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Perovskite Strontium Doped Rare Earth Manganites Nanocomposites and Their Photocatalytic Performances

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Abstract

Studying catalysts *in situ* is an important topic that helps us to understand their surface structure and electronic states in operation. Three types of materials are used in the degradation of organic matter, which has applications in the environmental remediation and self-cleaning surfaces. The technique is widely known but still hampered by one significant limitation. The materials generally absorb ultra violet UV light but we need to develop active materials for visible light. Utilizing the sunlight efficiently for solar energy conversion is an important demand in the present time. The research on visible-light active photocatalysts attracted a lot of interest. The perovskite-like compounds are found to be active catalysts for the oxidation of carbon monoxide. In the present chapter, we will focus on the application of the nano-sized strontium doped neodymium manganites within perovskite like structure as photocatalysis and studying their photocatalytic performance.

Keywords: photocatalytic, perovskite, manganites, nanocomposites, visible light

1. Introduction

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. The ability to generate electron-hole pairs and free radicals is very important parameters to understand the photocatalytic activity (PCA) in photogenerated catalysis [1]. On other words we can describe the photocatalysis process as two parts, “photo” and “catalysis”. Let us define the catalysis as the process in which a material participates in modifying the rate of a chemical transformation of the reactants without altering or consuming in the end. This material is so called catalyst,

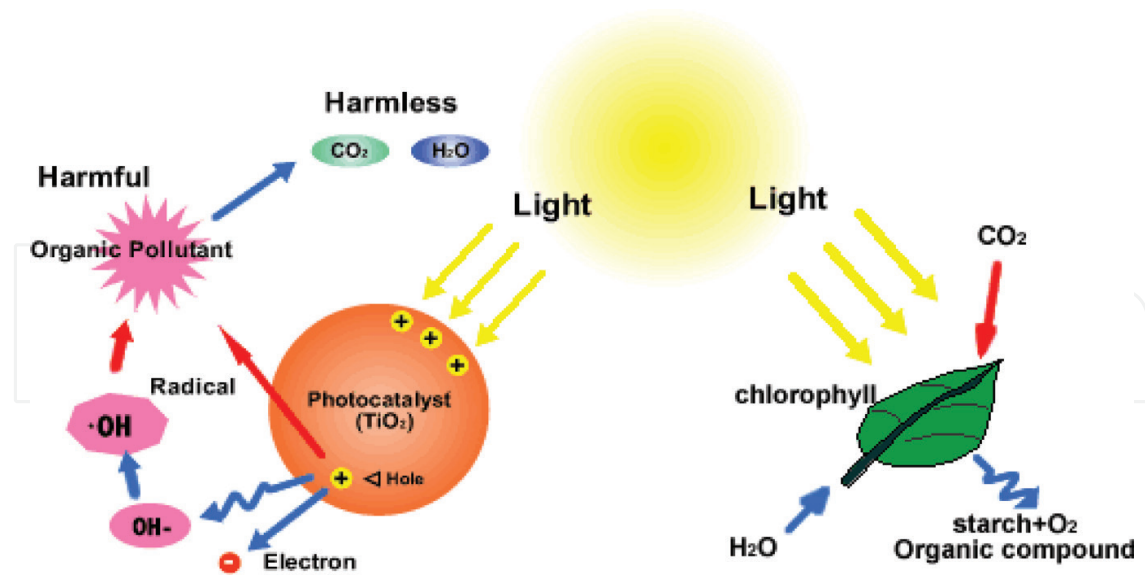


Figure 1. Nano TiO_2 photocatalyst and chlorophyll of plants is a typical natural photocatalyst [2].

which the activation energy is reduced that may lead to acceleration of the reaction. In general, light is used to activate a substance, which modifies the rate of a chemical reaction without being involved itself, and the photocatalyst is the substance, which can modify the rate of chemical reaction using light irradiation [1]. Chlorophyll of plants is good example for the natural photocatalyst. The difference between chlorophyll photocatalyst and nano TiO_2 photocatalyst (see **Figure 1**) [2] is, usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, while photocatalyst creates strong oxidation agent and electronic holes to breakdown the organic matter to carbon dioxide and water in the presence of photocatalyst, light and water [2]. So many materials are developed daily to be applied as photocatalysis and nanocomposites that have perovskites-like structure are promising materials for these applications.

