Chapter

Theories, Hypothesis and Rules for Morphology Transition Engineering of 1D, 2D and 3D Nanomaterials

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Abstract

Most of the chemical and physical properties of nanomaterials vary remarkably according to their size, shape, and structure. Thus morphology is a crucial parameter that controls the properties and functionality of materials. On the basis of Abdelmohsen et al.'s theories and hypothesis, which are theory for morphology transition engineering (ATMTE), theory for morphology engineering of solid compounds (ATMESC), and hypothesis for engineering of micro- and nanostructures (AHEMNS), novel approach was modified for fabricating one-, two-, and three-dimensional hybrid nanomaterials, such as hybrid ZnO nanosheets (38–150 nm), hybrid ZnO nanorods, hybrid nanocomposites, and hierarchical hybrid Cu_2O nanostructures. In addition, by the help of this novel method, the fabrication of metal-oxidene (one/few atoms thick layer of metal oxides) is assumed and hybrid ZnO thin film that is expected to have extraordinary physicochemical properties. A series of selection rules and morphology engineering rules are discussed. Throughout this chapter, we will come across this novel approach as a promising technique for nanofabrication and discuss the suggested mechanisms for the evolution process during fabrication of nanomaterials. By the help of this method, we have fabricated 1D, 2D and 3D nanomaterials that are expected to have potential use for energy, catalysis, biomedical, and other applications.

Keywords: Abdelmohsen et al. Theory 1 (ATMTE), Abdelmohsen et al. Theory 2 (ATMESC), Abdelmohsen et al. Hypothesis (AHEMNS), selection rules (SRs), morphology engineering rules, 1D, 2D and 3D nanomaterials, morphology transition, dangling bonds, morphology engineering, metal oxides, polyoxometalates (POMs), structural directing materials, Zn-oxidene, hybrid thin film

1. Introduction

Since the evolution of the field of nanotechnology "The field of research concerned with building up materials and devices on the scale of atoms and molecules" by the help of the pioneer work of R. Feynman, K. Drexler, and N. Taniguchi; the nanofabrication techniques evolved and developed enormously [1]. Nanomaterial is one-billionth of meter which is ten times the diameter of a hydrogen atom. More precise definition was postulated by B. Fahlman which state that "Nanotechnology is the creation of functional materials, devices and systems through control of matter on the nanometer length scale (1–100) nanometers and exploitation of novel phenomenon and properties (physical, chemical, biological, mechanical electrical, etc.) at that length scale" [1]. At such scales, the classical rules of chemistry and physics cannot be applied like melting point, reactivity, conductivity, strength and color can differ remarkably when the materials converted from bulk to nano-scale [2]. For example, in case of gold, there is a change in color from the bright yellow to red and a drop in melting point from 1336 K to 310 K when the size decreased [3]. There is a change in mechanical properties of carbon-based nanomaterials like fullerenes, nanotubes, and graphene. At nano-scale these materials become lighter and stronger than other structural materials like steel [4, 5]. Finally, other materials like ionic and metal carbon compounds experience changes in electrochemical and electronic properties at the nano-scale in terms of function or magnitude [6].

The concept of materials fabrication/engineering was expanded by Abdelmohsen et al. to include "controlling and designing the oriented structures of materials by re-scaling their dimensions or varying their external morphologies, favorably with functionalization, decoration, doping or mixing with other materials to attend the synergistic effect which enhance their properties" [7]. Nanofabrication techniques are classified into two main approaches which are top-down and bottom-up approaches [8]. The top-down approach involves the breaking down of the materials and converting it from bulk to nano-scale. On the other hand, bottom-up approach involves the building up of nanomaterials atom by atom and molecule by molecule. Scientists recommended the latter over the former approach, because it can fabricate structures with homogenous chemical composition, with better short- and long-range ordering, and less defects [8]. **Figure 1** illustrates an example for the bottom-up approach for engineering of nanomaterials like metal oxides atom by atom in solution. During this process the starting materials can be engineered to miscellaneous nanostructures like particles, rods, tubes, thin films, plates and stars [7]. **Figure 2** illustrates an example for the top-down approach for engineering of nanomaterials like carbon nanoparticles (CNPs). This process involves the breaking down of the bulk carbon black particles into smaller particles by ultra-sonication in the presence of polyoxometalates (POMs) like phosphomolybdic acid (PMA) which stabilizes the etched nanoparticles [7].

A precise definition for morphology transition engineering was postulated by Abdelmohsen et al. which is "The morphology evolution of materials under the effect of external stimulus (chemically, physically or mechanically) to build up new materials with various dimensions under easily attainable conditions (e.g., one step synthesis)" [9]. The role of the external stimulus is the inducing of the surface polarity by etching of the outer surface atoms to create reactive dangling bonds. The chemical stimulus is the acids which etch and dissolve the outer surface atoms to form the dangling bonds [7]. The physical stimulus is the accelerated particles that etch the outer surface atoms to form the dangling bonds [10, 11]. Finally, the mechanical stimulus involves the breaking down of the bulk particles or etching their outer atoms by ball milling to form also the dangling bonds [11, 12]. After the formation of reactive dangling bonds there are four possibilities that takes place which cause morphology transition engineering. The first possibility is the fusion of the etched particles to form different morphologies [7, 9]. The second possibility is the reconstruction

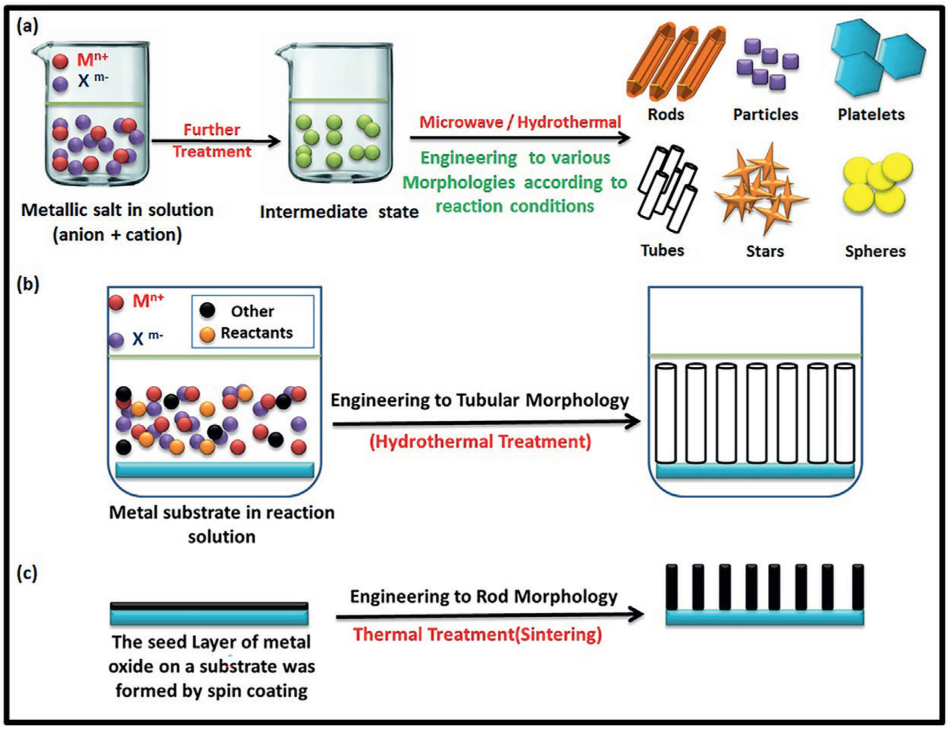

Figure 1.
Schematic illustration for the morphology engineering of metal oxides by bottom-up approach. Reproduced with permission [7] 2017, Springer Nature.

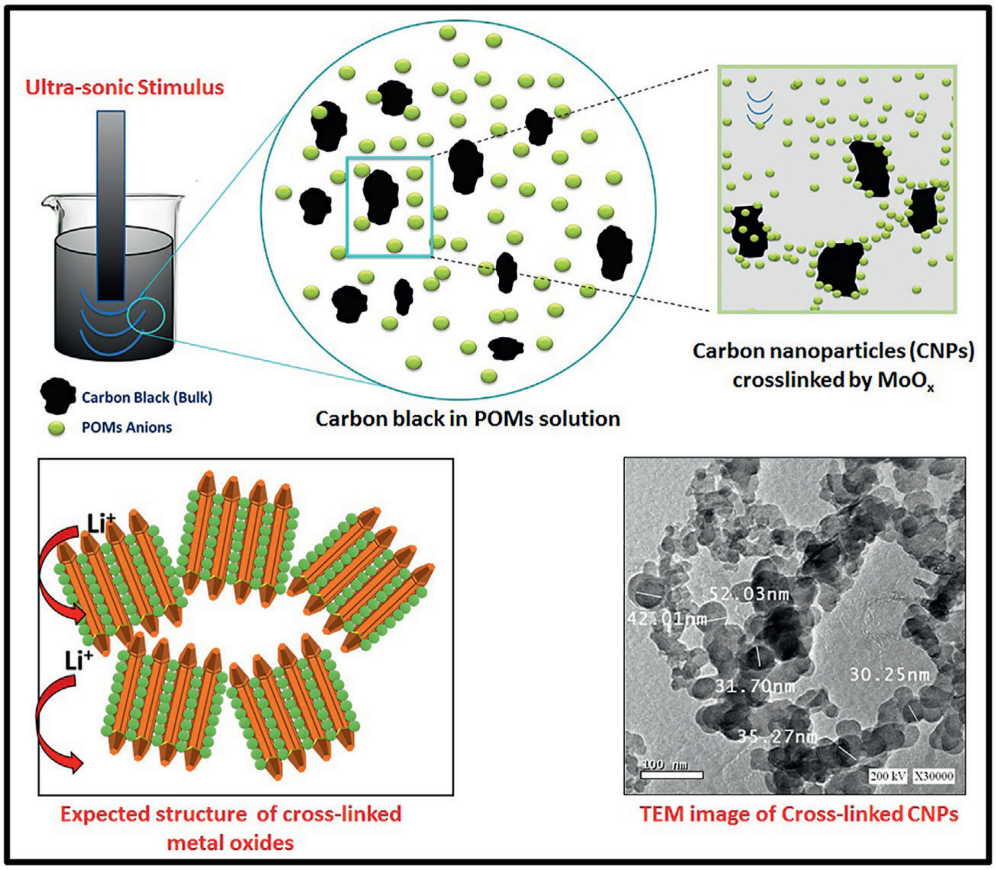

Figure 2.
Schematic illustration for the morphology engineering of carbon nanoparticles (CNPs) by top-down approach [Polyoxometalates assisted-solution technique]. Reproduced with permission [7] 2017, Springer Nature.

