to the broad peak centered at 425 nm. (b) The same experiment was repeated by replacing the PbBr<sub>2</sub> solution with 15  $\mu$ L of Cs-oleate (400 mg Cs<sub>2</sub>CO<sub>3</sub>, 1,75 mL OA, 15 mL 1-octadecene (ODE), according to<sup>92</sup>). The black dashed line refers to the PL spectrum of Cs<sub>4</sub>PbBr<sub>6</sub> NCs treated with Cs-oleate (a control experiment demonstrating that Cs-oleate does not convert Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub>@SiO<sub>2</sub> was monitored over time. Modified with the permission of Chemistry of Materials.<sup>84</sup>

To deal with the low stability of CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs towards polar solvents, the CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs were exposed again to a silica source aiming at a thicker shell (*Figure 6, step 4*). The as-obtained CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs showed a thicker shell (*Figure 13a, c, further images in Figure A4*) as expected. Atomic-number contrast HAADF-STEM imaging and EDS mapping prove that the core is made of CsPbBr<sub>3</sub> NCs and the darker shell of silica (*Figure 13c*). The second silica growth step removed the unconverted Cs<sub>4</sub>PbBr<sub>6</sub> NCs as shown by the disappearance of the absorption feature at 314 nm (*Figure 7b*) and by the XRD pattern (*Figure 7d*). The PL peak was red shifted from 507 nm to 513 nm after the second silica coating, this behavior can be related with the removal of small CsPbBr<sub>3</sub> NCs or the further growth of CsPbBr<sub>3</sub> NCs from the consumed Cs<sub>4</sub>PbBr<sub>6</sub> NCs.



Figure 13: Structural, morphological and optical characterization of  $CsPbBr_3@SiO_2@SiO_2NCs$  and stability tests in ethanol. (a) Overview HAADF-STEM image, (b) absorption and PL spectra and their enlargement in the inset, (c) high-magnification HAADF-STEM image and corresponding EDS elemental maps, (d) XRD pattern of the CsPbBr\_3@SiO\_2@SiO\_2NC sample and the reference powder diffraction data for rhombohedral Cs\_4PbBr\_6 (black bars, ICSD code 162158) and orthorhombic CsPbBr\_3 (red bars, COD code 4510745).<sup>84</sup> Modified with the permission of Chemistry of Materials.<sup>84</sup>

The effect of the additional silica coating onto the stability was tested. CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs, CsPbBr<sub>3</sub>@SiO<sub>2</sub> NCs and CsPbBr<sub>3</sub> NCs were exposed to ethanol to evaluate the resistance towards polar solvents, to 470 nm illumination for the photostability, and to an iodine source for the chemical stability towards anion exchange. When CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs were immersed in ethanol they experienced a loss of 5% of their initial PL intensity after 9 days of ethanol exposure while the PL intensity of CsPbBr<sub>3</sub>@SiO<sub>2</sub>, CsPbBr<sub>3</sub> NCs converted with MANH and CsPbBr<sub>3</sub> NCs prepared trough hot-injection was quenched within 30 min of exposure (*Figure 14a*). It is worth to say that, before the beginning of the stability test, CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs were exposed to ethanol for 10 minutes in order to remove unprotected material and enhance the PL stability in presence of polar solvents. While, when CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs were exposed to a mixture of water and toluene the PL quenching was much faster than in

ethanol, a loss of 60% of the initial PL was recorded after about 30 min of exposure (Figure 14b). Regarding the photostability, when the samples were exposed to 1 h of continuous illumination of a 470 nm LED ( $I_{exc} = 100 \text{ mW} \cdot \text{cm}^{-2}$ ), the CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs retained 90 % of their initial PL intensity, slightly better than the 80% of CsPbBr<sub>3</sub>@SiO<sub>2</sub>. This performance is much higher than for both the MANHconverted and the hot injected CsPbBr<sub>3</sub> NCs that retained only about 25 % of the initial PL (already after 30 min in the case of hot injected CsPbBr<sub>3</sub> NCs) (Figure 14c). Lastly, the resistance towards anion exchange was tested exposing the samples to oleylammonium iodine (OLAM-I), an iodine source prepared according to<sup>120</sup>. It is widely accepted that iodine replaces bromine in the perovskite crystal causing a shift of the PL peak from green to red.<sup>132</sup> When CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> NCs were treated with OLAM-I the green PL peak increased in intensity in the first ~5 min, then steadily decreased. At the same time, from ~1 h onwards, a PL peak in the red spectrum range (~ 660 nm) gradually grew and shifted up to 675 nm after ~21 h. On the other hand, the CsPbBr<sub>3</sub> NCs synthesized via hot-injection showed a red shift of the PL peak in just a few seconds (Figure 14d, e, f). It is concluded that the double silica coating improves the resistance towards iodine exchange.

The CsPbBr<sub>3</sub>@SiO<sub>2</sub> synthesized in this work presents lower PLQY than the state of the art. In fact, single core-shell have been reported with a PLQY of ~90 % and the highest PLQY reported for CsPbBr<sub>3</sub> dispersed in a silica matrix is  $89\pm10$  %<sup>113</sup> while the one measured in this study was only 8 %. The ethanol stability reached in this work was pretty good, it is difficult to find comparable stabilities in the single shell material, while the matrixes achieved even higher stability with negligible PL variation after 50 days of immersion in water<sup>112</sup>. However, from a chemical view-point, this study is interesting since exploits the poorly studied reactivity of surface capping ligands in a novel way and the phase transformation from Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub> to let the desired reaction happen. Hopefully, such an approach will be useful to let LHP NCs react with selected molecules or to favor ligand exchange, ligand stripping, etc.



**Figure 14:** Stability tests. (a) comparative quenching of PL intensity over time for four nanomaterials exposed to ethanol: CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub>, CsPbBr<sub>3</sub>@SiO<sub>2</sub>, CsPbBr<sub>3</sub> converted (MANH) and CsPbBr<sub>3</sub> prepared trough colloidal synthesis (hot-injection). (b) The relative variation of the maxima of the PL spectra as a function of the treatment time for CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> when exposed to a heterogeneous mixture of toluene and water. (c) The relative variation of the maxima of the PL spectra intensity (integrated PL spectra) as a function of exposure time for CsPbBr<sub>3</sub>@SiO<sub>2</sub>, CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> (MANH) and CsPbBr<sub>3</sub> (hot-injection) exposed to 470 nm LED for 30-60 min. (d) Green PL peak intensity variation as a function of the exposure time for CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> and CsPbBr<sub>3</sub> NCs prepared trough hot-injection. (e, f) PL spectrum variation after 1 μL OLAM-I addition for CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> and CsPbBr<sub>3</sub> NCs (hot-injection), respectively. (g, h) Images after the OLAM-I treatment of CsPbBr<sub>3</sub>@SiO<sub>2</sub>@SiO<sub>2</sub> and CsPbBr<sub>3</sub> NCs (hot-injection), respectively.<sup>84</sup> Modified with the permission of Chemistry of Materials.<sup>84</sup>

# 2.2. Zn<sub>(1-x)</sub>Mg<sub>x</sub>O thin film via chemical bath deposition for PV

# 2.2.1. Project overview

As described in the introduction, PV is one of the most promising solutions to address climate change. Scientists have been studying several photoactive materials in order to boost solar cells efficiency and stability, decreasing the module price and the energy consumed to fabricate them. The first PV technologies that have been developed are made of silicon and are called *first generation* PV. They consist of single-junction solar cells made of mono-crystalline or poly-crystalline silicon. First generation PV is currently leading the solar cell production, in fact, about 80% of the cells available in the market are silicon cells. The strengths of silicon PV are its high-power conversion efficiency (PCE, among the highest between all PV technologies) and long certified working life, both of which are features strongly related to decades of development. On the other hand, the main drawbacks of silicon PV regard its energy and labor-intensive manufacturing process that requires high temperatures and the rigidity of the panels that cannot be bent. The second generation PV was developed in order to address the flaws of the first generation. Those technologies exploit thin films that require considerably less active material (thus less energy and labor) and is amenable to flexible configurations. There are 3 main technologies in this class which are CdTe, CIGSe, and amorphous silicon. The third generation PV tries to preserve the thin film organization of the second one but increasing the efficiency of the device in order to compete with mono and poly-crystalline silicon modules.<sup>133</sup> It includes solar cell technologies like microconcentrators, quantum dot, multijunction, etc.<sup>134</sup>

CIGSe technology offers remarkable values compared to Silicon one. For instance, CIGSe bandgap can be tuned changing the ratio between In and Ga and Se and S. Generally, the first strategy is involved which allows to change the bandgap from 1.1 eV (CuInSe<sub>2</sub>) to 1.7 eV (CuGaSe<sub>2</sub>).<sup>135</sup> The deposition temperature required for CIGSe is lower than for Silicon paving the way for a cheaper and greener manufacturing process.<sup>136</sup> CIGSe solar cells have been experienced an impressive efficiency growth from ~6 % in 1976 to about 23 % in 2019 by Solar Frontier.<sup>137,138</sup> Such an improvement has been obtained thanks to the overall improvement of the whole cell architecture. Following the light path, a CIGSe solar cell is made of a top electrode of ZnO:Al, a resistive window layer made of i-ZnO or Zn<sub>1-x</sub>Mg<sub>x</sub>O, the CIGSe p-type material that is coupled with a n-type CdS buffer layer prepared via chemical bath deposition (CBD) and a back contact made of molybdenum, typically sitting on a glass or flexible polymeric substrate. The shorter lifespan of CIGSe technology compared to silicon one makes CIGSe more expensive than silicon which is currently the main motivation for the large supremacy of

the latter in PV market. Secondly, CIGSe solar cells present a toxic CdS layer in the device architecture. For this reason several alternative buffer layers have been proposed  $(Zn(O,S)^{139}, Zn_{1-x}Sn_xO^{140}, Zn(O,S,OH), Zn(O,S,OH)/Zn_{1-x}Mg_xO, etc.)$  which sometimes gave comparable or even higher efficiency compared to CdS as shown in Table A1. Remarkable examples are Zn(O,S,OH)/Zn<sub>1-x</sub>Mg<sub>x</sub>O double buffer layer which showed enhanced efficiency, Voc, Jsc and FF compared to the CdS reference achieving the record efficiency of 23.35 % higher by 0.4 % absolute efficiency showed by CdS.<sup>138</sup> In(O,OH,S) reported a 12.55 % efficiency, while the corresponding CdS gave only 12.10 % thanks to an higher  $J_{sc}$ .<sup>141</sup> In<sub>2</sub>S<sub>3</sub> buffer layer showed the same 12.9 % efficiency of CdS with slightly higher Voc and FF, but slightly lower Jsc compared to CdS.<sup>142</sup> Also Zn<sub>0.8</sub>Mg<sub>0.2</sub>O displayed comparable efficiency than CdS, 18.1 and 18.2 % respectively because of an higher  $J_{sc}$  a lower V<sub>oc</sub> and FF.<sup>143</sup> Zn(Se,OH)/Zn(OH)<sub>2</sub> reported a 14.2 % efficiency very close to the CdS reference value of 14.4 % according to an higher J<sub>sc</sub> and lower FF than CdS.<sup>144</sup> Other alternative buffers like Zn<sub>(1-x)</sub>Sn<sub>x</sub>O, ZnTiO, Zn(O,S), Zn(OH)<sub>2</sub> and ZnO showed a lower efficiency compared to CdS (for further details see section 4.4.).<sup>139,144-147</sup> Other remarkable performance obtained with alternative buffer layers are a 19.7 %<sup>148</sup>, 19.1 %<sup>149</sup>, 18.8 %<sup>150</sup> efficiency from a chemical bath deposited Zn(O,S) further examples are reported in *Table 2A*<sup>151</sup>. The reasons for the higher efficiency of some alternative buffer layers compared to CdS are generally identified in the larger bandgap of the alternative buffers and in its tunability, a degree of freedom which is not allowed in case of CdS. The control over the position and the width of the bandgap is crucial to optimize the band alignment within the solar cell, in fact, in order to minimize charge recombination, it is crucial that electrons and holes can travel from the active layer to the respective electrode without encounter any potential barrier.