2. Mechanism of photocatalysis

When photocatalyst such as titanium dioxide (TiO_2) absorbs Ultraviolet (UV)* radiation comes from sun or any other illuminated light source (e.g., fluorescent lamps), pairs of electrons and holes are produced, see **Figure 2**. As a result of the light illumination, the electron of the valence band of titanium dioxide becomes excited. Excited electron transits to the conduction band of titanium dioxide with excess energy to create pair of charges; the negative-electron (e^-) and positive-hole (h^+). This behaviour is well known as the semiconductor's photo-excitation' state. The 'Band Gap' is defined as a result of the difference in energy between the valence band and the conduction band. The necessary wavelength of the light required for the photo-excitation is given according to 1240 (Planck's constant, h)/ 3.2 eV (band gap energy) and equal to 388 nm [3]. The hole with positive charge in titanium dioxide may split the water molecule into both of the hydrogen gas and hydroxyl radical. On the other side, the electron with negative charge reacts with oxygen molecule forming the super oxide anion. The continuity of this cycle depends on the availability of the light [3].

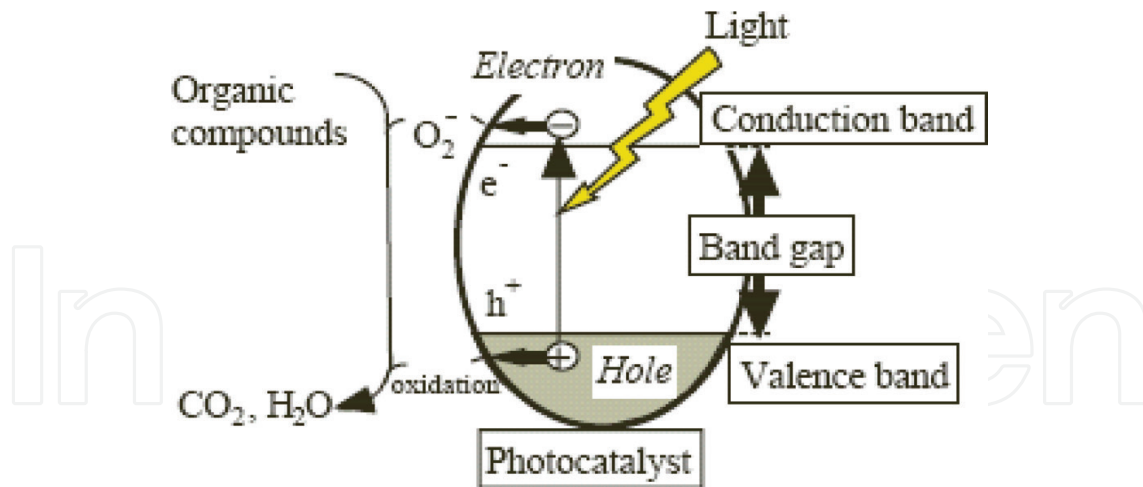


Figure 2. Schematic diagram showing the photocatalysis mechanism by producing both holes and electrons as a result of illumination [3].

Solar energy is clean and till now its utilization is limited. A strong need to develop a sustainable and cost-effective manner for harvesting solar energy to satisfy the growing energy demand of the world with a minimal environmental impact [4]. Photo-catalysis plays an important role for the conversion of solar energy into chemical fuel, electricity, the decomposition of organic pollutants etc.

The degradation behaviors were studied by Sher Bahadar Khan et al. [5] and the degradation pattern of AO by Langmuir–Hinshelwood (L–H) model was defined and given from the relationship between the rate of degradation and the initial concentration of AO in photo-catalytic reaction [6].

The rate of photo-degradation was calculated according to the following equation; Eq. (1)

$$r = -dC/dt = KrKC = KappC \quad (1)$$

where r in this equation is defined as the degradation rate of organic pollutant, Kr is describing the reaction rate constant, K is constant equal to the equilibrium constant, C is the concentration of the reactant. From Eq. 1, we can neglect KC when C becomes very small so this equation could describe the first order kinetic. Applying the following initial conditions, ($t = 0, C = C_0$) in Eq. (1), that may lead to a new equation; Eq. (2).

$$-\ln C/C_0 = kt \quad (2)$$

Half-life, $t_{1/2}$ (in min) is

$$t_{1/2} = 0.693/k \quad (3)$$

The photo degradation of AO in the presence of CeO_2 1 nano-particles is shown in **Figure 3**.

Different materials are used as photocatalysis and research is going on to apply a new material for this applications. The rare earth manganite is one of the promising materials for

photocatalysis and so in the present proposal we develop the strontium doped neodymium manganites nanocomposites within perovskite like structure as photocatalysis and studying its performance and so the main goals are; –synthesis new perovskite materials enhanced the photocatalysis performance applying the obtained results for solar energy utilizations.