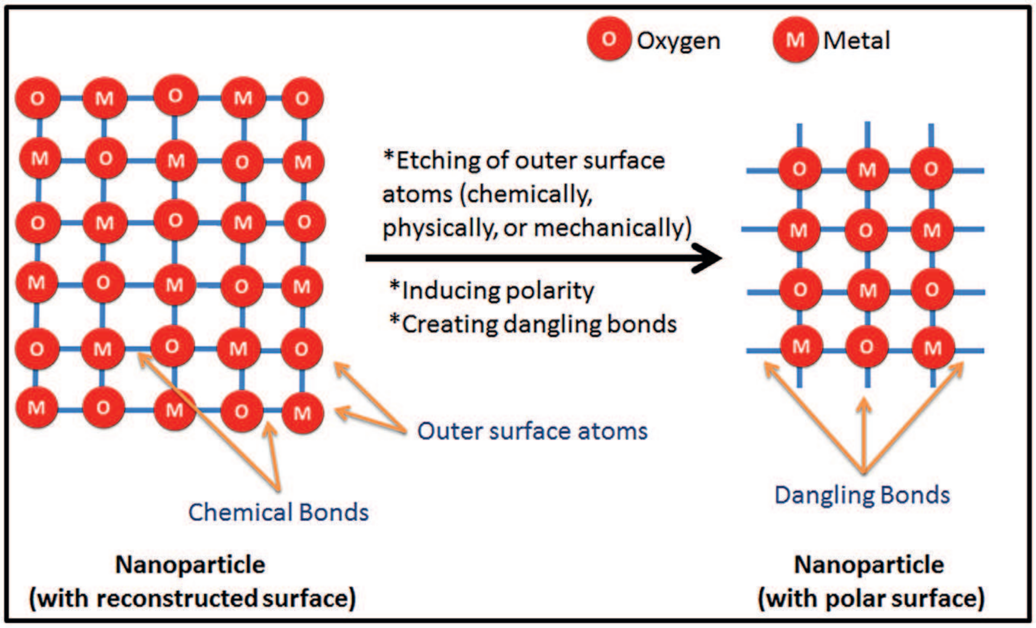

Figure 3.
Illustrates the chemical etching of MO nanoparticles to form smaller particles with reactive surfaces.

of the etched particles to form different morphologies [7, 9]. The third possibility is the adsorption of charged species to form also different morphologies by formation of atomic layers [11, 13]. The fourth possibility is the further growth of materials to different dimensions [7, 9]. The mechanism will be illustrated in details in Section 3. **Figure 3** shows the chemical etching of metal oxide (MO) nanoparticles to form smaller particles with reactive surfaces (polar surfaces/surfaces with dangling bonds). **Figure 4** illustrates the four possibilities that take place after etching/inducing surface polarity of nanoparticles. Reconstruction is a complementary process in all occasions as the particles tend to acquire the stable state after being in the active unstable state [7, 9]. The morphology transition process involves the top-down and bottom-up techniques. Precisely, inducing the surface polarity by etching the materials (chemically, physically, or mechanically) breaks down the bulk materials to smaller ones. This process refers to the top-down approach. The four possibilities mentioned take place to form further morphologies 1D, 2D and 3D nanostructures, refers to the bottom-up approach [7, 9].

2. Different studies on morphology transition engineering

The phase evolution of ZnO films that deposited electrochemically is greatly depending on the concentration of SO_4^{2-} ion as discovered by Wang and co-workers. As discovered by this group, the SO_4^{2-} ion concentration plays a critical role in engineering the morphology of the films from rod-like to plate-like structure. **Figure 5** shows the morphology evolution of ZnO from nanorods to nanoplatelets at different $ZnSO_4$ concentrations [14]. Das et al. studied the morphology evolution in hexagonal $V_{10}O_{28}$ – type polyoxometalate macrocrystals as a function of sonication temperatures. The morphology transformed from nano-rods to microflowers passing through intermediate hexagonal shaped microcrystals by raising the sonication temperature from 50°C to 80°C [15].

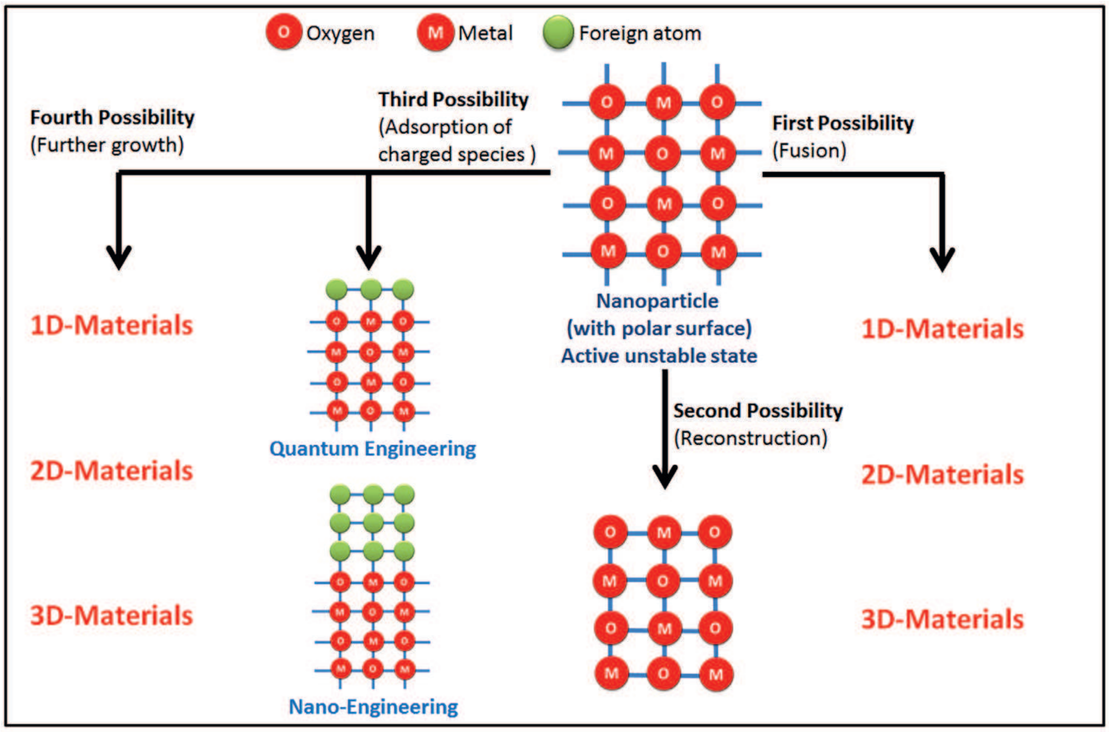

Figure 4.
Illustrates the four possibilities that take place after etching/inducing surface polarity of nanoparticles.

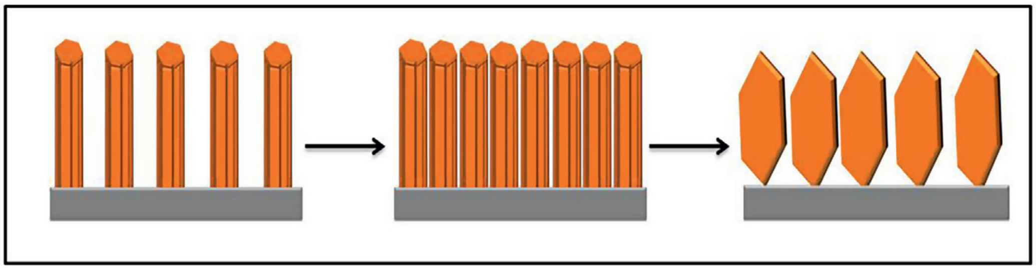

Figure 5.
Shows the morphology evolution of ZnO from nanorods to nanoplates by increasing concentration from left to right.