As remarked by the recent record efficiency achieved in 2019 by replacing CdS with  $Zn(O,S,OH)/Zn_{1-x}Mg_xO$  double buffer layer in a CIGSSe solar cell, the understanding and the improvement of the interface between the absorber material and the buffer plays a key role in the device optimization underlying the need for further studied on this topic.

 $Zn_{1-x}Mg_xO$  was selected as an alternative buffer layer since it already showed its suitability as a buffer layer in CIGSe technology when prepared trough sputtering<sup>143,152</sup> and atomic layer deposition<sup>153</sup>. Tuning the Mg amount the bandgap of  $Zn_{1-x}Mg_xO$  bandgap can span from about 3.3 eV of ZnO to about 3.9 eV when  $x = 0.48^{154}$  and in principle even to more than 7.0 eV<sup>155</sup> since this modification is almost entirely related to the shift of the valence band minimum towards lower energies, the Mg amount control allows a precise band alignment among valence band minimum with potentially positive effects on the device performance.<sup>152</sup>

In this work  $Zn_{1-x}Mg_xO$  buffer layers have been prepared trough CBD for this purpose. This project was developed at INL in the Laboratory for Nanostructured Solar Cell headed by Dr. Sascha Sadewasser, PhD. The starting procedure involved for  $Zn_{(1-x)}Mg_xO$  was optimized by the master student Diego Alejandro Garzon<sup>156</sup> starting from the method reported by *Kokotov et al.*<sup>157</sup> he also participated during the preparation of  $Zn_{(1-x)}Mg_xO$ thin film with some experimental work, sharing opinions, etc. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) measurements were performed by Francesco Soggia at DCCI. The modification of the order of the regents was investigated thanks to the help of Dr. Chiara Lambruschini and Dr. Andrea Galatini.

# 2.2.2. Intrinsic & doped ZnO: physical, structural and morphological properties

ZnO is a direct bandgap (~3,4 eV) semiconductor oxide with unique chemical and physical properties involved in many fields such as optoelectronics, catalysis, etc. In particular, ZnO absorbs UV light and reemits it in the UV-VIS range, it is highly biocompatible, low toxic and chemically stable, which are all properties that allow successful applications in UV absorption, antibacterial treatments, catalysts, photocatalysts, liquid crystals displays and solar cells.<sup>158–166</sup> These properties are closely connected to the ZnO crystal structure that can be cubic zinc blende, wurtzite, or cubic rock salt as depicted in *Figure 15*. The wurtzite crystal structure is the most common since it shows the higher stability under typical working conditions.<sup>167</sup> In particular, ZnO has a hexagonal lattice with a P63mc space group, and lattice parameters a = b = 0.3296 nm and c = 0.52065 nm. Zn<sup>2+</sup> and O<sup>2-</sup> have a tetrahedral coordination that results in a noncentral symmetric structure composed of positively charged layers alternated with negatively charged ones. In fact, the difference in electronegativity between Zn and O makes ZnO between ionic and covalent materials.<sup>168</sup>



Hexagonal wurtzite Cubic zinc blende Cubic Rock salt

*Figure 15: Crystal structure of ZnO polymorphs.* From left to right hexagonal wurtzite, cubic zinc blend and cubic rock salt.

As a result of this crystallographic organization, polar surfaces perpendicular to the c axis display different surface energies than non-polar ones parallel to the same axis. In other words, the crystallographic structure gives rise to a normal dipole moment and a polarization along the c axis. These structural properties strongly influence the crystal habit. In fact, it is widely reported in the literature<sup>169,157</sup>, and confirmed in this study, that ZnO crystals can grow with a peculiar columnar shape. Such a behavior can be justified comparing the relative growth rates in the different crystallographic directions. In fact, the slower the growth along a particular crystallographic direction, the larger the plane perpendicular to that direction.<sup>170</sup> Since polar surfaces (0001, Figure 16b) are thermodynamically less stable than non-polar ones (e.g. 1100, 1010, *Figure 16a*) due to the unbalanced surface charge, they have a higher tendency to rearrange to minimize energy. As a result, the growth rate is higher along the (0001) plane than along the other directions<sup>171</sup>, hence the columnar growth will be favored. However, the polar and high energy (0001) facet is generally not observed at Field Emission Scanning Electron Microscopy (FE-SEM) while the non-polar and low energy  $(1\overline{1}00)$ ,  $(10\overline{1}0)$  and  $(10\overline{1}1)$ are typically displayed<sup>164–166</sup> (*Figure 18e-i*). This behavior can be justified considering that the faster facet to form (0001) eventually grows itself out of existence leaving behind the lower growth rate facets  $(10\overline{1}0)^{172,173}$ . Consequently, the  $(1\overline{1}00)$  and the  $(10\overline{1}1)$  are generally observed at FE-SEM. However, the (0001) facet can be stabilized and preserved in the final product (*Figure 18e*).<sup>174</sup>



Figure 16: Schematic of the columnar growth of ZnO. Schematic of a ZnO column showing the (a)  $(1\overline{1}00)$ ,  $(10\overline{1}0)$  and  $(10\overline{1}1)$  non-polar low energy facets and (b) (1100) polar high energy facet.

Concerning the electronic properties, the most common crystallographic defects in ZnO are the oxygen vacancies ( $V_0^0$ ). In fact,  $V_0^0$  has the lowest formation energy compared

to other kinds of defects in  $ZnO^{175}$ . It was believed that V<sub>0</sub> are responsible for the native n-type character of ZnO.<sup>176</sup> However, it was later shown that  $V_0$  generate deep donor levels in ZnO, which means that their energy state is far below the conduction band minimum (CBM). In particular, the energy level of the CBM (E<sub>cbm</sub>) minus the energy level of the defect (E<sub>d</sub>) is it reported as 0.5  $eV^{177}$ , 1  $eV^{178}$ , or 1.4  $eV^{179}$ .<sup>176</sup> Since the bandgap of ZnO is  $3.37 \text{ eV}^{180}$ , such levels are much deeper than for shallow defects such as the Zn interstitial donor ( $E_{cbm}$  -  $E_d = 0.050$  eV). Since thermal energy of room temperature is insufficient to promote the electrons from such deep levels to the conduction band,  $V_0$  are not expected to influence the ZnO semiconductor character. On the contrary, a shallow donor is close enough to the CBM that electrons can be easily promoted to the CB even at room temperature, this makes Zn interstitials the most probable source of n-type character in ZnO.<sup>176</sup> This property is exploited to fabricate optoelectronic devices, such as solar cells, LEDs, etc. However, often the native n-type character of ZnO is not sufficient for optoelectronic applications, hence ZnO has been widely doped to properly tune its conductivity (e.g.  $Zn_{(1-x)}Al_xO$ , etc.)<sup>181</sup>, as well as its bandgap (e.g.  $Zn_{(1-x)}Mg_xO$ ,  $Zn_{(1-x)}Sn_xO$ , etc.)<sup>181–184</sup>.

The crystallographic sites occupied by Mg in ZMO is still under debate (*Figure 17*), in some works it is reported that substitutional Mg is favored according to the ionic radius similarities between  $Zn^{2+}$  and  $Mg^{2+}$ , other authors suggest that Mg occupies interstitial and substitutional sites.<sup>185,186</sup> ZMO has a non-negligible ionic character, even stronger than in ZnO due to the lower electronegativity of Mg compared to Zn (1.31 and 1.65, respectively), hence his crystal structure was represented in *Figure 17* both involving covalent and ionic radii. In both cases the radii of Zn and Mg are very similar making possible the Mg incorporation.



*Figure 17: How different radii influence ZnO crystal structure. Hexagonal wurtzite represented considering covalent radii (a) and ionic ones (b).* 

CIGSe solar cells require buffer layers with a suitably large bandgap in order to enable an appropriate band alignment between the top contact and the CIGSe layer. Buffer layers also need to be highly transparent to allow light to be absorbed by the CIGSe, properties that the traditionally involved CdS buffer layers do not possess. To this end, CBD was involved to grow Zn<sub>(1-x)</sub>Mg<sub>x</sub>O thin films, due to their low/non toxicity and tunable electronic properties changing the Mg content.  $Zn_{(1-x)}Mg_xO$  thin films have been already synthesized following several techniques (e.g. atomic layer deposition<sup>187</sup>, radio frequency reactive magnetron sputtering<sup>188</sup>, thermal evaporation<sup>189</sup>, pulsed laser ablation<sup>190</sup>, CBD<sup>174</sup> itself, etc.). Some of the aforementioned synthetic procedures were able to incorporate a large amount of Mg e.g. 62 %<sup>190</sup> (measured trough ICP) without any phase separation, such a doping control is still very far from CBD deposited ZMO reported in the literature (Table A3, section 4.5.). In fact, only few papers report high concentration of Mg: Maekawa et al.<sup>154</sup> reports a 48 mol% of magnesium without secondary phase formation, despite this, as noted by Winkler et al.<sup>174</sup>, XRD did not show any variation in position (they should experience a shift towards higher 2 theta degrees according with the lower radius of Mg compared to Zn), in addition the author tried to reproduce such a procedure without success. Chawla et al.<sup>191</sup> reported a 30 mol% Mg content but no measurement were provided to support such a value involving ammonia as the complexing agent. Winkler et al.<sup>174</sup>, measured with ICP an Mg content as high as 2.1% exploiting citric acid (CA) and ammonia. Presat et al.<sup>192</sup> obtained a 1.5% Mg quantified trough SEM-EDS exploiting ammonia capability to complex Mg and Zn. Lastly, Polat et al.<sup>193</sup>, reported a 0.85 mol% from SEM-EDS measurement exploiting hexametilentetrammine. As a result, no or few reports successfully obtain a reliable Mg concentration higher than 2 mol% underlying the need for further understanding of the best conditions for Mg incorporation.

Despite this CBD is typically selected to prepare buffer layers for CIGSe solar cells due to its scalability and its mild deposition conditions that minimize damage to the underlying photovoltaic material.