Metal oxide photocatalysis is based on metal oxide like titanium dioxide as light-activated catalysts [7]. Three types of materials are used in the degradation of organic matter which has

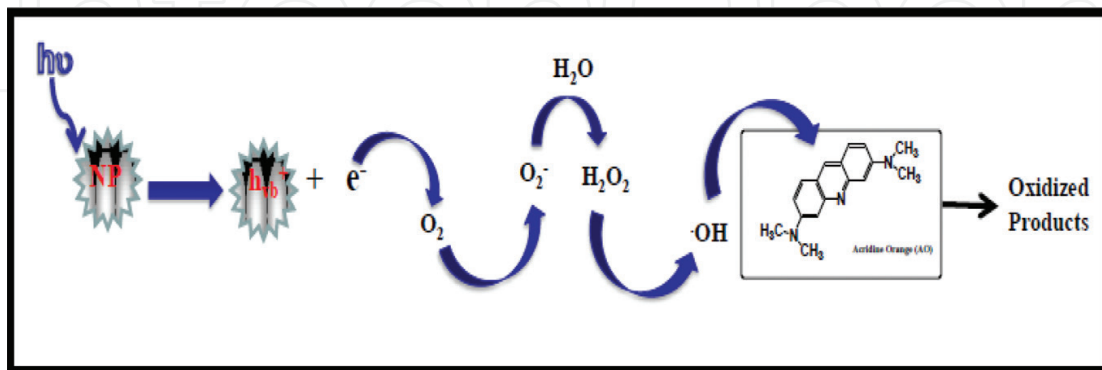


Figure 3. Photo-degradation of AO in the presence of CeO₂ 1 nanoparticles [5].