Xiong et al. used a facile binary-solution route and sequential thermal decomposition at atmospheric pressure to synthesize mesoporous 2D and 3D architectures of the oxide semiconductor Co_3O_4, including nanosheets, monodisperse microspheres are self-assembled from nanosheets, and copper-coin-like nanosheets. The volume ratio of H_2O and ethanolamine (EA) play a crucial role in the morphology of the precursor [16]. Yan et al. has reported the morphology evolution of single-crystalline octahedron CeO_2 to multi-nanostructure and nanorods using $Ce(NO_3)_3$•$6H_2O$ as cerium resource and Na_3PO_4•$6H_2O$ as mineralizer, the morphology evolution between the nano-octahedron and nanorod was observed by tuning the hydrothermal treatment time as shown in **Figure 6a** [17]. The Morphology Evolution of ZnO Thin Films from aqueous solutions was demonstrated by Goa and co-workers. A two-step approach was employed for the epitaxial growth of ZnO by beginning with the preparation of a (002)-oriented ZnO seed layer electrochemically. The substrate was soaked in an aqueous solution containing $ZnCl_2$ and complex agents. A large-scale fabrication of ZnO nanorods arrays on transparent conductive oxides has been

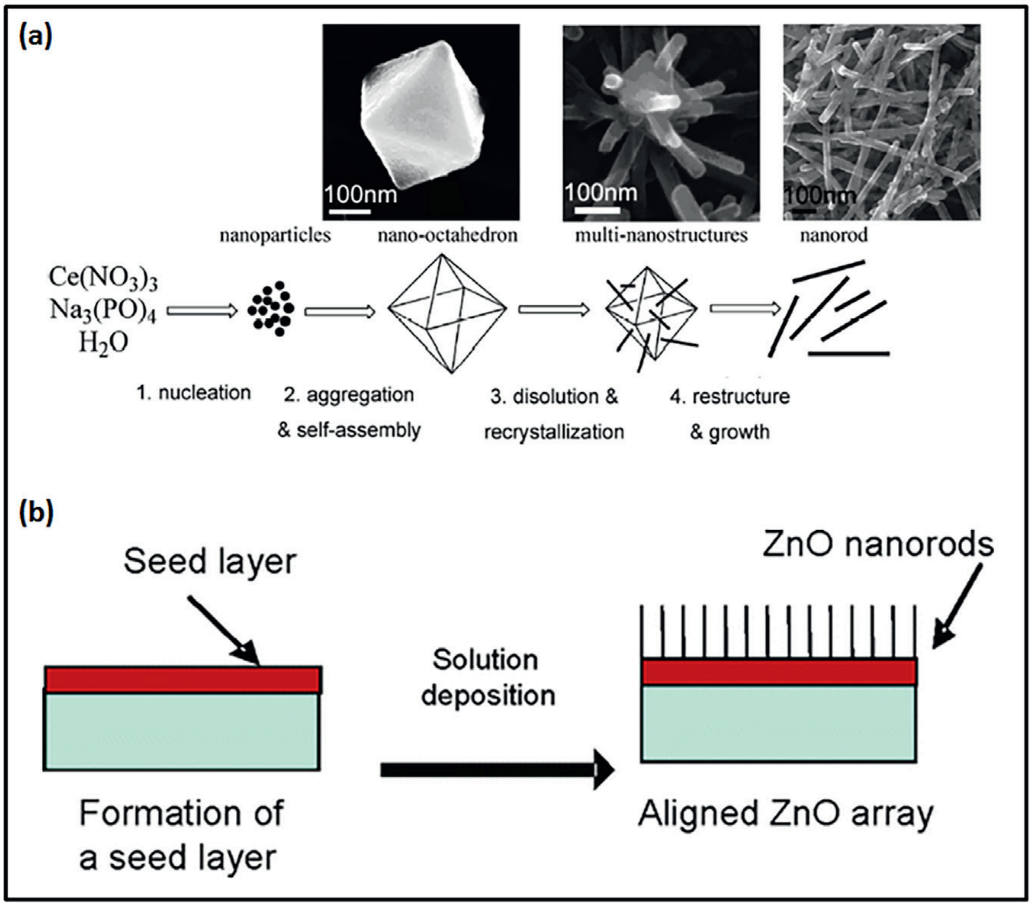

Figure 6.
Shows (a) schematic illustration for the multinanostructures evolution of CeO_2*, (b) the morphology evolution of ZnO nanorods of ZnO thin films from aqueous solutions. Reproduced with permission [17] 2008, American Chemical Society. Reproduced with permission [18] 2006, American Chemical Society.*

achieved after soaking at 95°C for 1–48 h as shown in **Figure 6b** [18]. Sweegers et al. discovered that the reaction conditions have a great effect on the formed morphology of gibbsite, g-$Al(OH)_3$. While the process of growth the gibbsite crystals morphology changed from thin, rounded hexagons and faceted lozenges into plates and blocks with well-formed basal, prismatic faces. The alkali ions of solution play the major role to control the morphology of gibbsite. An evidence for this fact is the engineering of different morphologies from potassium and cesium hydroxide solutions [19]. Morphology evolution of urchin-like $NiCo_2O_4$ nanostructures from urea was reported by Wang and co-workers. A'rods-to-straw-bundles-to-urchins' mechanism was proposed. Images of the $NiCo_2O_4$ products obtained by hydrothermal process are shown in **Figure 7** [20].

3. Mechanism and rules of morphology transition engineering

On the basis of chemical and physical explanation we will illustrate the mechanism of morphology transition of pure zinc oxide (ZnO) nanorods to nanoplatelets grafted Mo_8O_{23}-MoO_2 mixed oxide, when react with polyoxoxmetalates (POMs) like phosphomolybdic acid (PMA) under ultra-sonication. In addition, we will discuss a series of selection rules (SRs) which account for the ability of ZnO to experience morphology transition among other binary compounds. The

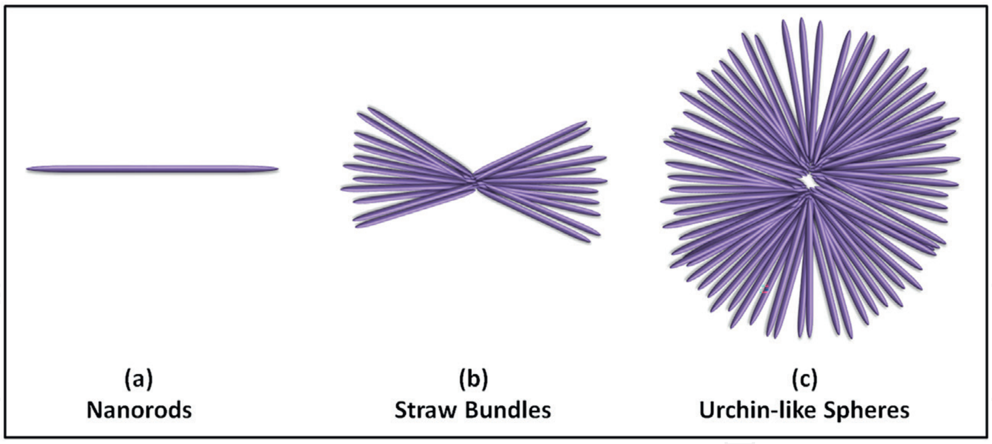

Figure 7.
Shows schematic illustrations of the growth mechanism of the urchin-like $NiCo_2O_4$ *nanostructures evolving from nanorods, straw bundles to urchin-like spheres.*

explanation of the nano-scale reaction mechanism depends on some theories and models like hard and soft (Lewis) acids and bases (HSAB) theory, Brønsted-Lowry acid/base theory, frontier molecular orbital (FMO) theory, the perturbation theory of reactivity, and site-binding model [21–25]. According to HSAB theory; elements in periodic table can be classified as acids and bases [26]. So we suggest that the cationic metal centers (Zn^{2+}) act as Lewis acid sites [LUMO: Lowest Unoccupied Molecular Orbital] while the anionic oxygen (O^{2-}) centers act as Lewis bases [HOMO: Highest Occupied Molecular Orbital] [27]. We can conclude that the fusion process is due to the interaction between (LUMO) of cations with (HOMO) of ligand (empty-filled interaction) which produce a bonding molecular orbital [28]. When the energy of the interacting orbitals is close the newly formed molecular orbital needs greater stabilizing energy to be formed [29]. Hence, we introduce the first selection rule (SR1) as follow “The appropriate energy difference between LUMO (acid orbital) and HOMO (base orbital) may account for ability of ZnO to experience morphology transition when react with POMs under specific conditions” [7].

Acid/base sites are quite important in determining the catalytic activity of metal oxides [27]. In highly acidic medium (PMA solution (pH ~2)), ZnO surface will act as Brønsted bases and can accept protons according to site-binding model and become positively charged as illustrated in **Figure 8b**. The isoelectric point (IEP) is the point at which the MO carries zero charge [30]. At pH values above the IEP, the MO carries a negative charge, while at pH values below the IEP; the MO carries a positive charge [31]. The IEP of ZnO lies within the pH range (8.0–10.0) [32]. The positively charged ZnO nanorods will be surrounded by the Polyoxomatalate anions $[PO_4\ (MoO_3)_{12}]^{3-}]$ as illustrated in **Figure 8a–c**. Hence, by considering these two factors which are; at pH value lower than the IEP, OH^{2+} species are dominant, and our reaction takes place at extremely acidic medium (pH ~ 2); we introduce the second selection rule (SR2) as follow; “The suitable isoelectric point (IEP) which locates in basic region (8–10) account for the tendency of ZnO to experience morphology transition when react with POMs, as this guarantees the predominant of OH^{2+} species which attract POM anions to metal oxide surface” [7].