#### 2.2.3. Experimental part

**Materials.** Potassium permanganate ( $\geq 99.0\%$ ), n-butanol (99.9%), ammonium hydroxide solution (28-30%), magnesium acetate tetrahydrate ( $\geq 99\%$ ), zinc sulfate heptahydrate ( $\geq 99\%$ ), were purchased from Sigma Aldrich. The solutions were prepared using ultrapure water produced by Milli-Q Advantage A10 system (Millipore) with resistivity of 18.2 M $\Omega$ ·cm.

### **Experimental procedures.**

**SLG cleaning and activation.** SLG with an area of ~1 inch<sup>2</sup> and ~1 mm thickness were sonicated for 20 min in DI water at room temperature, followed by 20 min of sonication in DI water and MicroSon soup at 60 °C. The substrates were rinsed several times with DI water and lastly, they were sonicated again for 20 min in DI water at 60 °C. Following *Kokotov et al.*<sup>157</sup>, the as-cleaned SLG was activated by dipping it into a 50 mM KMnO<sub>4</sub> aqueous solution, to which 2.5  $\mu$ L of n-butanol were added per mL of KMnO<sub>4</sub> solution. The SLG container was covered with an Al foil and placed in a water bath at 85 °C for 20 min. After that, the activated substrates were rinsed 10 times, sonicated for 20 min and stored in DI water.

Zn<sub>(1-x)</sub>Mg<sub>x</sub>O thin films preparation through chemical bath deposition. Zn<sub>(1-x)</sub>Mg<sub>x</sub>O (ZMO) thin films were prepared starting from the synthesis jointly developed with Diego Garzon at INL for the chemical bath deposition of Zn<sub>(1-x)</sub>Sn<sub>x</sub>O<sup>156</sup> that was likewise optimized from *Kokotov et al.*<sup>157</sup> The chemical bath was prepared by weighting the desired amount of magnesium acetate tetrahydrate in a 100 mL beaker, followed by its dissolution in DI water. Then various amounts of Zn<sup>2+</sup>, ammonia (NH<sub>3</sub>), ethanolamine (EA) and CA stock solutions were added in this order. The water volume was adjusted to obtain a final volume of 75 mL. Zn<sup>2+</sup>, NH<sub>3</sub>, EA and CA stock solutions were prepared by dissolving 14.37 mg of zinc sulphate heptahydrate, 15 mL of NH<sub>3</sub> solution at 28-30 wt.%, 25 mL of EA and 0.9606 g of CA, respectively, in 50 mL of DI water (100 mL for CA stock solution). Once all the components were introduced, two cleaned and activated substrates (see "SLG cleaning and activation" section of the experimental part for further details) were typically inserted in the bath, the beaker was closed with an Al foil and placed in a thermostatic water bath at 92 °C for various reaction times. The film growth was monitored by eye after 15 min, 30 min and 1h 30 min; when a film was clearly distinguishable they were removed from the bath, rinsed with DI water, dried with an N<sub>2</sub> gun, sonicated for 15 min at 55 °C, and lastly dried again with an N<sub>2</sub> gun.

# 2.2.4. Zn<sub>1-x</sub>Mg<sub>x</sub>O (ZMO) thin films results & discussion

In the following, the Mg content of the ZMO films is expressed as the MMZ ratio ([Mg]/([Mg]+[Zn])). The standard experimental procedure described 2.2.3. was modified by varying the Mg and CA contents with the final aim to maximize the Mg incorporated in the layer.

The Mg content was tuned (MMZ of 1, 5, 25, 35, 50 %) without adding any CA, only EA (1.618 M) and ammonia solution (0.220 M) were present as complexing agents. The asprepared films were investigated with XRD, UV-VIS and FE-SEM. Films were obtained

only when the nominal MMZ was equal to or lower than 25% (Figure 18a, b). It is worth to note that the highest nominal Mg content that yielded a film (25%) required a longer reaction time (~1 h 30 min - 2 h) than those performed with 1 % and 5 % MMZ (15 min), suggesting that a higher nominal MMZ slows down the ZMO growth kinetics. The XRD pattern of ZMO thin films showed a reasonable match with the ZnO reference with no extra reflections. UV-VIS spectra showed the expected threshold at about 375 nm related to the intrinsic material bandgap (~3.3 eV) (Figure 18c, d). FE-SEM images displayed a columnar morphology in all the samples (Figure 18e-i), which is a typical crystal habit for ZnO reported in the literature<sup>157,173,194</sup>. It is worth noting that samples with 1% and 5% MMZ obtained after 15 min of reaction time showed different exposed facets compared to 1% 30 min and 25% 120 min. In particular, experiments run with 1% and 5% MMZ after 15 min of reaction display columns ending with a pyramidal shape, due to the presence of terminal ( $\overline{1011}$ ) and (0001) facets (*Figure 18a*), whereas in the cases of 1% 30 min and 25% 120 min, the terminal facet is the flat (0001) represented in *Figure* 18b. Consequently, a longer reaction time and a higher nominal MMZ appear to stabilize the (0001) facet with a resulting truncated columnar shape. Despite such a stabilization, each column is separated from the others and this space might be detrimental for the solar cell device because it could lead to short circuit between the underlying CIGSe and the top electrical contact.



Figure 18: Characterization of ZMO thin films grown without CA with different MMZ and reaction times. (a, b) XRD patterns and the correspondent hexagonal zincite reference (HighScore 96-900-8878, black bars) and (c, d) UV-VIS spectra after 15 min

and longer reaction times, respectively. (*e*, *f*, *g*, *h*, *i*) FE-SEM images of the samples that display deposited material on the top of the soda lime glass substrate.

In order to improve the compactness of the film, CA was introduced in the chemical bath as a complexing agent following the study of Winkler et al.<sup>174</sup> who reported a more compact ZMO layer and an higher % of Mg incorporated after CA addition. A starting concentration of 0.005 M CA was employed in the presence of EA (1.618 M) and ammonia solution (0.220 M). The nominal MMZ was tuned from 0 to 50 % and the assynthesized films were characterized by XRD, UV-VIS and FE-SEM. XRD patterns showed a reasonable match with the hexagonal zincite reference, except for 1 % MMZ 30 min which showed an additional peak at about 40  $^{\circ}$  2 theta (*Figure 19a*, *b*). The 10 % MMZ showed a strong modification in the XRD pattern due to a preferential orientation, compared to the samples with lower nominal Mg, probably because in the latter the columnar morphology is still predominant. UV-VIS spectra show interference fringes in all the samples probably originated by the strong morphological modification induced by CA (Figure 19c, d). Higher nominal MMZ caused a red-shift of the transmittance threshold in UV-VIS spectra probably related to the higher Mg content that enlarges the band gap. FE-SEM showed a columnar morphology with enhanced lateral growth compared to the case without CA (Figure 19e - m). At higher MMZ (10%) the lateral coalescence of the columns resulted in a pseudo-cuboidal morphology as depicted in Figure 19m.



Figure 19: Characterization of ZMO thin films grown with a CA concentration of 0.005 *M*, different MMZ and reaction times. (a, b) XRD patterns and the correspondent

hexagonal zincite reference (HighScore 96-900-8878, black bars) and (c, d) UV-VIS spectra after 15 min and longer reaction times, respectively. (e-m) FE-SEM images of the samples with some deposited material on the top of the substrate.

The enhanced lateral growth provided by CA is consistent with the literature where this behavior is motivated considering that the (0001) facet presents the highest density of positive charges and the highest energy, hence the 3 binding groups of citrate anions can efficiently passivate this facet. Preferential binding slows down the growth of the (0001) facet promoting the lateral growth of the columns as qualitatively shown in *Figure 20a*- $c^{173,174}$ . Then, it is proposed that the columns intersect together yielding the pseudo cubical morphology (*Figure 20d*).



Figure 20: Schematic depiction of the different morphologies observed in ZMO thin films with the corresponding FE-SEM images. The crystallographic orientations of the facets refer to the axis reported in each image as shown in the legend at the top of the figure. (a) Truncated pyramid terminated columns obtained without CA at 1% MMZ after 15 min of reaction time. (b) Truncated columns prepared as in (a) but after 30 min of reaction. (c) Laterally connected columns synthesized with 0.005 M CA solution at 5% MMZ after 30 min of reaction. (d) Cuboidal morphology obtained from the coalescence of columns as a result of 30 min of reaction in a 10% MMZ bath with CA 0.010 M.

Notably, when CA (0.005 M) was involved without EA, no film was obtained for any of the MMZ tested (1%, 5%, 10%), even after 1 h 30 min of reaction time. In other words, both EA and CA are required for the formation of a compact thin film. Given that CA improved the compactness of the layer, and since both CA and EA are essential, the concentration of CA was tuned at a fixed MMZ (10%) and in the presence of EA (1.618 M), in order to further explore its beneficial role onto ZMO. The as-prepared films were analyzed by XRD, UV-VIS and FE-SEM. XRD patterns showed a reasonable match with hexagonal zincite reference. UV-VIS spectra showed enhanced transparency and a small

blue-shift of the threshold at 375 nm with increasing CA content (*Figure 21b*). Interference fringes appeared in UV-VIS spectra when CA was added; this peculiar behavior is hypothesized to originate from the strong morphological modification obtained upon CA addition. In fact, similarly to previous experiment, FE-SEM analyses showed that the columnar shaped crystals prepared without CA were replaced by cuboidal shaped ones with a higher substrate coverage, which is expected to be beneficial for photovoltaic applications. It is worth to note that doubling the CA concentration, the compactness of those cuboidal shaped crystals increased (*Figure 21d, e*).

The described samples were dissolved in HCl and analyzed with ICP-AES order to quantify the amount of Mg incorporated in the films. In agreement with the study by *Winkler et al.*<sup>174</sup>, the analysis revealed that the actual Mg content within the film is about 1 order of magnitude lower than the nominal MMZ of the solution. Notably, the measured MMZ slightly grew increasing the CA amount and the nominal MMZ until about 0.55% MMZ (CA 0.010 M, MMZ 10 %) (*Figure 21c*), underlying the beneficial role of CA also from a compositional viewpoint. Unexpectedly, when the film with the highest measured Mg concentration was analyzed at X-ray photoemission spectroscopy (XPS) it showed an MMZ of 18 % a value almost forty times higher than measured by ICP-AES. Since the latter is sensitive to the whole volume of the sample, whereas XPS is a surface sensitive technique, the presence of a bilayer was hypothesized. This hypothesis was also supported by the Tauc plot calculated from the transmittance spectrum<sup>195</sup> that showed two linear regions, one corresponding to a band gap of ~3,2 eV compatible with ZnO and the other one of ~4,2 eV that might originate from Zn and Mg oxide or hydroxide.