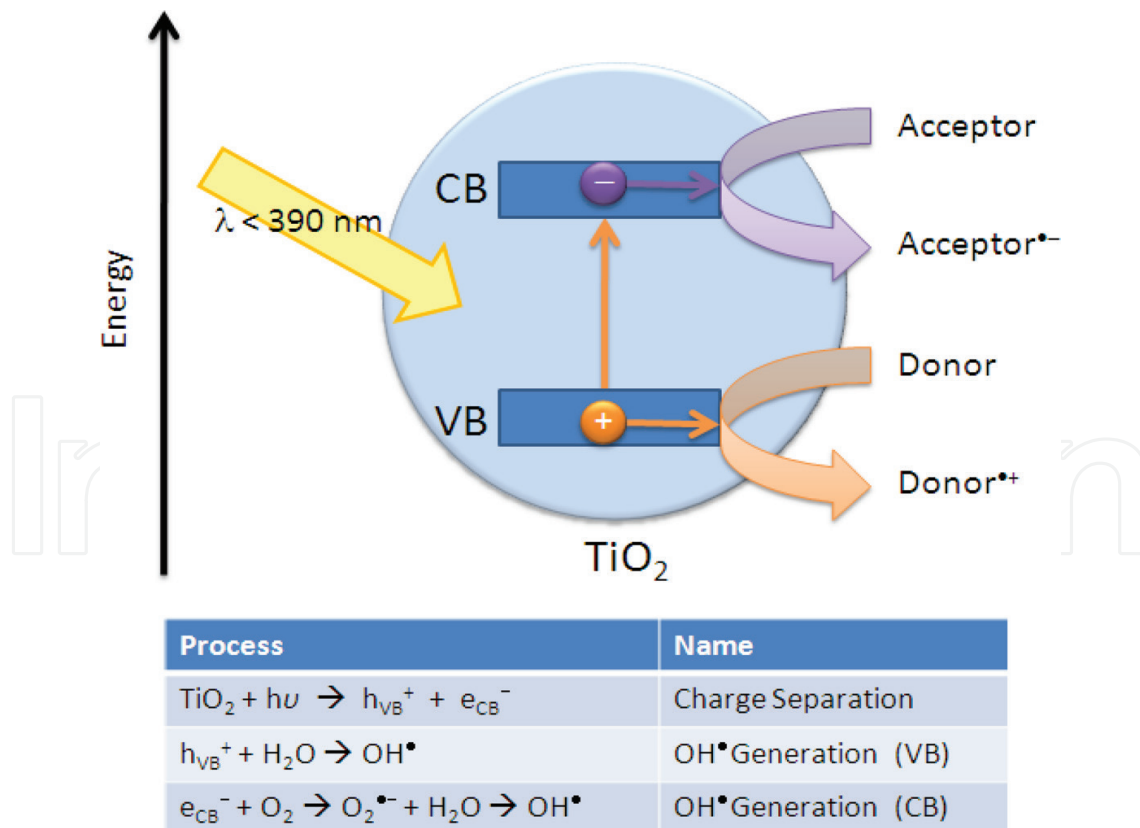


Figure 4. Schematic representation; top light with energy higher than band gap leads to charge separation, with electron reducing a donor (usually oxygen) and hole oxidizing a donor (usually water); summary of processes occurring. Image based on Bahnemann (2004) [7].

applications in the environmental remediation and self-cleaning surfaces. The technique is widely known but still hampered by one significant limitation. The materials generally absorb ultra violet UV light but we need to develop active materials for visible light, see **Figure 4**.

3. Perovskites as photocatalytic

ABO_3 perovskites are very essential family of oxide materials because they possess very interesting physical and chemical properties. These unusual properties may lead to use these materials in potential applications. The corner-shared octahedral BO_6 lattice site in these materials play very important role in transfer of oxygen and electrons easily and may lead to nonstoichiometry of oxygen [8–23]. Moreover, the mixed valence states of the transition metal at B-site are also important term in such perovskite-type oxides, which affect their activity. Nevertheless a lot of applications depend on the A and B cations in the ABO_3 perovskites, such as electrocatalysts for O_2 evolution [8–10], catalysts [11, 12], photo/electro-catalysts for hydrogen production and pollutants degradation [13–19] and electrode material used in fuel cells [13]. The synthesis of perovskite materials could be done using different methods such as solid state reaction [24–28], chemical co-precipitation [29–33], sol-gel [34–38]. In each method there are parameters to play with in order to improve the properties of the required materials. A lot of perovskite oxides have been synthesized such as tantalate [39–43], titanate [14, 44–50], ferrite, [51, 52] vanadium-and niobium-based perovskites [53–56], and manganites [57, 58] and they have shown visible light photocatalytic activity as a result of their unique electronic properties and crystal structures [59]. The reduced band-gap energy values in the doped alkaline rare-earth transition metal perovskite-like structure oxides focus more attention because this property enhances the separation of charge carriers (photogenerated electrons and holes) [60]. Intensive studies have been done on these materials because of the capability of tuning their electrical and optical properties, indicating a control of their rational design structure by substitutions of cationic in ABO_3 perovskite [61, 62]. Therefore, we can say that the perovskite compounds are one of the promising structure that are adapting the bandgap values to harvest visible-light absorption and the potentials of band edge to tailor the needs of particular photocatalysis.

Furthermore, the lattice distortion existed in the rare earth transition metal perovskite compounds strongly affects the separation of photogenerated charge carriers [59, 63, 64]. The distortion in the bond angles resulted from both; metal-ligand or the metal-ligand-metal into perovskite framework are significantly related to their charge carriers and band gap values [65–67]. The crystallinity, phase structure, size, and surface area affect the efficiency of photocatalysts. Consequently, control of the shape of perovskites and the size and crystal phase is essential and significant parameter for assessing their phase-dependent photoactivity and promoting perovskites-based driven visible light photocatalysts. According to Abdel-Latif et al. [66], $Nd_{0.6}Sr_{0.4}MnO_3$ was studied as superior photocatalyst under visible light, different modifications of perovskite $Nd_{0.6}Sr_{0.4}MnO_3$ to get high harvesting of photons and enhancing the migration and separation of the photogenerated charge carriers through the photocatalytic reaction [61–65]. For the first time, the impact on phase structures and photocatalytic efficiencies under visible light of the annealed $Nd_{0.6}Sr_{0.4}MnO_3$ perovskite which prepared by sol-gel