Surface polarity helps to explain the morphology transition of ZnO, which refer to “the status of the surface plane whether it contains a stoichiometric ratio of cations (Zn^{2+}) and anions (O^{2-}) or not, which refer to non-polar or polar surface

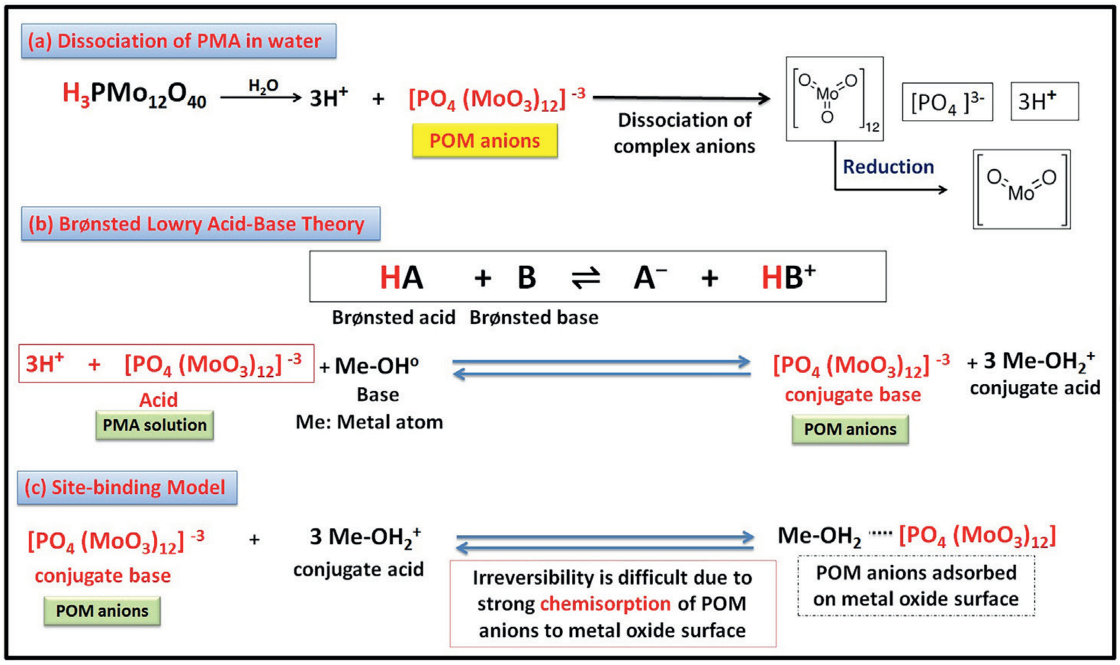

Figure 8.
Shows (a) dissociation equation for phosphomolybdic acid (PMA) in water, (b) the behavior of OH group on MO surface as Brønsted base site (accept protons), and (c) the adsorption of (POM anions) to amphoteric MO surface according to site-binding model. Reproduced with permission [7] 2017, Springer Nature.

respectively" [33]. Physical explanation was suggested on the basis of 'the perturbation theory of reactivity' which state that as a pair of reactants approach one another, their orbitals interact and begin to undergo a "perturbation". Hence, we suggested that when an acid is adsorbed on the oxide surface a perturbation of the acid-base sites [(Zn^{2+}) and (O^{2-}) sites] take place induces the surface relaxation and surface polarity [25]. The polarity may be induced more by chemical etching of surface atoms by PMA. Tasker et al. and other researchers reported that the unstable polar surfaces can attain stability by different methods like metallization (fusion of nanorods), surface reconstruction, adsorption of hydroxyl groups and other charged species, finally further growth occurred due to the presence of other reactants [34–38]. To sum up the mechanism of morphology transition engineering, we conclude three steps for complete morphology transition of ZnO nanorods to hybrid nanoplatelets. First step, involves the chemisorption of POM anions on the surface of ZnO nanorods cause surface relaxation by disrupting the neighboring atoms, which induce the polarity of the non-polar faces (the physical explanation) [7, 9, 11]. According to ZnO Pourbaix diagram, the pH of POM solution (~2) allows the dissolution/chemical etching of ZnO [39]. This chemical etching causes surface relaxation and induces polarity by removing zinc cations or oxygen anions from the outer surfaces (the chemical explanation). These etched species are taking part in self-assembly (fusion) process. Second step involves three main mechanisms; the first one, is the metallization process which involves fusing of two faces with different polarity by bonding Zn-atom to O-atom through their dangling bonds [empty Zn 4 s-orbitals and filled O 2p-orbitals] to form bonding molecular orbital with lower energy and high stability [36]. The second and third ones involve the incorporation of dissolved Zn^{2+} and O^{2-} species within the fused faces which have similar polarity. Schematic illustration for the three possible fusion mechanisms is illustrated in **Figure 9a** [7]. We supposed that PMA acts as a catalyst for binding ZnO nanorods together to nanoplatelets accompanied with deposition of Mo_8O_{23}-MoO_2 mixed oxide on their surfaces. Both of (Mo^{IV}) and (Mo^{VI}) species are oxidized in the air to Mo_8O_{23}-MoO_2 mixed oxide. A brief schematic illustration for proposed morphology transition mechanism is shown in **Figure 9b** [7]. We suggest the formation of intermediate compounds Zn-molybdates (ZM) or/and Zn phosphomolybdate (ZMP) (pigments) during morphology transition process [9, 11].

In addition, we have suggested that, magnetic properties of cations that form the binary compounds may account well for the fluctuation of their behavior when

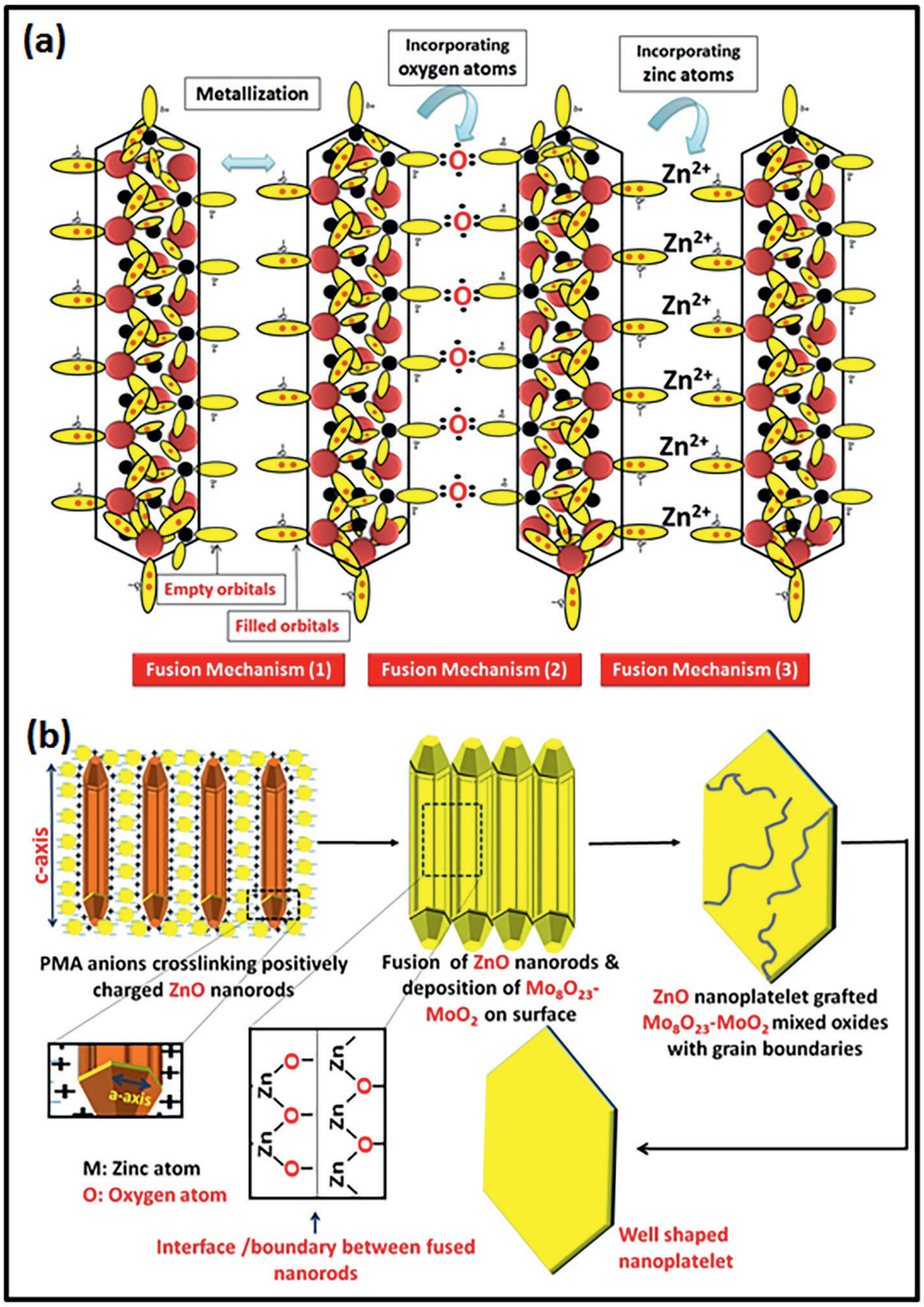

Figure 9.
(a) Schematic illustration for the three possible fusion mechanisms of ZnO nanorods in PMA solution, (b) the proposed mechanism for the morphology transition (self-assembly) of hexagonal ZnO nanorods to ZnO nanoplatelets grafted Mo_8O_{23}-MoO_2 *mixed oxide. Reproduced with permission [7] 2017, Springer Nature.*