Figure 21: Characterization of ZMO thin films grown without CA and with a concentration of CA equals to 0.005 and 0.010 M. (a) XRD patterns and the correspondent hexagonal zincite reference (HighScore 96-900-8878, black bar) and (b) UV-VIS spectra. (c) MMZ measured by ICP-AES as a function of the nominal MMZ; the values for the CA-free deposition at 1 and 5% MMZ and for the 0.005 M at 1% MMZ are not displayed because they are lower than the detection limit of the instrument. (d) Tauc plot obtained from transmittance spectra of the sample with the highest MMZ. (e-g) FE-SEM images.

In conclusion, the preparation of ZTO thin films through CBD has been investigated in order to develop a non-toxic buffer layer for CIGSe solar cells alternative to CdS. It turned out that CA complexing agent was able to improve the compactness of the layer along with its transparency and an increased Mg incorporation. The highest MMZ obtained of 0.55 % is not so far from the 2.1 % reported by *Winkler et al.*<sup>174</sup>. Further tuning of the CA concentration and investigation of different complexing agents could be valuable strategies to overcome the 2 % MMZ limit, with the final aim of achieving a homogeneous layer and a fine control over the Mg concentration.

The large precipitation in solution has detrimental effects onto the yield of the entire deposition process. In the procedure developed here (called *solution A*) it is difficult to minimize such a precipitation, because it occurs already at the beginning of the process when NH<sub>3</sub> is added. Interestingly, it was observed that a modification of the order of the reagents successfully yielded a transparent solution without any precipitate (*solution B*). In fact, when the precursor solutions were added in the following order: Mg<sup>2+</sup>, Zn<sup>2+</sup>, H<sub>2</sub>O DI, CA, EA and NH<sub>3</sub>, the precipitate formed upon the addition of EA is redissolved once

NH<sub>3</sub> is introduced, yielding a transparent solution. Such a bath was kept sealed at room temperature for a long time to investigate its potential capability to deliver a thin film. However, after 48 h, neither films nor precipitates were observed in the solution. Then, the same bath was heated up to 92 °C in order to favor the decomposition of the complexes. As expected, 30-40 min later, a white precipitate formed in the solution. The total homogeneous nucleation suggested a kinetically driven process that did not allow the desired heterogeneous nucleation, suggesting the need for a slower heating ramp. In order to explain which complexes form in the solution, speciation diagrams were plotted through *Hyss software*<sup>196</sup> with data reported from the NIST database<sup>197</sup>. Hyss software investigate chemical equilibria calculating the variation of the concentration of the species under study as a function of the pH. For instance, it calculates the concentration of the free reagents by solving the mass-balance equation taking into account the equilibrium constant for metal-complex equilibria (log $\beta$ ), the stoichiometric coefficients of the species and their analytical concentration provided by the user (*Table A4*, section 4.5.)<sup>196</sup>.

In particular, the concentrations of the solution under study were inserted in the software together with the log $\beta$  values at the temperature desired. Log $\beta$  and formation enthalpies of metal-ligand complexes at room temperature were critically selected from NIST database e.g. stability constants measured at a similar ionic strength than the solution under study were chosen. When required, according to *Winkler et al.*<sup>174</sup> the integrated Van't Hoff equation was exploited to calculate the log $\beta$  value at 92 °C (details in section 4.3.). *Figure 22a-d* shows the dissociation of the ligands as a function of the pH, revealing that the ligands are present in their deprotonated form in the system under study (pH~11).



*Figure 22: Speciation of ligands computed with Hyss software. (a) Ammonia, (b) EA, (c) CA (expressed in percentage of the ligand) and (d) the molar concentration of all the previous species are plotted as a function of the pH.* 

In order to understand which complexes are present in the solution, all the possible complexes between the three ligands and the two metals (Mg and Zn) reported in the NIST database were plotted as a function of the pH. Each plot reports all the complexes formed for a particular species (Mg, Zn, CA and EA) whose concentration is expressed in % of that specie. In case of Mg (*Figure 23a*), from low to high pH Mg<sup>2+</sup> firstly forms a complex with citrate anions (Mg-cit)<sup>-</sup>, secondly with EA (Mg-EA)<sup>+</sup> and lastly with hydroxyl groups  $[Mg_4(OH)_4]^+$  and  $[Mg(OH)]^-$ . In the case of Zn (*Figure 23b*), from low to high pH, Zn<sup>2+</sup> firstly forms a complex with citrate (Zn-cit)<sup>-</sup> then also by hydroxyl groups  $([Zn_2(OH)_3]^+$  and  $[Zn(OH)_4]^{2-}$ ). From OH<sup>-</sup> point of view (*Figure 23d*), strong -OH complexes form at a pH higher than 11. Looking at EA speciation, only the dissociation of the ligand is visible, whereas no complexes are formed (Figure 23e). From the citrate point of view (Figure 23f), it is clear that (Zn-cit)<sup>-</sup> forms at lower pH than (Mg-cit)<sup>-</sup> and at a pH higher than 6  $(cit)^{3-}$  is released due to the hydroxyl complexes formation. Lastly, when the concentration of all the species is plotted as a function of the pH (*Figure 23g*), the large abundance of EA and successively of NH<sub>3</sub> in their protonated and deprotonated forms is clearly evident, and suggests that EA and ammonia do not participate in the complexation of metals despite their large excess; hence their contribution is mainly related with their influence onto the pH. As a consequence,  $Zn_{(1-x)}Mg_xO$  can probably be deposited without EA in agreement with *Winkler et al*<sup>174</sup>. In conclusion, the transparency of the system under study (pH ~ 11) is related to the formation of (Mg-cit)<sup>-</sup>, (Mg-EA)<sup>+</sup> and  $[Zn_2(OH)_3]^+$  (*Figure 23a, b*).

Similar speciation plots can be prepared also for solution A, where a precipitate forms in solution by taking into account the formation of the solid including in the model their solubility equilibrium and the corresponding solubility product constant. Such a study, including the identification of the precipitate in solution, is still under development. As a preliminary hypothesis, it is proposed that the precipitates observed in solution A are oxides and/or hydroxide of Zn and/or Mg and that the remaining Zn and Mg cations form complexes with the ligands in solution similarly to solution A. The slight enhancement of the Mg content in the film increasing the CA amount from 0 to 0.010 M (Figure 21c) suggests that CA is one of the complexing agents for Mg, similarly to solution B. The only Mg complex with a higher log $\beta$  is  $[Mg_4(OH)_4]^{4+}$  that, according to Figure 23a, should form from pH 12 up. Despite the lower logβ (*Table 1*), the same plot suggests the formation of [Mg(OH)]<sup>+</sup> from pH 10-11, which may also form. In conclusion, it is hypothesized that Mg forms complexes with citrate and hydroxyl groups in solution A, whose decomposition releases  $Mg^{2+}$  that heterogeneously nucleates onto the substrate in the form of hydroxide. As widely accepted, at 92 °C hydroxides can spontaneously dehydrate forming oxides<sup>198</sup>. Regarding Zn, since most of the citrate anions are already complexing Mg, it is proposed that zinc-hydroxy complexes ( $[Zn_4(OH)_4]^{4+}$ ) form due to their higher logβ compared to zinc-EA (*Table 1*), zinc-ammonia complexes and any other selected from NIST database (Table A4), similarly to solution A (Table A4).



Figure 23: Speciation of the equilibria in chemical bath deposition solution computed with Hyss software. (a) Magnesium, (b) zinc, (c) ammonia, (d) EA, (e) CA, (e)  $OH^-$  (and  $H^+$ ), and (g) all of them.

Species	Logβ (25 °C)	Logβ (92 °C)	ΔH (kJ/mol)
[Mg-cit] <sup>-</sup>	3.52	3.26	8
[Mg-EA] <sup>2+</sup>	0.24		
$[Mg(NH_3)_2]^{2+}$	0.15	0,31	-5
[Mg4-OH4] <sup>4+</sup>	17.1	24	
[Mg-OH] <sup>+</sup>	2.225	1.84	12
[Zn-cit] <sup>-</sup>	7.835	7.58	8
[Zn-EA] <sup>2+</sup>	2.50	4.12	-50.45
$[Zn(NH_3)_4]^{2+}$	9.175	11.15	-61.5
[Zn4(OH)4] <sup>4+</sup>	16.23	10.19	188*

*Table 1.* Average values of metal-complex stability constants from NIST database<sup>197</sup>.

\*Selected from<sup>199</sup>

# 2.3. TiO<sub>2</sub> thin films via spin coating and oxygen vacancies control for PV

# 2.3.1. Project overview

TiO<sub>2</sub> (titania) is widely exploited in photovoltaics. In perovskite solar cells it is often employed as an electron transporting layer and as the n-type semiconductor in the p-n or in the p-i-n junction.<sup>17</sup> Recently, titania thin films have been finding applications also in Sb<sub>2</sub>Se<sub>3</sub> solar cells as a replacement to the toxic n-type CdS buffer layer.<sup>200</sup> Sb<sub>2</sub>Se<sub>3</sub> is an emerging p-type semiconductor whose laboratory-scale solar cells have already achieved 10.12 % record efficiency.<sup>201</sup> In this study, titania thin films were prepared through spin coating and treated post-synthesis with diluted HCl in order to generate and control V<sub>0</sub>.<sup>202</sup> It is proposed to enhance the Sb<sub>2</sub>Se<sub>3</sub> solar cell efficiency by controlling the n-type carrier density of the TiO<sub>2</sub> by tuning its V<sub>0</sub> concentration.

This study was developed in collaboration with CNR-IMEM Parma and in particular with Dr. Stefano Rampino, PhD, and the PhD candidate Giulia Spaggiari who performed the FE-SEM and Raman analysis reported in this study. The supervison over the XPS spectra analysis and the acquisition of the spectra were done by *Dr. Letizia Savio, PhD.* Lastly, transmission spectra were acquired with the help of *Dr. Paola Lova*.

# 2.3.2. Titania: structure, morphology and physical properties

TiO<sub>2</sub> is a semiconductor material that natively displays n-type doping and a bandgap in the UV spectral range (3.0 - 3.2 eV depending on the crystal structure). TiO<sub>2</sub> is transparent in the visible and is a low/non-toxic and chemically stable compound amenable to relatively easy and cheap synthesis. Such properties make titania widely used in photocatalysis<sup>203</sup>, self-cleaning surfaces in air<sup>204</sup>, lithium ion batteries<sup>205</sup> and solar cells<sup>17,206</sup> The aforementioned properties derive from its structure; titania presents three main polymorphs (Figure 24): rutile, anatase and brookite. In all the three structures each Ti<sup>4+</sup> cation is surrounded by six O<sup>2-</sup> anions, forming an octahedron. Rutile is the thermodynamically stable phase with least distorted octahedra and with a tetragonal crystal structure. Anatase possesses a structure similar to rutile, but with highly distorted octahedra. The brookite phase has an orthorhombic crystal structure and is the least stable among the three structures. Compared to rutile, anatase has a shorter distance between titanium ions and a longer distance between titanium and oxygen ions. This structural anisotropy generates different mass density and band structure. Regarding the morphology, titania thin films have been prepared without and with controlled mesoporosity spanning from disorganized pores to hexagonal and cubical arrangements.206



Figure 24: Crystal structure of TiO<sub>2</sub> polymorphs.