method in the presence of polyethylene glycol and citric acid was studied by Abdel-Latif et al. [66], and the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite annealed at 500°C was found to be a superior photocatalyst than that annealed at 800 , 1000 and 1150°C . $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ semiconductor has a narrow band gap energy values ranged from 2 to 2.98 eV, which we can control its value by changing its annealing temperatures. Charge carriers created by absorbing visible light (photogenerated electrons and holes) depend on the excitation by this visible light. The hole, which photogenerated in the valence band reacts either with the adsorbed $-\text{OH}$ ions or H_2O onto the surface of NSMO producing OH^\bullet . On the other side, the electron, which photogenerated in the conduction band reduces O_2 to get $\text{O}_2^\bullet-$ give rising to other oxidative O_2 species (i.e., OH^\bullet and H_2O_2). The photocatalytic efficiencies of the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ nanocomposites were evaluated in Ref. [66] for the MB photodegradation, where they calculated the MB photodecomposition under visible light illumination by recording absorption spectra. They found that MB is negligible at the photolysis and it is stable after visible light illumination for 3 h. Furthermore, there is a slight decrease in MB concentration as a result of adsorption onto $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ surface when it is suspended with MB solution in dark as shown in **Figure 5**. The observed MB absorption bands at $\lambda = 663$ and 291 nm gradually decreased upon boosting illumination times.

As it is clear from the photocatalytic performance of the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite, the crystalline size (55 nm), which depends on the annealed temperature (500°C). The mixed perovskite structure $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (26.18% orthorhombic "Orth" and 73.82% monoclinic "Mon") obtained at annealing temperature 500°C is a superior photocatalyst candidate than that of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite obtained at annealing temperature 1150°C and with mixed structure (82.22% cubic "Cub" and 17.78% orthorhombic "Orth" phases). The observed photo degradation was 100% by the annealing temperature 500°C of the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite [66]. However, as a result of the increase in the annealing temperature to 1150°C , reduction in the photocatalytic efficiency was observed to be 60%. Looking at the effect of the annealing temperature in $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite according to Abdel-Latif et al., [66], the overall photodegradation rate of the sample annealed at 500°C is significantly 3-times higher than that of the other sample, which annealed at 1150°C . The superiority of the neodymium strontium doped manganite, which annealed at 500°C is attributed to the mixed crystallographic structure with double phases (Mon/Orth) framework, high crystallinity, and the Mn-O polyhedron distortion. From this work on can say that key factors for the high photocatalytic activity of the obtained neodymium strontium doped manganite with annealing temperature 500°C are the high visible-light absorption, lattice distortion and narrow band gap.

Another example of the rare earth manganites is the non-stoichiometric perovskites; $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ ($x = 0.35, 0.50, 0.65, 0.80$) series, which was examined by Antoine Demont and Stéphane Abanades [67] in the context of solar-driven two-step thermo-chemical dissociation of CO_2 . All the performance characterization measurements such as X-ray diffraction and thermochemical characterizations were carried out in order to the evaluation of the redox activity of these materials toward the thermal reduction under inert atmosphere followed by the re-oxidation process and carbon oxide generation from CO_2 . They found that, the control of introducing strontium into lanthanum manganite allowed tuning the redox thermodynamics within the series. The high activity observed toward both thermal reduction and CO_2 dissociation occurred. As a result of analysis of experimental measurements they found that the $\text{La}_{0.50}\text{Sr}_{0.50}\text{MnO}_{3-\delta}$ composition is a promising candidate for thermochemical CO_2 splitting **Figures 6** and **7**.