react with POMs [40–42], as by increasing the para-magnestism of cation, the repulsion between the d-orbital of cation and 2p-orbital of anion also increases which does not allow the binding of the latter with 4s-orbital of cations, and restrict the morphology transition process. This may account for the different behavior of metal oxides when react with POMs. We introduce the third selection rule (SR3); as follow "The completely filled 3d-orbital (diamagnetism) of ZnO can account well for its ability to experience morphology transition when react with POMs and recommend other binary compounds of cations like (Cd^{2+}, Hg^{2+}, Cu^{+}, Au^{+}, Ag^{+}) to obey ATMTE" [7]. This third rule still needs more computational studies and experimental evidences to be clear. Amphoteric behavior of ZnO accounts very well for the phenomenon of morphology transition when react with POMs [30, 43]. Amphoterism of ZnO means that, it has the tendency to dissolve in both acidic and basic medium, which guarantees the presence of dissolved cationic and anionic species during all stages of reactions. These species play a critical role in fixing the grain boundaries between the merged nanorods to produce nanoplatelets. Hence, we introduce the fourth selection rule (SR4) as follows; "The amphoteric nature of ZnO accounts well for its ability to experience morphology transition when react with POMs at specific conditions, and recommend other amphoteric oxides to obey ATMTE" [7]. On the basis of experimental evidences we have postulated the morphology engineering rules (MERs) that control the morphology (dimension and thickness) of fabricated materials [9]. We introduce the first MER (MER1) as follow, "Under controlled conditions, as the temperature increases, the possibility to engineer higher dimensions (2D,3D) decreases and vice versa" [9], while the second MER (MER2) "Thickness Rule" states that, "Under controlled conditions, ultra-sonication at low temperature and POM concentrations increases the possibility to engineer higher dimensions (2D,3D) with few atoms in thickness" [9]. The detailed mechanism and discussion about the rules are illustrated in [7, 9, 11].

4. Abdelmohsen et al. theories and hypothesis for morphology transition engineering (ATMTE, ATMESC and AHEMNS)

Theory defined as "the explanation of the general causes of certain phenomenon with evidences or facts to support it" [44]. So, on the basis of our phenomenon that discussed in Section 3 and other experimental evidences that will be mentioned later, we can postulate a theory about morphology transition engineering of micro and nanomaterials. Abdelmohsen et al. theory for morphology transition engineering (ATMTE) was proposed on the basis of the phenomenon of morphology transition of ZnO nanorods to nanoplatelets when reacts with POMs under ultra-sonication [7]. This theory (ATMTE) states that "Binary compounds especially amphoteric/diamagnetic pure and doped metal-oxides like (ZnO, Cu_2O) that have appropriate energy difference between their LUMO (acid site/cation) and HOMO (base site/anion), may experience morphology transition to various dimensions (1D, 2D and 3D) when reacts with polyoxometalates under specific conditions, with a possibility to manipulate their surface catalytic properties" [7]. By further study and reading about the morphology transition of materials, another theory was proposed which discuss the ability of most solid materials to experience morphology transition after inducing their surface polarity [11]. This theory is Abdelmohsen et al. theory for morphology engineering of solid compounds (ATMESC), which state that "Most solid compounds may experience morphology transition by inducing their surface polarity (creating dangling bonds); chemically, physically or mechanically. For instance, chemically we can induce polarity of amphoteric compounds which include diamagnetic cations (d^{10}) within their structure (e.g., doped/pure ZnO or Cu_2O and their hydroxides, and composites) with a possibility to manipulate the engineered morphologies, and surface catalytic activity depending on the morphology engineering rules (MERs)" [11]. A hypothetical study for the morphology transition of Cu_2O and other solid materials was proposed as Cu_2O dissolves completely by POMs at high temperature but still need a precipitating-agent to be precipitated to different morphologies. In order to control this reaction we proposed Abdelmohsen et al. hypothesis for engineering of micro and nanostructures (AHEMNS). This hypothesis supposes dissolving any chemical compound by a specific dissolving agent, such as acids, e.g., PMA. Then these dissolved seeds can be precipitated by an alkali like NaOH to synthesize various nanostructures. It is a modification for the aforementioned two theories (ATMTE and ATMESC) and is expected to be applied for nearly all solid compounds by using different dissolving and precipitating-agents [9]. This hypothesis (AHEMNS) states that "Most Solid compounds may be engineered by dissolving starting materials by dissolving agents (e.g., phosphomolybdic acids) which acts also as structural directing-agent, followed by co-precipitating by precipitating agent like (NaOH)" [9]. The produced materials by this method are mostly hybrid materials due to the co-precipitation of both the precursor and the dissolving agent together. In addition, we assumed the fabrication of different morphologies like rods, wires, and needles. Also we look for fabrication of 3D nanostructures when carbon fillers like graphene, and carbon nanotubes, are added during synthesizing. The used dissolving agents is not limited to PMA, as we assume also other types of POMs which widely used for self-assembling of materials and other types of acids to be used as structural-directing agents. The growth of MO over carbonaceous materials is strongly recommended for critical applications like energy storage as this enhance electron diffusion through the whole structure. Two samples of ZnO nanoparticles which are (ZnO (1)) and (ZnO (2)) were prepared by a simple co-precipitation at room temperature and micro-wave assisted technique as reported here. XRD charts and SEM images for them are shown in **Figure 10** [9].

4.1 Fabrication of 1D nanostructures

1D nanostructured materials possess a variety of advantages which make them promising materials in different applications like alkali metal ion batteries due to the high capacity, long-term cycling, and superior rate performance. They also used in electronics, water splitting, photocatalysts, and water treatment [45]. On the basis on our theories, we have fabricated various 1D nanostructures as reported here [7, 9]. For instance, by stirring of ZnO (2) at high temperature (~90°C) in POM solution, a hybrid ZnO nanorods (ZnO grafted MoO_x) was produced which have a diameter in the range of (100–130) nm and length of few micrometer [9]. Few nanosheets are formed but the predominant structure is the nanorods. SEM images of the nanomaterial are shown in **Figure 11** [9]. As noticed by experiments, at room temperature Cu_2O has not experienced any morphology transition, but under ultra-sonication at high temperature (~90°C) hybrid nanowires were produced by addition of NaOH as a precipitating-agent as reported here [9]. XRD charts and SEM images are shown in **Figure 12** [9]. A hybrid (1D) ZnO/MWCNTs nanocomposite was produced by

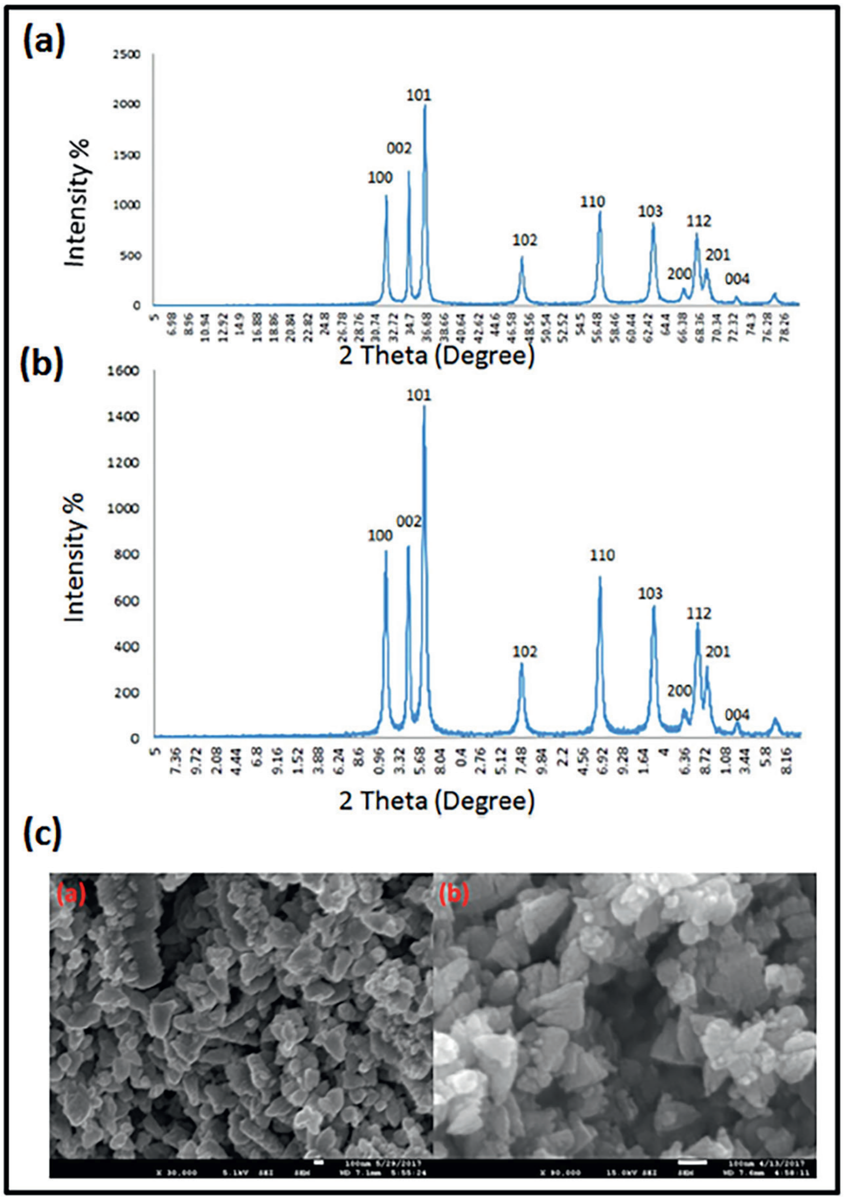

Figure 10.
XRD charts for (a) (ZnO (1)), (b) (ZnO (2)), (c) SEM images for (ZnO (1)) (left) and (ZnO (2)) (right). Reproduced with permission [9] 2019, Springer Nature.