Scientists discovered that selected defects, namely  $V_o$ , can boost the properties of titania in terms of photocatalytic activity. Subsequently, several ways to control the defects in TiO<sub>2</sub> have been investigated: HCl treatment<sup>202</sup>, annealing in hydrogen atmosphere<sup>207</sup>, laser treatment<sup>208</sup>, and many others.<sup>209</sup> V<sub>o</sub> can largely influence the properties of titania. In fact, upon oxygen removal, the crystal structure rearranges in order to reinforce the bonds between the remaining atoms, causing the reduction of the Ti-O bond length<sup>209–211</sup> and resulting into the octahedral distorsion.<sup>212</sup> Optically, titania free from V<sub>o</sub> would absorb only in the UV range, whereas V<sub>o</sub> generate defect levels within the bandgap, causing light absorption in the visible range that attributes a color to the typically colorless titania<sup>213,214</sup>. Electronically, the lower the oxygen content the larger the octahedral distortion, which pushes titanium ions closer to each other enhancing its conductivity.<sup>215</sup>

Regarding the effect of the dopant onto the device performance, when selected dopants are incorporated in a sufficient amount, they are able to strongly modify the bandgap of  $TiO_2^{216}$ , another effect is related to the charge density of the layer which can influence the recombination probability. Lastly, the dopant generally has a slightly different atomic/ionic radius with the consequent favored enhanced or decreased material stress with the overhanging layer. As an example, the doping of titania with Nb improves the carrier collection but decreases the open circuit voltage because of the Fermi level is moved closer to the middle of the bandgap of  $Sb_2S_3$ .<sup>217</sup> Further doping of Nb enhance the recombination resistance, the authors identified the origin of this behavior in the decreasing of the TiO<sub>2</sub> defects and capacitance at the interface of  $Sb_2S_3$  layer. In addition, a decreasing of the conductivity and of the series resistence were observed at the

 $FTO/TiO_2$  interface. It is supposed that the effect of the oxygen vacancy onto the device performance is very similar to the one of the aforementioned dopants.

### 2.3.3. Experimental part

**Materials.** Titanium ethoxide, ethanol and HCl were purchased from Sigma Aldrich and used without any further purification. DI H<sub>2</sub>O was produced in the laboratory.

# **Experimental procedures.**

TiO<sub>2</sub> thin films via sol-gel spin coating. Titania thin films were spin coated onto 1 inch<sup>2</sup> fluorine doped SnO<sub>2</sub> (FTO) substrate trough a sol-gel spin coating technique following *Luther et al.*<sup>17</sup> First, FTO substrates were cleaned by sonicating them in DI water, ethanol and acetone for 10 minutes each in this order at room temperature. The sol-gel precursor solution was prepared by mixing 325  $\mu$ L of titanium ethoxide, 5 mL of ethanol, and 125  $\mu$ L of DI water that caused the formation of a white precipitate; hence, a few droplets of HCl 35% were added until the solution turned clear again. The resulting sol-gel precursor solution was magnetically stirred for 1 h and stored in a fridge before use. The spin coater was set at 3000 rpm for 25 s, loaded with a cleaned FTO substrate and run at 3000 rpm for 25 s; after 5 s, 200  $\mu$ L of the sol-gel precursor solution were dynamically supplied with a micropipette onto the spinning substrate. For the deposition of additional layers, the same amount of solution was statically supplied onto the top of the sample and then spin coated at 3000 rpm for 20 s. When all the layers were prepared, the samples were annealed in a muffle in air at 115 °C and 450 °C for 30 min each (heating ramp: 20-25 °C/min).

Acid treatment for V<sub>0</sub> formation. In order to yield a controlled concentration of V<sub>0</sub> inside the TiO<sub>2</sub> thin films, the samples were exposed to three acidic solutions according to *Zhang et al.*<sup>202</sup>. In three different crystallization dishes, DI water and HCl 35% were mixed to obtain 2, 4 and 6 M solutions. Titania thin films were immersed horizontally in each aforementioned acidic solutions for about 12 h and 30 min; during the entire treatment, the dishes were covered with parafilm. Then, samples were rinsed with DI water several times, annealed in a muffle in air at 500 °C for about 1 h, cooled down in air outside of the muffle, and lastly stored in argon atmosphere inside a glove box.

**XPS fitting procedure.** The data analysis of the XPS spectra was performed trough CasaXPS software by calibrating the spectra respect to C 1s peak (284.8 eV) and the spectra were analyzed as follow. Ti peaks were fitted with GL(50) functions (50% Lorenzian and 50% Gaussian function) by imposing the area of 1/2 peak as double of the one of 3/2 peak for both Ti<sup>3+</sup> and Ti<sup>4+</sup>. The FWHM of the Ti<sup>3+</sup> 1/2 was imposed equal to

the one of Ti<sup>4+</sup> 1/2, the same was done for Ti<sup>4+</sup> peaks. Peak positions were imposed according to reported values with the possibility to change of 0.2 eV. O peaks were fitted with GL(30) imposing the peak position of ~531.2, ~532.25 eV allowing a variation of 2.0 eV, 0.2 eV, for V<sub>o</sub>, -OH, respectively. Oxygen vacancy and O<sup>2-</sup> peaks were fit simply imposing GL(30) as functions.

**Thermodynamic calculations.**  $G^{0}(T)$  for the Ti<sub>x</sub>O<sub>y</sub> reported in *Eq.* 24-28, was calculated according to *Eq.* 22:

$$G^{0}(T) = 10^{3}[H_{(+)} - S_{(+)}y - ay(\ln(T) - 1) - b/2y^{2} - c/2y^{-1} - d/6y^{3}]$$
(22)

Were  $H_{(+)}$ ,  $S_{(+)}$ , a, b, c, d are tabulated coefficients<sup>218</sup>, y is 10<sup>-3</sup> T (temperature, K). The plots in *Figure 30a*, *b*, *c*, *d* are prepared with this equation (22).

Then also the effect of pressure was considered (Eq. 23)

$$G^{0}(T) = z \cdot (10^{3}(H_{(+)} - S_{(+)}y - ay(\ln(T) - 1) - b/2y^{2} - c/2y^{-1} - d/6y^{3})) + x/yRT \cdot \ln(P)$$
(23)

Where z is the number of moles of the reagent in equations 23-27, R is 8.31 J/(K·mol), x are the number of moles of oxygen and y are the atoms in the O<sub>2</sub> molecule (y = 2.) The pressure P is in bar. The plot in *Figure 30e* is obtained with this equation (23).

#### 2.3.4. Results & discussion

TiO<sub>2</sub> spin coating procedures are widely available in the literature, but often the volume of solution required to completely and homogeneously cover the rotating substrate is not reported. Firstly, the procedure published by Luther et al.<sup>17</sup> (details in section "2.3.3. Experimental part") was tested with various volumes of precursor solution from 50 µL to 350  $\mu$ L onto an FTO substrate of 1 inch<sup>2</sup> area followed by a drying process at 3000 rpm for 25 s. By visual inspection, the best coverage of the substrate was obtained when 200 µL were involved. Then, it was observed that the film quality was not really affected by the drying process, hence it was removed. An additional spin coating step was introduced in order to improve the coverage of the substrate onto the edges. In particular rotation speeds of 4000, 5000 and 6000 rpm for 25 s were tested in three different samples, but the substrate coverage remained almost unchanged. Hence the final procedure involved for the preparation of all the sample of this study entails a rotation speed of 3000 rpm for 25 s and 200  $\mu$ L of precursor solution which are supplied after 5s of rotation if not differently specified. Secondly, the long stirring time of the precursor solution reported by Luther et al.<sup>17</sup> (48 h) was optimized. Titania thin films onto FTO substrates where spin coated after magnetically stirring for 1, 24 and 48 h and analyzed with Raman spectroscopy for phase identification and with SEM-EDS to check any evident thickness modification (*Figure 25a*). In fact, due to the limited thickness of the samples (from ~50 to ~450 nm depending on the sample) XRD do not give enough signal to determine the phase of the material. As a consequence, Raman spectra were acquired at University of Parma by *Dr. Giulia Spaggiari* and revealed the presence of anatase phase in all the samples. Since the EDS penetration depth is much higher than the sample thickness and since the samples only contain Ti in the form of titania, Ti at% measured at SEM-EDS was considered proportional to the titania thickness. SEM-EDS analysis showed a limited variation of Ti at% (~10 % maximum modification at both 10 and 20 kV) (*Figure 25b*). Since no important changes were observed among the samples, the shortest stirring time (1 h) was selected for further experiments.



Figure 25: Study of the precursor solution stirring time, thickness and heating/cooling speed. (a) SEM-EDS data and (b) Raman spectra of  $TiO_2$  thin films prepared after a stirring time of 1, 24 and 48 h. (c, d) FE-SEM and SEM images for thickness estimation and (e, f) for cracks analysis.

The films thickness was controlled involving multiple spin coating steps. FE-SEM analysis performed at CNR-IMEM of Parma estimated a thickness from ~400 nm (*Figure 25c*) to ~50 nm (*Figure 25d*) when 3 and 1 layers were deposited, respectively. FE-SEM analysis also showed the presence of cracks onto the titania surface (*Figure 25e*) which were considered the reason of short-circuit of the Sb<sub>2</sub>Se<sub>3</sub> solar cells grown onto TiO<sub>2</sub> prepared at CNR-IMEM in Parma. In order to deal with this issue, the heating speed of the annealing steps from room temperature to 115 and then to 450 °C was decreased from ~25 °C/min to ~10 and ~5 °C/min and the air quenching of the sample from 450 °C to room temperature was replaced by a slower cooling inside the furnace. The new samples

showed a lower quantity of cracks especially in the center of the film as shown by *Figure* 25*f* which was collected in one of the regions of the sample with the highest density of cracks, despite this, their number is still lower than before *Figure 25e*.

In order to control the n doping density of the material, following *Zhang et al.*<sup>202</sup>, titania thin films spin coated onto FTO were dipped into HCl at different concentrations (2, 4 and 6 M) (further details in section 2.3.3. "*Acid treatment for V<sub>o</sub> formation*") and analyzed at XPS before and after the treatment. XPS surveys (*Figure 26*) showed the presence of both Ti and O, together with impurities i.e. Sn, Na, C probably coming from the substrate (Sn), from handling contamination (Na) and from the precursor solution (C).



Figure 26: XPS surveys before and after 4M HCl treatment.