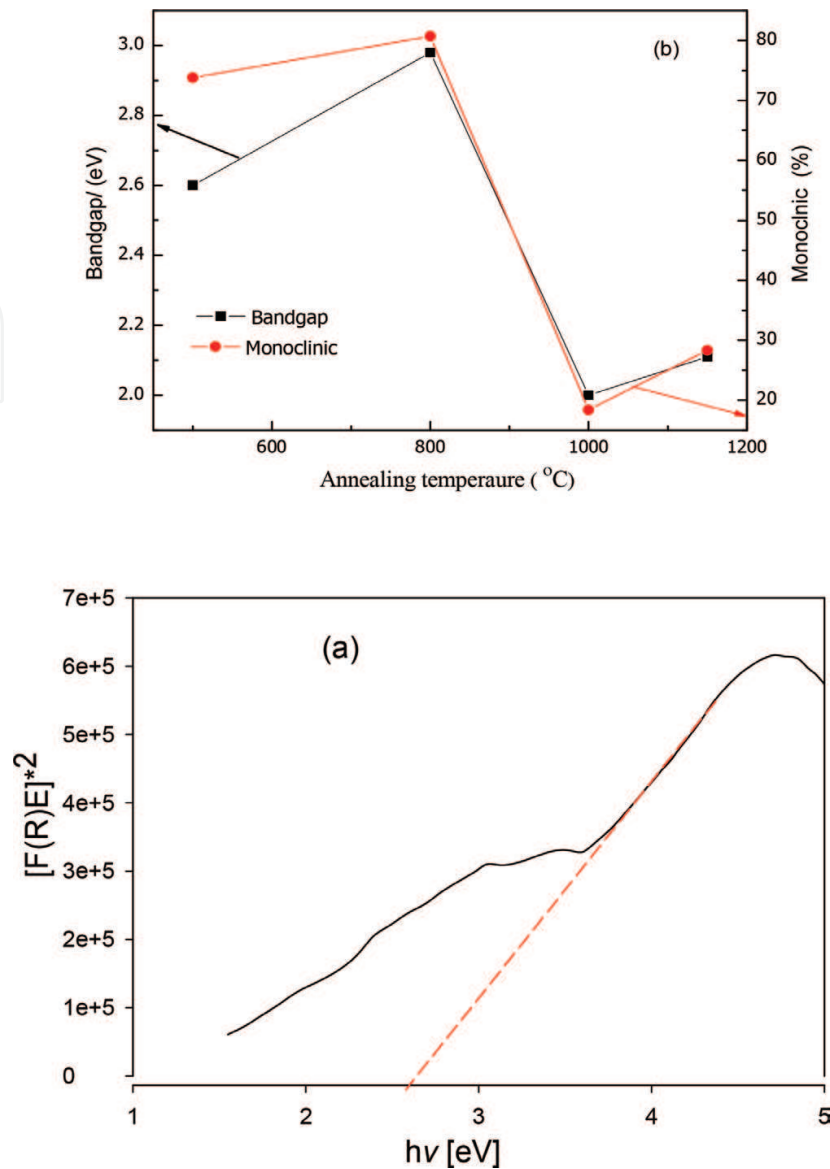


Figure 5. Optical bandgap energy E_g for nano $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite annealed at 500°C (a), relation between the bandgap energy E_g values and the percentage of the monoclinic phase (b) [66].

Maximum production of carbon oxide is reached in the range of $270 \mu\text{mol g}^{-1}$ during the carbon dioxide splitting step with an optimal temperature of re-oxidation 1050°C (thermal reduction performed under Argon gas at 1400°C), in spite of the re-oxidation yield limitation “50%”. The evolution of the manganese oxidation state reveal partial re-oxidation of Mn^{3+} into Mn^{4+} , thus the activation of $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox pair in the perovskites was confirmed. They concluded that the mixed valence perovskites have clear potential for displaying redox properties suitable for efficient solar-driven thermochemical CO_2 dissociation [67].

Oxygen diffusion and desorption in oxides have been developed for slightly defective and well crystallized bulky materials in Ref. [68]. The relation between nanostructure and the change of the mechanism of oxygen mobility has been studied in this work. Temperature programmed oxygen desorption and thermogravimetric analysis applied to study some nanostructured perovskite-like structure $\text{La}_{1-x}\text{A}_x\text{MnO}_{3\pm\delta}$ samples (A = Sr. and Ce, 20–60 nm

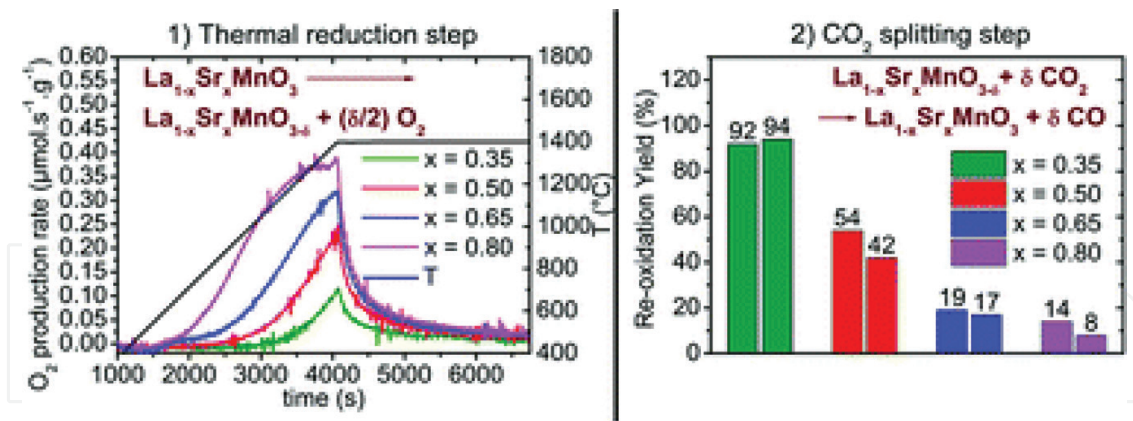


Figure 6. Solar-driven two-step thermochemical dissociation of CO_2 in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ [67].