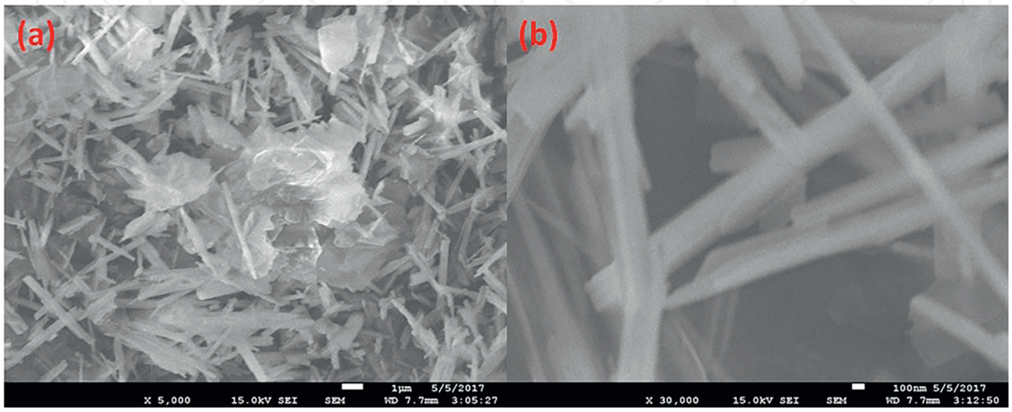

Figure 11.
SEM images of hybrid ZnO nanosheets prepared by stirring of "ZnO (2)" in polyoxometalate (POM) solution at ~90°C. reproduced with permission [9] 2019, Springer Nature.

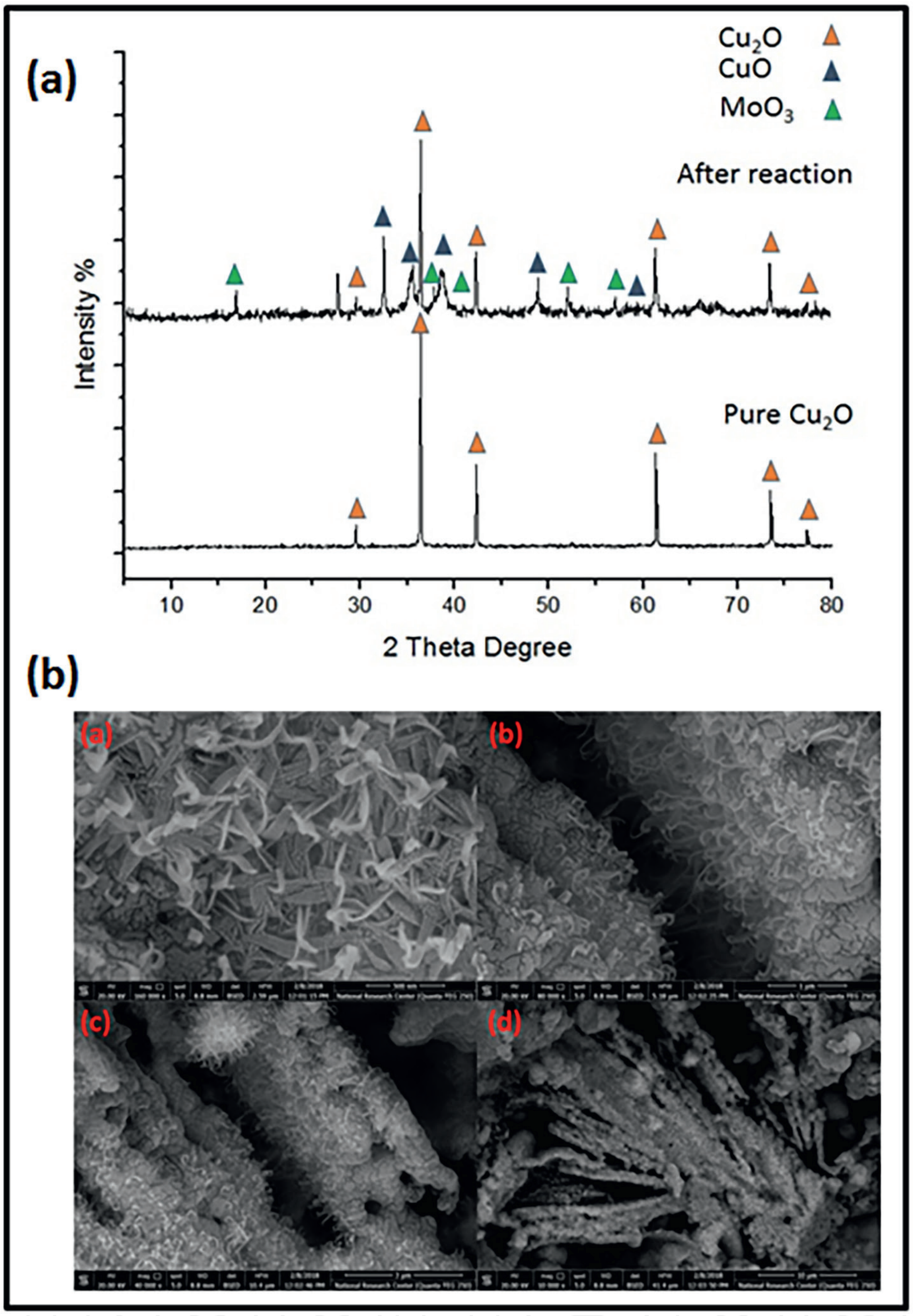

Figure 12.
(a) XRD charts for pure Cu_2O and the formed materials after reaction under ultra-sonication, (b) SEM images of Cu_2O that experienced morphology transition to nanowires under ultra-sonication conditions at high temperature. Reproduced with permission [9] 2019, Springer Nature.

ultra-sonication at room temperature of mixture of ZnO and MWCNTs in POM solution [9]. This will be discussed in details in Section 5.

4.2 Fabrication of 2D nanostructures

2D nanostructured materials possess a variety of advantages which make them promising materials in different applications like energy storage and conversion. They also used in cancer therapy, biomedical applications, piezophototronics, and water treatment [46, 47]. On the basis of our theories, we have fabricated various 2D

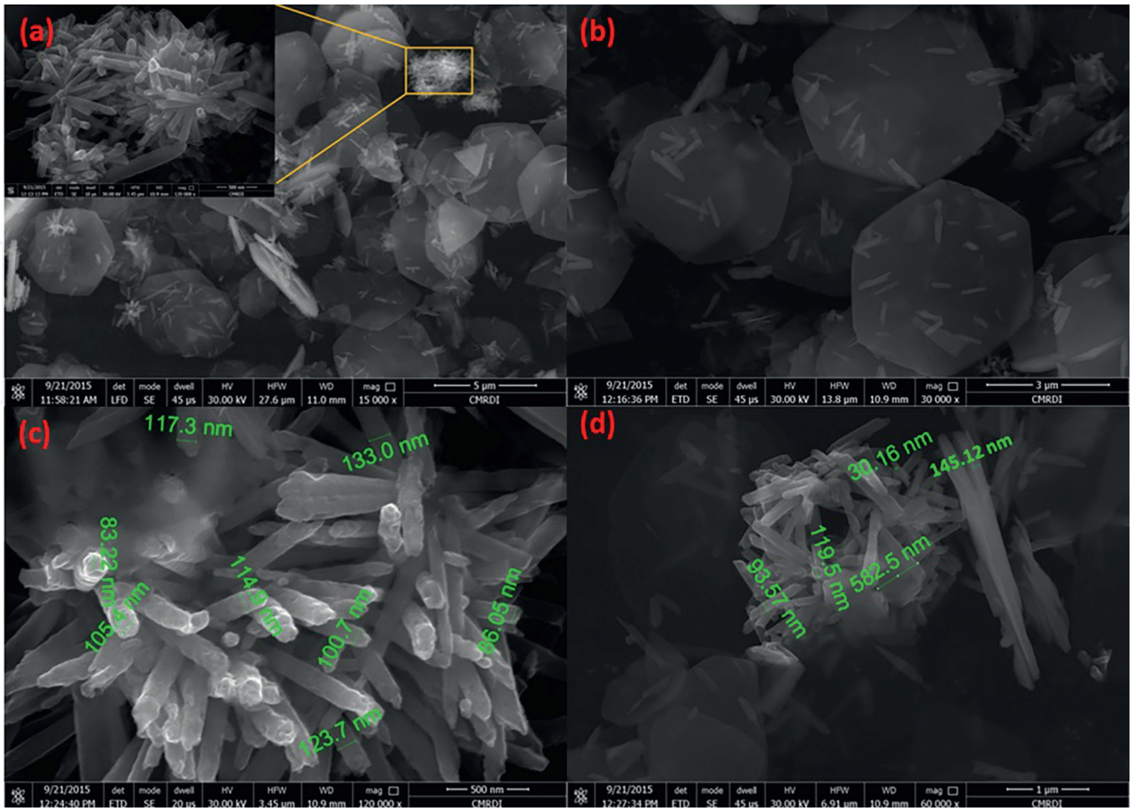

Figure 13.
(a) FESEM images of ZnO nanoflower over nanoplatelets, (b) dispersed ZnO nanorods over nanoplatelets, (c) collection of ZnO nanorods, (d) and ZnO nanocage over nanoplatelets. Reproduced with permission [7] 2017, Springer Nature.

nanostructures as reported here [7, 9]. For instance, we have fabricated this hybrid nanocomposite (ZnO nanoplatelets grafted Mo_8O_{23}-MoO_2 mixed oxide) decorated ZnO nanostructures, by ultra-sonication a mixture of ZnO nanorods and POM at room temperature for nearly 15 minutes. Nanoplatelets with thickness (100–130) nm and micrometer length were produced as shown in **Figure 13** [7]. Under different conditions, thin nanosheets (exfoliated graphite-like structure) were produced with thickness (38–50) nm and micrometer length by also ultra-sonication of ZnO (2) in POM solution at room temperature as shown in **Figure 14** [9]. Moreover, 2D nanosheets were also fabricated by stirring of “ZnO (1)” in polyoxometalate solution at ~90°C as reported here [9].