High resolution XPS spectra of titanium and oxygen show clearly two peaks for both untreated and treated samples. All the aforementioned peaks were fitted in order to quantify the V<sub>o</sub> and under-coordinated titanium atoms potentially present. In the case of titanium fitting, when only the two components corresponding to Ti<sup>4+</sup> 3/2 and Ti<sup>4+</sup> 1/2 were involved, the resulting fit was rather different compared to the experimental data. Consequently, multiple functions simulating uncoordinated titania were introduced and the giving the best fit with the lowest number of components was obtained involving four components corresponding to Ti<sup>4+</sup> 3/2, Ti<sup>4+</sup> 1/2, Ti<sup>3+</sup> 3/2 and Ti<sup>3+</sup> 1/2. In the case of oxygen fit, two components resembling O<sup>2-</sup> and another one for any other oxygen specie (called other oxygens) provided a reasonable approximation of the experimental data. In order to quantify the amount of other oxygens and under-coordinated titania, the area of the corresponding peak was divided by the sum of all of them (*Figure 27a, b*). The acid treatment slightly enhanced the relative amount of under-coordinated Ti, leaving almost unchanged the other oxygen peaks together with the poor intensity of Ti<sup>3+</sup> peaks

compared to  $Ti^{4+}$  suggests that, if present, the formation of  $V_o$  and under-coordinated titania is much lower than the one reported by *Zhang et al.*<sup>202</sup>



Figure 27: XPS spectra before and after 4M HCl treatment. Ti 2p high-resolution spectrum for (a) pristine sample, (b) treated and the (c) corresponding normalized  $Ti^{3+}$  $\frac{1}{2}$  and  $Ti^{4+}$   $\frac{1}{2}$  relative intensity expressed as their peak area divided by the sum of  $Ti^{3+}$   $\frac{1}{2}$ and  $Ti^{4+}$   $\frac{1}{2}$  peak areas. O 1s high-resolution spectrum for (d) not treated sample, (e) after HCl 4M exposure and the (f) corresponding normalized other oxygens and O<sup>2</sup>-relative intensity expressed as their peak area divided by the sum of O<sup>2-</sup> and other oxygens peak areas. O 1s high-resolution spectrum for (g) pristine, (h) treated with acid and (i) corresponding normalized V<sub>o</sub>, -OH and O<sup>2-</sup> relative intensity expressed as their peak area divided by the sum of the area of the three peaks.

In order to investigate the reaction mechanism experienced by  $TiO_2$  during the acid treatment, the high-resolution XPS spectra of O 1s peaks were fitted with an additional peak in order to quantify the amount of V<sub>o</sub> reported at about 531.1 eV and hydroxyl groups (-OH), at about 532.2 eV (*Figure 27g, h*) (details in section "2.3.3."). Again, in

order to quantify the effect of the treatment onto the samples, the area of the peak of  $O^{2-}$ ,  $V_0$  and -OH was divided by the sum of the three (*Figure 27i*). It was found that the  $O^{2-}$  slightly decreased after the treatment,  $V_0$  remained basically unchanged and -OH slightly increased. The minimal variation of the peak areas often within the error of the measurement (both for Ti 2p and O 1s) requires further analysis in order to clarify the actual effect of the acid onto TiO<sub>2</sub>. However, in order to explain the experimental evidence observed, a tentative reaction mechanism is proposed (*Figure 28*). HCl dissociate in water favoring the formation of H<sub>3</sub>O<sup>+</sup> cations which react with surface oxygens (*Figure 28a*) forming hydroxyl groups. For each -OH group formed in this way a Ti atom decreases its coordination number from 4+ to 3+ (*Figure 28 b*). This simplistic model gives a qualitative explanation of the slight enhancement of Ti<sup>3+</sup> and -OH species according to the experimental evidence observed in XPS spectra.



**Figure 28:** TiO<sub>2</sub>-HCl reaction mechanism. Proposed reaction mechanism of TiO<sub>2</sub> surface and  $H_3O^+$  formed upon dissociation of HCl in water: a)  $H_3O^+$  interacts with titania surface forming (b) and hydroxyl group onto the surface and under-coordinated Ti ion.

There are several possible reasons to justify the low amount of defects generated by the acid treatment. First of all, (i) The HCl exposure is followed by an annealed at 500 °C for 1 h, defects may diffuse in the volume of the sample making them impossible to detect by XPS (analysis sensitive to the top most ~1-3 nm). Secondly, (ii) the V<sub>o</sub> might be passivated by the air exposure before the XPS measurement since they were exposed for some days (~2-4) in air, lastly, (iii) the treatment may not work properly. UV-VIS transmittance measurements (*Figure 29*), acquired with the help of Dr. Paola Lova, onto other acid treated TiO<sub>2</sub> samples (prepared with a different heating and cooling speed) did not reveal any appreciable absorption by the V<sub>o</sub> and Ti<sup>3+</sup>, that absorb light in the visible

when present in a sufficient amount<sup>213</sup>, leaving the last two hypothesis (ii, iii) the most probable.



Figure 29: Optical characterization of titania thin films prepared with different heating speed. (a) 5 °C/min and (b) 10 °C/min.

The understanding of the stability regions of TiO<sub>2</sub> and under-coordinated titania species might be very useful to control titania defectivity. Hence, the chemical potential of Ti<sub>x</sub>O<sub>y</sub> species was plotted as a function of temperature (*Figure 30a, b, c, d, Eq. 22*) according to *Eq. 24-28* (balanced in order to have the same number of atoms among them). Then, the role of O<sub>2</sub> pressure was taken into account by plotting the Gibbs free energy of Ti<sub>x</sub>O<sub>y</sub> species as a function of temperature and O<sub>2</sub> partial pressure (iii) (*Figure 30f, Eq. 23*). In the first two cases (i, ii), Ti<sub>x</sub>O<sub>y</sub> curves do not intersect each other, suggesting that the conversion of one phase into the other is not thermodynamically favored. Also the effect of O<sub>2</sub> partial pressure was also considered (iii), but again the resulting 3D surfaces do not show any intersection among them. In principle, the aforementioned plots suggests that thermodynamically the only stable phase at ambient condition is TiO<sub>2</sub> meaning that all the others are metastable. However, this thermodynamic study is still under development and requires further efforts in order to be exploited for the experimental work.

$$24\text{TiO}_{2(s)} \to 6\text{Ti}_4\text{O}_{7(s)} + 3\text{O}_{2(g)} \tag{24}$$

$$6Ti_4O_{7(s)} \rightarrow 8Ti_3O_{5(s)} + O_{2(g)}$$
 (25)

$$8\text{Ti}_{3}\text{O}_{5(s)} \rightarrow 12\text{Ti}_{2}\text{O}_{3(s)} + 2\text{O}_{2(g)}$$
<sup>(26)</sup>

 $12Ti_2O_{3(s)} \rightarrow 24TiO_{(s)} + 6O_{2(g)}$  (27)

$$24\text{TiO}_{(s)} \to 12\text{Ti}_2\text{O}_{(s)} + 6\text{O}_{2(g)} \tag{28}$$



Figure 30: Investigation of the thermodynamic stability of several  $Ti_xO_y$  species. Standard chemical potentials as a function of temperature for (a)  $TiO_2$  (Eq. 22), (b)  $Ti_4O_7$ (Eq. 23), (c)  $Ti_3O_5$  (Eq. 24), and (d) TiO (Eq. 25) decomposition reactions. (e) Gibbs free energy variations as functions of the  $O_2$  partial pressure and temperature. The Gibbs free energy of  $TiO_2$  was multiplied by  $10^{-1.5}$  to allow an easier comparison.
## **3.** Conclusions

In this study  $SiO_2$  nanostructured shells,  $Zn_{(1-x)}Mg_xO$  and titania thin films were investigated in three projects briefly summarized hereunder.

A SiO<sub>2</sub> shell was grown onto CsPbBr<sub>3</sub> NCs exploiting a novel synthetic route. In details, IIT researchers discovered that when the non-emissive Cs<sub>4</sub>PbBr<sub>6</sub> NCs are exposed to a solution of MANH in toluene the solution turned bright green emissive due to the formation of CsPbBr<sub>3</sub> NCs after few minutes. Such an interesting effect was further developed by Dr. Riccardo Scarfiello, who introduced TEOS in the reaction mixture and successfully prepared CsPbBr<sub>3</sub>@SiO<sub>2</sub> core@shell. By studying the reaction product as a function of time it was found that the two reactions ongoing (i.e. NCs conversion and silica shell growth) happen at different times, in fact, Cs<sub>4</sub>PbBr<sub>6</sub> NCs are firstly converted into CsPbBr<sub>3</sub> NCs and then the silica shell grows. The two reactions were successfully separated by postponing the addition of the silica precursor after the CsPbBr<sub>3</sub> NCs formation, yielding similar CsPbBr<sub>3</sub>@SiO<sub>2</sub> compared to the product obtained in the first process. The reaction mechanism was further investigated by IIT researchers trough NMR analysis revealing the formation of maleamic acid when MANH and OLAM were mixed together. This analysis suggested that the OLAM capping ligand of Cs<sub>4</sub>PbBr<sub>6</sub> NCs may react with MANH determining the formation of CsPbBr<sub>3</sub> NCs. The author investigated the reaction mechanism by involving alternative reaction condition e.g. air free atmosphere and different starting materials like a toluene suspension of CsPbBr<sub>3</sub> NCs prepared by hot-injection or by Cs<sub>4</sub>PbBr<sub>6</sub> conversion with MANH. The crucial role of Cs<sub>4</sub>PbBr<sub>6</sub> as a starting material was identified due to the related acidic reaction environment formation which is supposed to catalyze the silica growth. Also, the need for air atmosphere was observed since air-free environment prevents the silica growth. Regarding CsPbBr<sub>3</sub>@SiO<sub>2</sub> properties, it possesses weak light emission properties and poor stability that were improved by post-synthesis treatments which boosted the PL by almost eight times, and enhanced the material resistance towards ethanol, UV light and anion exchange. Despite the enhancement, light emission and stability properties did not reach the state of the art making clear that the importance of the work is mainly in the chemical processes ongoing rather than in the final product. In fact, this project paves the way for a deeper investigation and understating of the surface reactivity of LHP NCs which hopefully will favor the development of new reactions between LHP NCs and selected organic molecules with potential impact on many crucial aspects in optoelectronic materials such as ligand exchange, controlled NCs aggregation, enhanced passivation, enhanced NC surface reactivity, etc.