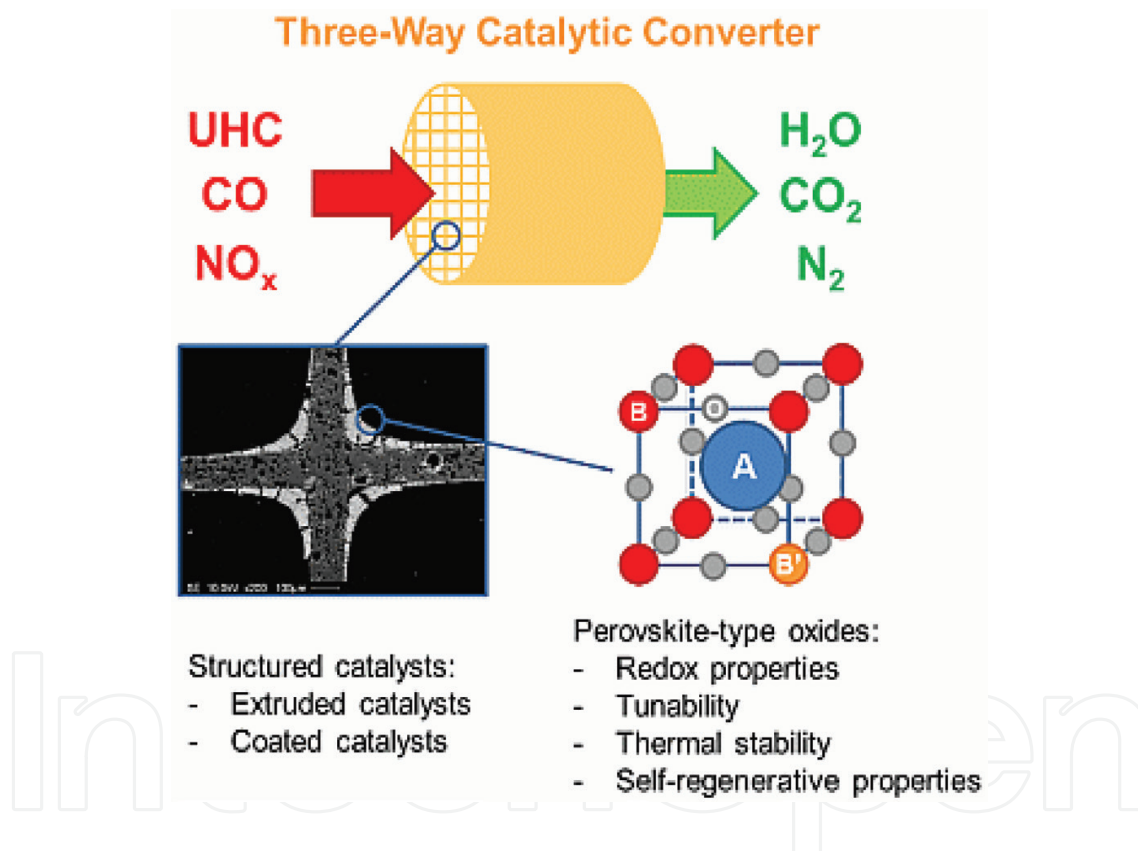


Figure 7. Three-way catalytic converter TWC [71].

particle size) [53]. Depending on the temperature range and oxygen depletion of the material different rate-determining steps have been identified. Particularly, oxygen diffusion was demonstrated at low temperature and defect concentration, whereas the oxygen recombination at the surface seems to be controlled at high temperature. However, the lower activation energy is responsible for the oxygen recombination step.

Utilizing the sunlight efficiently for solar energy conversion, the research on visible-light active photocatalysts attracted a lot of interest [4]. The photosensitization of transition metal oxides is a promising approach for achieving effective visible light photocatalysis. The world

of nanostructured photosensitizers, for example, plasmonic metal nanostructures, quantum dots, and carbon nanostructures engaged with the wide-bandgap in transition metal oxides that allow us to design a new visible-light active photocatalysts [4]. The implied mechanisms of the nanocomposite photocatalysts, for example, the charge separation inducing light and the visible-light photocatalytic reaction procedure in environmental treatment besides solar fuel generation fields, are also presented [10].