4.3 Fabrication of 3D nanostructures

3D nanostructured materials possess a variety of advantages which make them promising materials in different applications like electronics, environmental applications, energy storage, and energy conversion [47]. On the basis on our theories, we have fabricated various 3D nanostructures as reported here [9]. For instance, we have fabricated intersected (3D) hybrid ZnO nanosheets/nanoplatelets (ZnO grafted MoO_x) by ultra-sonication of pure ZnO nanoparticles in POM solution as shown in **Figure 15** [9]. In addition, 3D hybrid Cu_2O nanoflowers were fabricated by stirring of Cu_2O in POM solution at high temperature [9]. XRD charts of the starting material (Cu_2O) and the final product is shown in **Figure 16a** [9]. SEM images of the 3D nanoflowers are shown in **Figure 16b** [9].

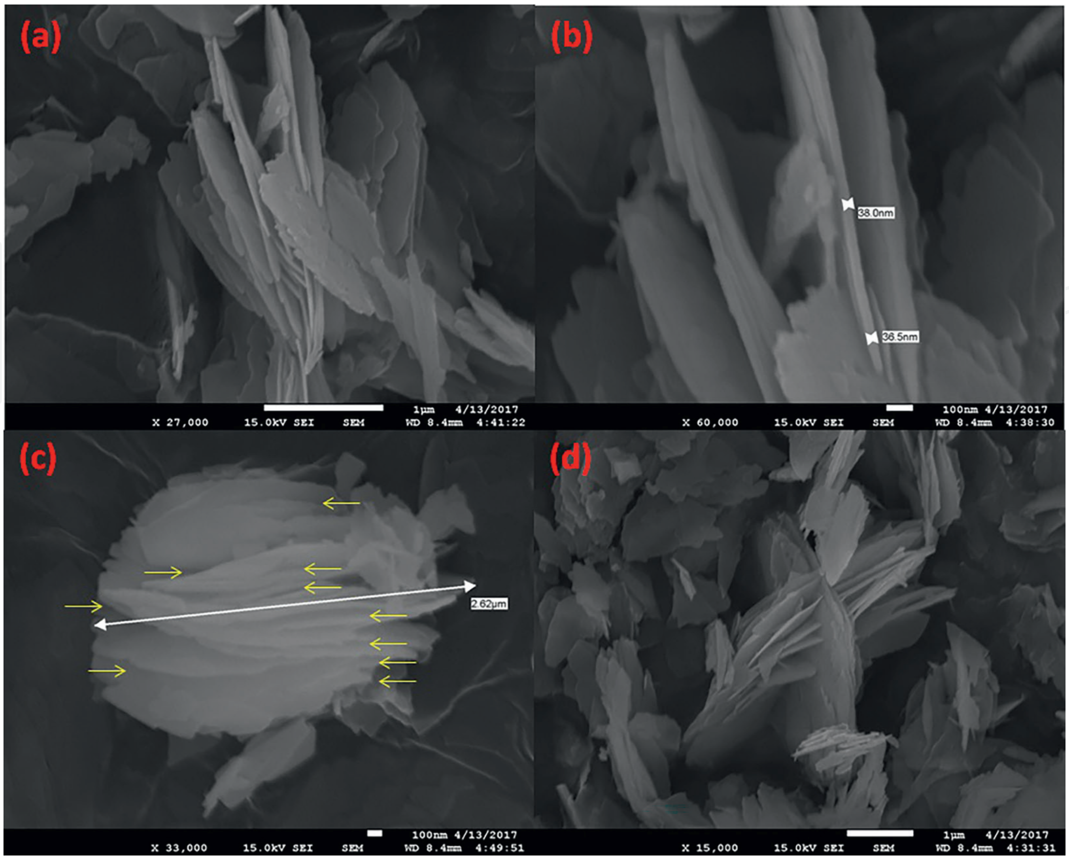

Figure 14.
SEM images of hybrid ZnO multi-layered nanosheets (exfoliated graphite-like structure) prepared by ultra-sonication of "ZnO (2)" at room temperature. Reproduced with permission [9] 2019, Springer Nature.

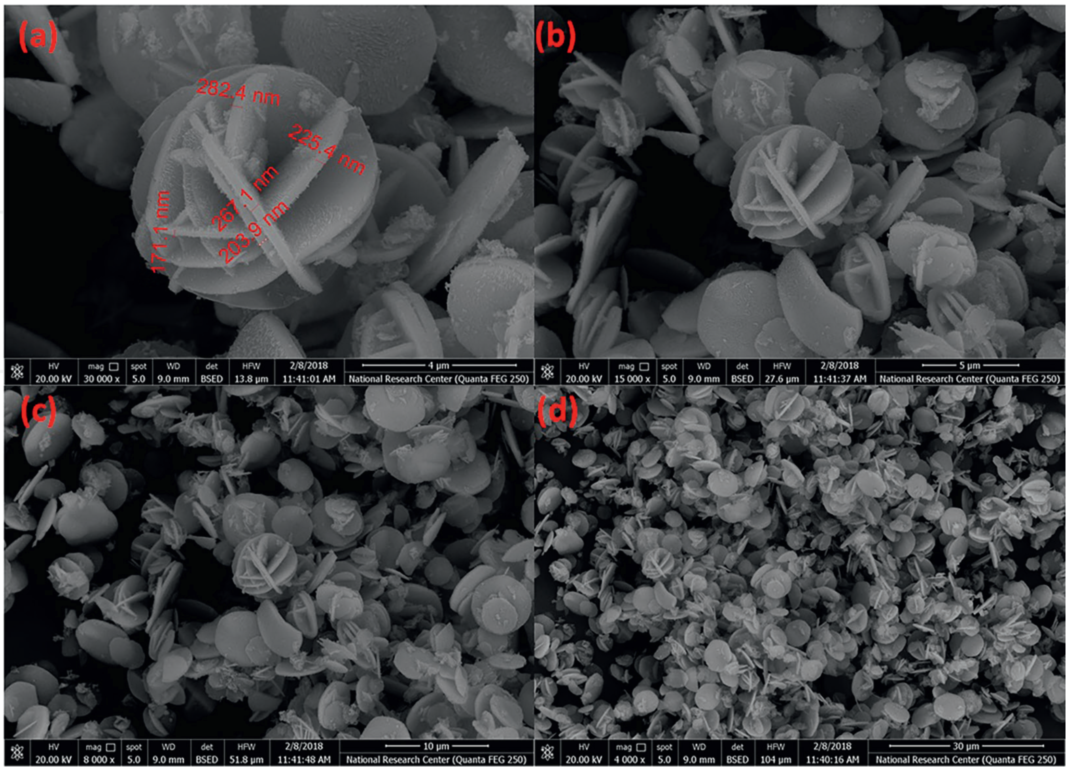

Figure 15.
SEM images of 3D- hybrid ZnO nanostructures prepared by ultra- sonication method. Reproduced with permission [9] 2019, Springer Nature.