Concerning ZnMgO thin film preparation trough CBD, the procedure developed by *Kokotov et al.*<sup>157</sup> and successively modified by Diego Garzon at INL to prepare ZnO was further investigated to incorporate Mg. In brief, Mg and Zn salts are mixed in presence of EA and ammonia at basic pH and the nominal Mg concentration was tuned. The samples were studied at different reaction times and showed the hexagonal zincite crystal structure typical of ZnO, high transparency (~80 %) until about 400 nm and a columnar morphology, but unfortunately a low amount of Mg is incorporated in the film (0.15% MMZ was the highest value measured by ICP). Hence, following the example of Winkler et al.<sup>174</sup> CA was added in the bath in order to increase the amount of Mg incorporated and to enhance the lateral growth of the material, as reported in the literature. The addition of CA enhanced the layer transparency, strongly improved the lateral growth of the columns allowing the preparation of a more compact layer and slightly increased the Mg incorporated in the layer with the consequent bandgap widening. Interestingly, the sample with the highest Mg concentration in the film was analyzed with both ICP and XPS revealing a strong difference in the Mg composition (0.55 % and 18 %, respectively). Since ICP measures the whole volume of the sample and since XPS investigates only its surface, such a result suggests the formation of a bilayer or a concentration gradient perhaps originated by a slower deposition kinetics of Mg compared to Zn. Hence, an higher incorporation of Mg might be obtained by controlling how fast Mg<sup>2+</sup> is released in the solution. In order to better elucidate which complexes form and how to decrease the homo-nucleation, the equilibria in solution were computed with the help of Hyss software. The latter was particularly suitable to understand which complexes may be present when the reagent order was tuned. In fact, it was discovered that by introducing CA and EA before NH<sub>3</sub> the resulting solution was stably transparent at room temperature paving the way for a decreasing of the homo-nucleation and allowing an easy investigation of the complexes at play through Hyss software. It was found that, at the pH of the transparent solution (~11), Mg forms complexes mainly with EA and CA. It is believed that a deep understanding of the coordination chemistry ongoing will strongly decrease the precipitation in solution hence improving the yield of the entire process. In addition, the control over the bond between the metal and the complexing agent will allow a much larger Mg incorporation which is crucial to optimize the band alignment in CIGSe solar cells improving the device efficiency and without the toxicity issues of the traditional CdS buffer layer.

Lastly, TiO<sub>2</sub> thin films were prepared trough spin coating technique, the optimization of the fabrication process was then followed by an acidic treatment to control the oxygen vacancy content. Firstly, the volume and the stirring time of the precursor solution were optimized by studying the samples with FE-SEM and Raman (by collaborators in Parma) that showed a film thickness from 50 to 450 nm involving 1 and 3 depositions,

respectively. FE-SEM revealed the presence of cracks in the film and identified the material as titania anatase. An acid treatment was then exploited to control the number of  $V_0$  in the material and hopefully the n-type doping of the layer. The defects formed onto titania surface were quantified by XPS analysis that revealed a slight enhancement of the Ti<sup>3+</sup> signal and of the -OH group. Transmittance spectra did not show any important variation after the acid treatment suggesting that also in the volume of the layer the number of defects produced is negligible from the view-point of optical properties. It is not excluded that the vacancies produced by the acidic treatment on the surface of the layer might diffuse in the whole volume after the annealing step. Further studies are required in order to successfully control the number of oxygen vacancies. Lastly, thermodynamic calculations showed the stability of the TiO<sub>2</sub> phase in a wide range of temperatures and oxygen partial pressures, showing that in principle the oxygen deficient  $Ti_xO_y$  phases are metastable at ambient condition. Hopefully, the control over titania defectivity may help not only to control its n-doping but also, as widely reported in the literature, to favor the incorporation of dopants able to properly tune TiO<sub>2</sub> properties and to tune the titania crystal orientation that may enable the control over the crystal growth orientation of Sb<sub>2</sub>Se<sub>3</sub> overlayer with the consequent solar cell efficiency boost.

It is hoped that the findings described in this thesis will help the development of optoelectronics devices, such as WLEDs and solar cells, which are considered among the most promising technologies to fight climate change.

# 4. Appendix

## 4.1. CsPbBr<sub>3</sub>@SiO<sub>2</sub> project: further images



*Figure A1: BF-TEM images of CsPbBr*<sub>3</sub>@*SiO*<sub>2</sub> *NCs obtain trough the one-step procedure. (a) After and (b) before centrifugation of the solution. Total reaction time 16 h, TEOS was involved as silica precursor. Modified with the permission of Chemistry of Materials.*<sup>84</sup>



Figure A2: NMR characterization of the reaction between maleic anhydride (MANH) and oleylamine (OLAM). 1H NMR spectra of (a) MANH. (b) OLAM and their mixtures in different molar ratios (c, d, e), (f) 1H-13C HSQC, and (g) 1H-13C HMBC of C=Oregion. All the NMR spectra were acquired by Dr. Luca Goldoni onto samples prepared by Dr.Riccardo Scarfiello and analyzed by Nanochemistry researchers. Modified with the permission of Chemistry of Materials.<sup>84</sup>



Figure A3: TEOS hydrolysis in air and in  $N_2$  filled glove box (GB) atmosphere. BF-TEM images of the reaction product at different reaction times including the pristine material (a, c, e, g) in air atmosphere and (b, d, f, h) in a  $N_2$  filled glove box. Modified with the permission of Chemistry of Materials.<sup>84</sup>



**Figure A4: Additional HAADF-STEM images of CsPbBr3@SiO2@SiO2.** CsPbBr3@SiO2@SiO2 images at (top row) lower and (bottom row) higher magnification. Acquired by Dr. Rosaria Brescia, PhD. Modified with the permission of Chemistry of Materials.<sup>84</sup>

#### 4.2. Thermodynamics of nucleation

The nucleation step consists in the process that brings to the formation of the smallest stable crystallite in the solution (homogeneous nucleation) or onto a substrate (heterogeneous nucleation) starting from a precursor solution. The thermodynamic description of the nucleation is known as classical nucleation theory and was based onto Gibbs' idea of nucleation<sup>219</sup>; then, the first complete theory of homogeneous nucleation was formulated by Volmer and Weber<sup>220</sup>, later implemented by Becker and Döring<sup>221</sup>, and further improved by Zeldovich<sup>222</sup>.<sup>223</sup>

In the following simplified calculation, the precursor solution is considered as an ideal gas, neglecting the solvent effect and in the absence of defined facets present in a real crystal.<sup>224</sup>

For both homogeneous and heterogeneous nucleation, there are 2 different energy contributions to the Gibbs free energy ( $\Delta G$ ) of the system:

#### a) Chemical potential difference ( $\Delta \mu$ ) between unbound and bound state of the monomers.

#### b) Surface energy of the growing crystals

**Homogeneous nucleation.** In this case the chemical potential difference (29) is described by the following equation:

$$\Delta G_{\rm V} = n(\mu_{\rm cryst} - \mu_{\rm sol}) = -\frac{v}{v_{\rm cryst}} \Delta \mu$$
<sup>(29)</sup>

Where n are the number of atoms in a nucleus,  $\mu_{cryst}$  and  $\mu_{sol}$  are the chemical potential of monomer species in the crystal and in the liquid, respectively. V and v<sub>cryst</sub> are the volume of the nucleus and that of each monomer forming the nucleus, respectively. Considering a spherical nucleus, the  $\Delta G_V$  can be written as:

$$\Delta G_{\rm V} = -\frac{4\pi}{3\rm vcryst} r^3 \Delta \mu \tag{30}$$

Regarding the surface energy of the growing crystals,  $\Delta G_V$  can be seen as the energy required to form an interface between the solution of monomers and the growing particles:

$$\Delta G_{\rm S} = 4\pi r^2 \,\gamma_{NL} \tag{31}$$

Where  $\gamma_{NL}$  is the surface energy for unit area when a nucleus is formed. Considering both (a) and (b), the total free energy for the formation of a nucleus is:

$$\Delta G = \Delta G_{\rm S} + \Delta G_{\rm V} = -\frac{4\pi}{3 \text{vcryst}} r^3 \Delta \mu + 4\pi r^2 \gamma_{NL}$$
(32)

The plot of  $\Delta G$  as a function of the particle radius r is qualitatively reported in *Figure A5*.



*Figure A5:* Depiction of  $\Delta G$  trend as a function of r (black curve), the volume contribution (green) and the surface one (blue).

By the first derivative of Eq. 32 it is possible to calculate the critical radius  $r^*$  and the energy barrier to be overcome to allow the free growth of the particles.

$$r_{hom}^* = \frac{2\gamma_{NL}\nu_{crys}}{\Delta\mu}$$
(33)

$$\Delta G^* = \frac{16\pi\gamma^3 NLv^2 cryst}{3\Delta\mu^2} \tag{34}$$

Heterogeneous nucleation. In this case the precursor solution is in direct contact with a substrate (*Figure A6*). The nucleus grows onto the substrate under the same hypothesis considered in the homogeneous nucleation (the initial solution of monomers in a solvent is considered as an ideal gas, the solvent is neglected, absence of defined facets present in a real crystal and the volume of the nucleus is imagined as a spherical cap). As before, the contribution to  $\Delta G$  is given by a chemical potential contribution (a) and a surface energy contribution (b).

$$\Delta G_{het} = -\frac{\nu_{het}}{\nu_{crys}} \Delta \mu + \gamma_{NP} A_{NP} + \gamma_{NS} A_{NS} - \gamma_{SP} A_{NS}$$
(35)

Setting the first derivative of  $\Delta G_{het}$  to 0, it is possible to calculate the critical radius r\*:

$$r_{het}^* = \frac{2\gamma_{NL}\nu_{crys}}{\Delta\mu} \tag{36}$$

Interestingly, the critical radius is the same for both homo and heterogeneous nucleation. Substituting the calculated value for  $r^*$  in the  $\Delta G_{het}$  expression:

$$\Delta G_{het} = \frac{(2 + \cos\theta)}{4} \cdot \frac{16\pi \gamma^3_{NL} v_{crys}^2}{3\Delta\mu^2}$$
(37)

 $\Delta G^*_{het} = \mathbf{f}(\theta) \cdot \Delta G^*_{hom}$ 



Figure A6: Schematic representation of surface tension onto play when a nucleus forms onto a substrate.

The heterogeneous nucleation presents the same  $r^*$  but a smaller energetic barrier compared to the homogeneous nucleation process, hence the heterogeneous nucleation is thermodynamically favored over the homogeneous one (*Figure A7*).



*Figure A7: Depiction of*  $\Delta G$  *trend as a function of r. In case of homogeneous nucleation (top curve) and heterogeneous one (bottom curve).* 

(38)

### 4.3. Equilibrium constants at different temperatures: Van't Hoff equation

Van't Hoff equation allows the calculation of the equilibrium constant at a particular temperature  $T_2$  by knowing its value at another temperature  $T_1$ , its enthalpy ( $\Delta_r H^\circ$ ) and assuming that the latter does not change in the temperature range of interest<sup>225</sup>:

$$\frac{d\ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$
(39)

Now it is necessary to integrate Eq. 39 between  $T_1$  and  $T_2$ :

$$lnK_2 - lnK_1 = -\frac{1}{R} \int_{\frac{1}{T_1}}^{\frac{1}{T_2}} \Delta_r \operatorname{H}^{\circ} \operatorname{d}\left(\frac{1}{T}\right)$$
(40)

$$lnK_2 = lnK_1 - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(41)

*Eq.* 41 provides a relation between the equilibrium constant and the temperatures where only the two temperatures,  $\Delta_r H^\circ$  and R (8.31 J/(K·mol)) appear.<sup>225</sup>

# 4.4. Photovoltaic performance of alternative buffer layers in CIGS PV

Composition	Efficiency (%)	V <sub>oc</sub> (mV)*	J <sub>sc</sub> (mA/cm <sup>2</sup> )*	FF (%)*	Ref.
Zn(O,S,OH)/	23.35	734	39.6	80.4	138
Zn <sub>(1-x)</sub> Mg <sub>x</sub> O					
CdS	22.92	746	38.5	79.7	
Zn(O,S)	11.0	537	38.6	53.0	139
CdS	11.4	537	38.1	56.0	
In <sub>2</sub> S <sub>3</sub>	12.9	27.8	0.64	72.6	142
CdS	12.9	27.6	0.65	71.5	
ZnTiO	11.79	0.57	33.09	62.13	145
CdS	15.44	0.63	34.37		
Zn <sub>0.8</sub> Mg <sub>0.2</sub> O	18.1	0.650	38.2	73.2	143
CdS	18.2	0.673	36.1	75.6	
Zn(OH) <sub>2</sub>	10.7	0.498	32.1	66.7	144
Zn(Se,OH)/	14.4	0.583	33.9	72.9	

Table A1: Comparison of the solar cell performance of alternative buffer with thecorresponding CdS device.