The rare earth manganites as well as the rare earth cobalt with perovskite-like structure (the rare earth like; lanthanum, praseodymium, or neodymium) are studied in Ref. [69], where they found that these materials are active catalysts for the oxidation of carbon monoxide. Comparing initial activity and lifetime in crushed single crystals of these composites and the commercial platinum catalysts showed its good performance. Therefore, one can say that these materials are considered as a promising alternate for platinum in devices for the catalytic treatment of auto exhaust.

The phonon-mode assignment of dysprosium chromate (DyCrO_3) nanoplatelets by Raman spectroscopy was reported recently [70]. They reported the effect of temperature on Raman spectra and they showed the shift in the phonon frequency of most intense modes in dysprosium chromate (DyCrO_3). The change in Raman line-width is observed, which is an indication to its correlation with the spin-phonon coupling. The impedance spectroscopy described in this work implied the anomalies in the dielectric constant *dependent on* temperature near the magnetic transitions point that may lead to postulate possible weak magnetoelectric coupling in DyCrO_3 nanoplatelets. Furthermore, UV-Vis absorption spectroscopy has been measured beside the photocatalytic activity measurement for DyCrO_3 nanoplatelets. The band gap deduced from the optical absorption spectrum was ~ 2.8 eV for DyCrO_3 nanoplatelets and this energy is considered as a good enough for the photocatalytic activity application. The efficient photocatalytic activity of DyCrO_3 nanoplatelets are described in this work, where degrading value was 65% for 8 h irradiation [70].

Three-way catalysts (TWC) were introduced more than 40 years ago and the development of a sustainable TWC still remains an important subject owing to the increasingly stringent emission regulations together with the price and scarcity of precious metals [71]. Perovskite-type oxides are alternatives to the conventionally used TWC compositions and it is suitable for a wide range of automotive applications, ranging from TWC to diesel oxidation catalysts (DOC). The interest in these catalysts has been renewed because of the catalyst regenerability of perovskite-based TWC concept. Principally, it is applicable to other catalytic processes and there is possibility to reduce the amounts of critical elements, such as valuable metals without industriously lowering the catalytic performance.

Studying catalysts *in situ* is of high interest for understanding their surface structure and electronic states in operation [72]. The epitaxial manganite perovskite thin films ($\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$) were found to be active for the oxygen evolution reaction (OER) from water splitting as a result of electro-catalytic water splitting. X-ray absorption near-edge spectroscopy (XANES), at the Mn L- and O K-edges, was measured and analyzed in Ref. [72], besides measuring the X-ray photoemission spectroscopy (XPS) of the O 1s and Ca 2p states. Both measurements were carried out under the following conditions; in water vapor under positive applied bias, in ultra-high vacuum and at room temperature [72]. According to the research in Ref. [72] under the oxidizing conditions of the OER a reduced Mn^{2+} species is generated at the catalyst surface and the Mn valence shift is accompanied by the formation of surface oxygen vacancies.

According to Madhavan and Ashok [73], perovskite materials exhibiting proton and oxide ion conductivities have been used for various energy-related applications such as solid oxide fuel cells (SOFCs), hydrogen production, gas sensors, etc. Nowadays, nanoperovskites were synthesized and were studied for catalytic activity and energy-related applications. The mechanism of proton and oxide ion conduction, and some specific properties and behaviors of few nanoperovskites as oxide ion and proton conductors and applications have been reported and discussed in this work [73].

4. Conclusions

As it is clear from the photocatalytic performance of the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite, the crystalline size (55 nm), which depends on the annealed temperature (500°C). The mixed phases (26.18% Orth and 73.82% Mono) in the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite as a result of annealing at 500°C is a superior photocatalyst than those of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite annealed at different temperatures. The maximum photodegradation of MB for the strontium doped neodymium manganites perovskite was achieved for those annealed at 500°C. As a result of the increase in the annealing temperature (annealing at 1150°C), the reduction to 60% in the photocatalytic efficiency was achieved. Comparing the overall photodegradation rates of the strontium doped neodymium manganites perovskite as a function of the annealing temperature we found 500°C annealing temperature is significantly 3-times higher than that of other temperatures. This superiority of the low annealing temperature in the case of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite is attributed to the forming these materials in mixed phases (double phases, Mono – Ortho phases) and its high crystallinity. Besides, the high Mn-O polyhedron distortion excited in these materials. So one can conclude that the annealing temperature plays very important role to improving the photocatalytic performance. The following factors; visible-light absorption, narrow band gap and lattice distortion are the key factors that determine the high photocatalytic activity of the obtained in such materials and good example for that the $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite annealed at 500°C.

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