CdS	14.6	0.588	33.7	73.7	
$Zn_{(1-x)}Sn_xO_y$	17.6	0.680	35.3	73.4	147
CdS	18.3	0.714	33.4	76.3	
ZnO	11.4	0.557	28.7	71.2	146
electrodeposited					
ZnO sputtered	7.8	0.508	27.8	55.4	
CBD CdS	13.3	0.621	30.7	69.5	
In(O,OH,S)	12.55	0.574	33.17	65.89	141
CdS	12.10	0.572	30.69	68.87	

\*  $V_{\rm oc}$  = open circuit voltage;  $J_{sc}$  = short circuit current; FF = fill factor

Table 2	2A:	Additional	examples	of	remarkable	high	-efficient	solar	cells	based	on
alterna	tive	buffer laye	<b>rs.</b> <sup>226</sup>								

Buffer	Preparation method for the buffer	Window	Efficiency (%)	Year	Ref.
Zn(O,S)	CBD	ZnO:B	19.7	2013	148
Zn(O,S)	CBD	(Zn,Mg)O/ZnO:Al	19.1	2011	149
Zn(O,S)	CBD	ZnO:B	18.8	2013	150

Zn(O,S)	CBD	i-ZnO/ZnO:Al	18.6	2003	227
Zn(O,S)	CBD	ZnO:Al	18.5	2012	228
Zn(O,S)	ALD	i-ZnO/ZnO:B	18.7	2013	229
Zn(O,S)	ALD	i-ZnO/ZnO:Al	18.5	2006	230
Zn(O,S)	ALD	(Zn,Mg)O/ZnO:Al	18.1	2013	231
In <sub>2</sub> Se <sub>3</sub>	Evaporation	ZnO:Al	18.3	2013	232
In <sub>2</sub> Se <sub>3</sub>	ILGAR	i-ZnO/ZnO:Al	16.1	2012	233
In <sub>2</sub> Se <sub>3</sub>	ALD	i-ZnO/ZnO:Al	16.4	2003	234
(Zn,Mg)O	ALD	ZnO:Al	18.1	2007	153
(Zn,Mg)O	Sputtering	ΙΤΟ	16.2	2002	235
(Zn,Mg)O	ALD	I:ZnO/ZnO:Al	18.2	2013	236

## **4.5. Data for speciation plots**

Table A3: Literature review of ZMO prepared trough CBD. Mg incorporated, technique involved in the measurement, potential complexing agents involved and the corresponding references are reported.

Mg (mol%)	Technique	Complexing agents	Ref.
2.1	ICP	CA, -OH <sup>-</sup> , NH <sub>3</sub>	174
1.5	SEM-EDS	NaOH, NH <sub>3</sub>	192
0.85	SEM-EDS	hexametilentetrammine	193
48	ICP	-OH <sup>-</sup> , NH <sub>3</sub>	154
30	Not measured	triethanolamine	191

**Table A4. Data for complexing agent investigation.** In this table the data involved to prepare the speciation plots in *Figure 14* and *13* are shown. For each complex the log $\beta$  is reported together with the temperature and the ionic strength found in NIST database<sup>197</sup>. While the log $\beta$  at 92 °C was calculated using Van't Hoff equation as described in section *4.3.* According to NIST database log $\beta$  values are reported as the equilibrium constant of the complex (ML) dissociation reaction into metal (M) and ligand (L) ions as followed reported:

$(ML)^x \rightarrow M^y + L^z$ ,	$\log\beta = [ML]$	$x/[M]^{y} \cdot [L]^{z}$
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Species	Logβ 25 °C	Logβ 92 °С	T °C	I	ΔH kJ/mol	Т <sub>ан</sub> °С	I <sub>AH</sub>	∆S J/K∙mol	Т <sub>лs</sub> °С	I AS
NH <sub>3</sub>	9.26		25	0.1	-52	25	0	2	25	0
	9.28		25	0.5	-51.8	25	0.1	2	25	0.1
	9.33		25	0.5	-53.1	25	0.5	0.4	25	0.5
	9.354		25	0.7	-53.9	25	1	-0.8	25	1
	9.41		25	0.7	-52.7			0.9		
	9.39		25	1						

(35)

	9.43		25	1						
	9.244		25	0						
	9.34	9.34								
ОН	13.78		25	0.1	-55.81	25	0	80.7	25	0
	13.69		25	0.5	-56.48	25	0.1	73.6	25	0.1
	13.73		25	0.5	-56.65	25	0.5	72.8	25	0.5
	13.75		25	0.5	-57.11	25	0.5	71.5	25	0.5
	13.75		25	0.7	-57.06	25	0.5	70.7	25	0.5
	13.71		25	1	-56.1	25	1	75.7	25	1
	13.77		25	1	-56.94	25	1	72.3	25	1
	13.94		25	1	-57.4	25	1	70.7	25	1
	13.997		25	0	-57.36	25	1	69.8	25	1
	13.79	13.79			-56.77			73.1		
CA([HL]/[H]*[L])	5.56		25	0.1	3.3	0				
	5.64		25	0.1	-1.3	1				
	5.69		25	0.1	1.9	0.1				
	5.8		25	0.1	1.3					
	5.57		25	0.15						
	5.64		25	0.15						
	5.73		25	0.15						
	5.58		25	0.2						
	5.3		25	0.5						
	5.36		25	0.5						
	5.13		25	1						
	5.23		25	1						
	5.33		25	1						
	5.34		25	1						
	5.49	5.49								
$CA([H_2L]/[HL]*[H])$	4.35		25	0.1	-2	25	0			
	4.25		25	0.2	-3.1	25	0.1			
	4.14		25	0.5	-4.47	25	1			
	4.06		25	1	-3.19					
	4.1		25	1						
	4.11		25	1						
	4.12		25	1						
	4.16	4.16								
	9.65	9.65								
$CA([H_3L]/[H_2L]*[H])$	2.9		25	0.1	-4	25	0			
	2.85		25	0.2	-4.6	25	0.1			
	2.8		25	0.5	-4.35	25	1			
	2.79		25	1	-4.32					
	2.835	2.83								
	12.49	12.49								
$Zn(NH_3)^{2+}$	2.31	2.66	25	0.1	-11		2			

	2.34	2.69			-24	25				
$Zn(NH_3)_2^{2+}$	4.77	5.54	25	1	-24		2	-1.3	25	2
	4.79	5.56			-40	25				
$Zn(NH_3)_3^{2+}$	6.86	8.14	25	0	-40		2	6.6	25	2
	7.085	8.37			-61.5	25				
$Zn(NH_3)_4^{2+}$	8.89	10.87	25	0	-61.5		2	-20	25	2
	9.17	11.15								
					8	25				
(Zn-cit) <sup>-</sup>	4.27	4.01	25	0.5	8		0.1	125	25	0.1
	11.4	11.14	25	0						
	7.83	7.58			25	25				
(Zn-cit <sub>2</sub> ) <sup>4-</sup>	5.9	5.09	25	0.5			0.1	213	25	0.1
Zn-HL	4.71	3.90	25	0						
					-50.45	25				
(Zn-EA) <sup>2+</sup>	2.50	4.12	25	0.5	-50.45	25	0			
$(Zn-EA_2)^{2+}$	2.50	4.12	25	0.5			0			
					0	25				
					0	25				
(Zn-OH) <sup>+</sup>	4.6	4.6	25	0.1	0	25	0	104	25	0
	4.7	4.7	25	1	0		0	104	25	0
	4.7	4.6								
(Zn-(OH) <sub>2</sub> ) [ML2]	11.1		25	0						
	11.2									
(Zn-(OH) <sub>3</sub> ) <sup>+</sup> [ML3]	13.6		25	0						
	13.87					25				
(Zn-(OH) <sub>4</sub> ) <sup>+</sup> [ML4]	14.8	8.7	25	0						
	16.23	10.18			8	25	0			
$(Zn_2-(OH)_3)^+$ [M2L]	5	4.74	25	0						
$(Zn_4-OH_4)^{4+}$ [M4L4]	27.9		25	3	26	25	3	125	25	3
[ML <sub>2</sub> (s,am)]	-14.84	-15.67	25	0.1						
[ML2(s,beta1)]	-15.56		25	0.1			2	-209	25	0
[ML2(s,beta2)]	-15.52		25	0.1						
[ML2(s,gamma)]	-15.58		25	0.1						
[ML2(s,delta)]	-15.47		25	0.1	33	25				
[ML2(s,epsilon)]	-15.79	-16.85	25	0.1	22	25				
[MO(s)]	-16.1	-16.80	25	0.1			0	204	25	0
Mg(NH <sub>3</sub> ) <sup>2+</sup>	0.24		25	2	-5	25	2	-246	25	0
$Mg(NH_3)_2^{2+}$	0.2	0.36	25	0	-5	25				
	0.1	0.26	25	2			0	-12	25	0
	0.15	0.31					0	-12	25	0
Mg(NH <sub>3</sub> ) <sub>3</sub> <sup>2+</sup>	1			1						
Mg(NH <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	1			1						
					8	25				

(Mg-cit) <sup>-</sup>	3.52	3.26	25	0.1						
(Mg-cit <sub>2</sub> ) <sup>4-</sup>							0.1	96	25	0.1
(Mg-citH) [MHL]	1.2		25	0.5						
	1.66		37	0.15						
	2.05									
	2.05									
(Mg-citH <sub>2</sub> ) [MH2L]	0.7		25	0.1						
(Mg-EA) <sup>2+</sup>	0.24		25							
					12	25				
(Mg-OH) <sup>+</sup>	1.87	1.48	25	0.1	12					
							0	92	25	0
	2.225	1.84								
(Mg-OH) <sup>+</sup> [M4][L4]	17.1		25	3						

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### 6. Published papers

Christian Rossi, Riccardo Scarfiello, Dmitry Baranov, Rosaria Brescia, Luca Goldoni, Gianvito Caputo, Luigi Carbone, Luca De Trizio, Liberato Manna, Diego Colombara. Exploiting the Transformative Features of Metal Halides for the Synthesis of CsPbBr<sub>3</sub>@SiO<sub>2</sub> Core-Shell Nanocrystals. *Chemistry of Materials* 2022, 34, 1, 405–413 https://doi.org/10.1021/acs.chemmater.1c03749