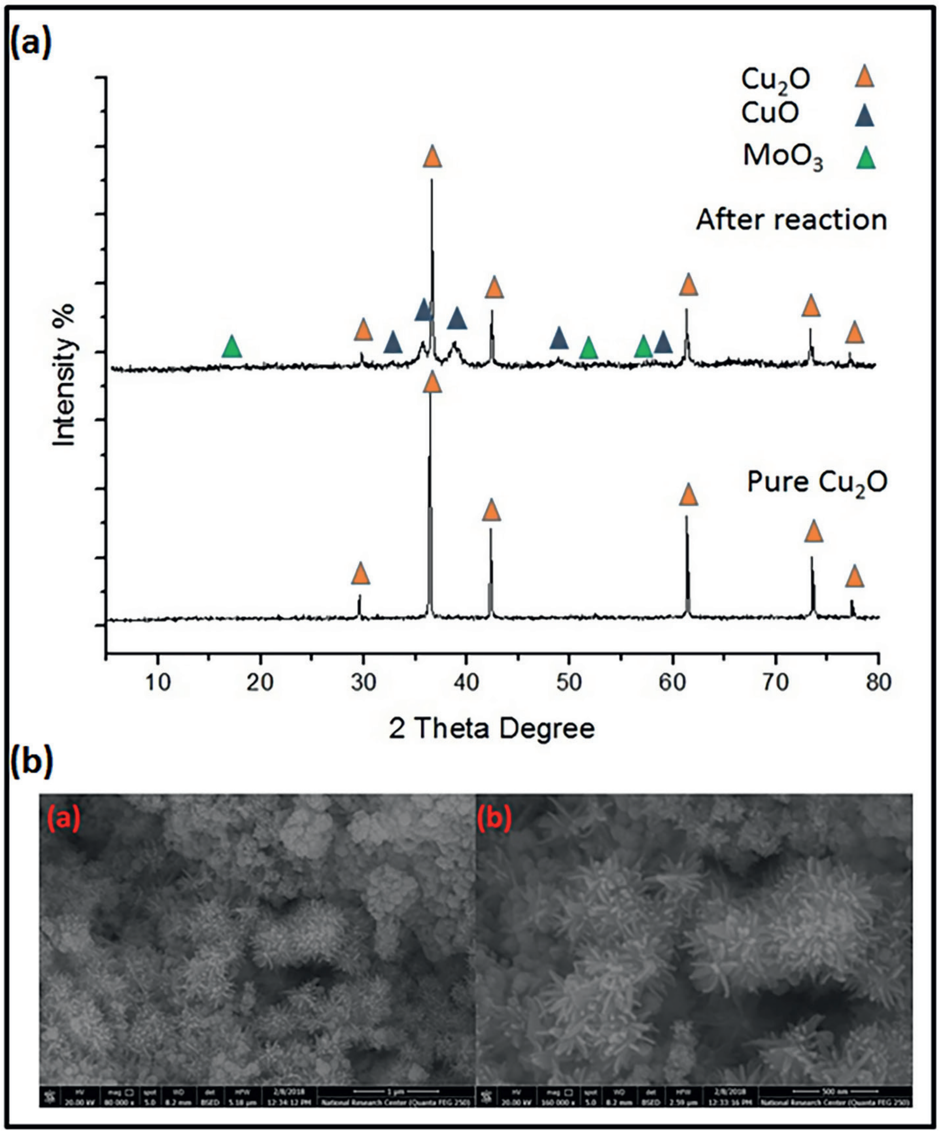

Figure 16.
(a) XRD charts of the starting material (Cu$_2$O) and the final product, (b) SEM images of the formed 3D nanoflowers. Reproduced with permission [9] 2019, Springer Nature.

5. Influence of carbonaceous materials on morphology transition of ZnO nanoparticles

Carbon-based materials which called the carbon fillers are used for enhancing the mechanical and electrical properties of the nanocomposite. They can be classified in to two types; which are the traditional fillers and the advanced fillers. The traditional fillers are carbon black and graphite. On the other hand, the advanced fillers are expanded graphite, graphene derivatives (graphene oxide, graphene, and porous graphene), carbon nanotubes (multi-walled carbon nanotubes and single-walled carbon nanotubes) and carbon aerogel [48]. These carbon fillers are acting as structural-directing materials which control the structure and morphology of hybrid ZnO during morphology transition process in the presence of POMs which act as structural-directing agent [9]. In our experiment, the effect of the presence of carbon fillers like carbon nanotubes (MWCNTs) was investigated. We have added (0.25 g) of both pure ZnO and MWCNTs in 50 ml deionized water under ultra-sonication for 45 minutes in the presence of PMA at 25°C. Under this reaction conditions we expected the fabrication of nanoplatelets (nanosheets) as usual, but we get a mixture of nanorods and nanosheets. For this unexpected phenomenon we have assumed this mechanism. We assumed that the carbon filler (MWCNTs) which act as structural-directing materials for the polar ZnO nanoparticles can inhibit the dangling bonds on ZnO surfaces that are in contact with them. By this way, they can allow the fusion of ZnO nanoparticles in only one-dimension. This leads to the formation of 1D nanomaterial which is the nanorods. In other words, due to the high strength of MWCNTS, we supposed the ability of them to control the way by which the ZnO nanoparticles will fuse with each other. Growth mechanism of hybrid ZnO nanorods in the presence of multi-walled carbon nanotubes is shown in **Figure 17** [9]. SEM images of hybrid ZnO/multi-walled carbon nanotube nanocomposites are shown in **Figure 18** [9].

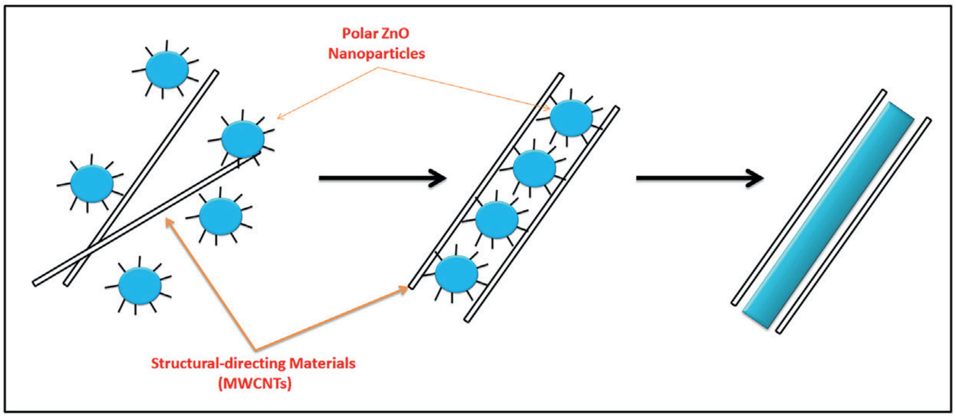

Figure 17.
Growth mechanism of hybrid ZnO nanorods in the presence of MWCNTS.

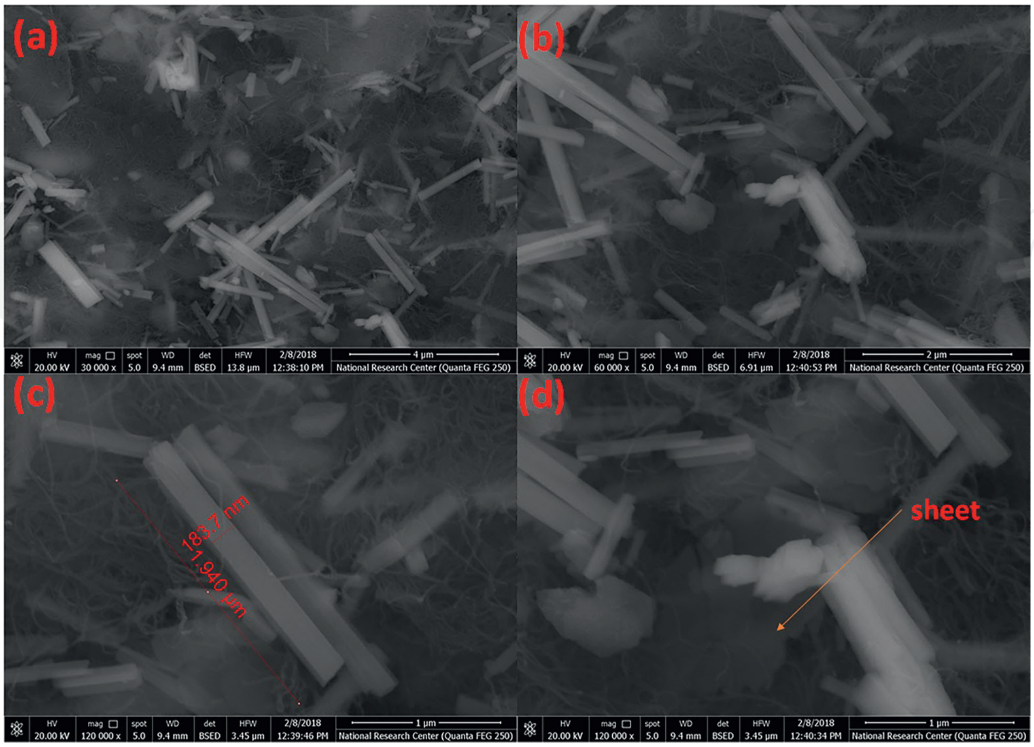

Figure 18.
SEM images of hybrid ZnO/ MWCNTS nanocomposites. Reproduced with permission [9] 2019, Springer Nature.

6. Zinc-oxidene, double layer thin film and expected applications

We suggested the controlling of nanosheets thickness to few nanometers by controlling the reaction conditions like temperature, sonication power and concentration. This will help us to engineer the quantum nanosheets (few/one-atoms thick layer) of hybrid ZnO, which was nominated as hybrid zinc-oxidene [9, 49, 50]. By similar or different methods metal-oxidene can be prepared for a variety of MO. Pure ZnO nanosheets can be produced by chemical etching of MoO_x deposited layers on ZnO nanosheets as shown in **Figure 19a** [9]. Hybrid and pure Zn-oxidene is expected to have extraordinary physico-chemical properties similar to that of graphene and silicone [51]. Fabrication of double layers or hybrid ZnO thin film is conceivable by soaking up of ZnO thin film in POM solution under specific conditions. This will lead to the polarity inducing of top surface, then the deposition of MoO_x layer epitaxially over ZnO substrate as shown in **Figure 19b** [9]. Hybrid and pure 1D, 2D and 3D nanomaterials that are engineered by Abdelmohsen et al. theories (ATMTE, ATMESC, and AHEMNS) are expected to have potential applications in different field if science likes solar cells that strongly depend on thickness [52]. Expected high piezoelectricity of ultra-thin ZnO nanosheets/nanoplatelets will make it an excellent candidate for nanosensors and nanoactuators [53]. ZnO is a promising anode material for alkali metal-ion batteries like lithium-ion battery, sodium-ion batteries and potassium-ion batteries, because it is not expensive, environmentally friendly, and biocompatible [54]. Pure ZnO has a high theoretical capacity (978 mAh g^{-1}) and can be used in its pure form as anode or doped with other oxides like transition metal oxides such as CoO (715 mAh g^{-1}), NiO (718 mAh g^{-1}) and CuO (674 mAh g^{-1}). Pure and doped ZnO nanostructures are also used as an electrode in supercapacitors [55].

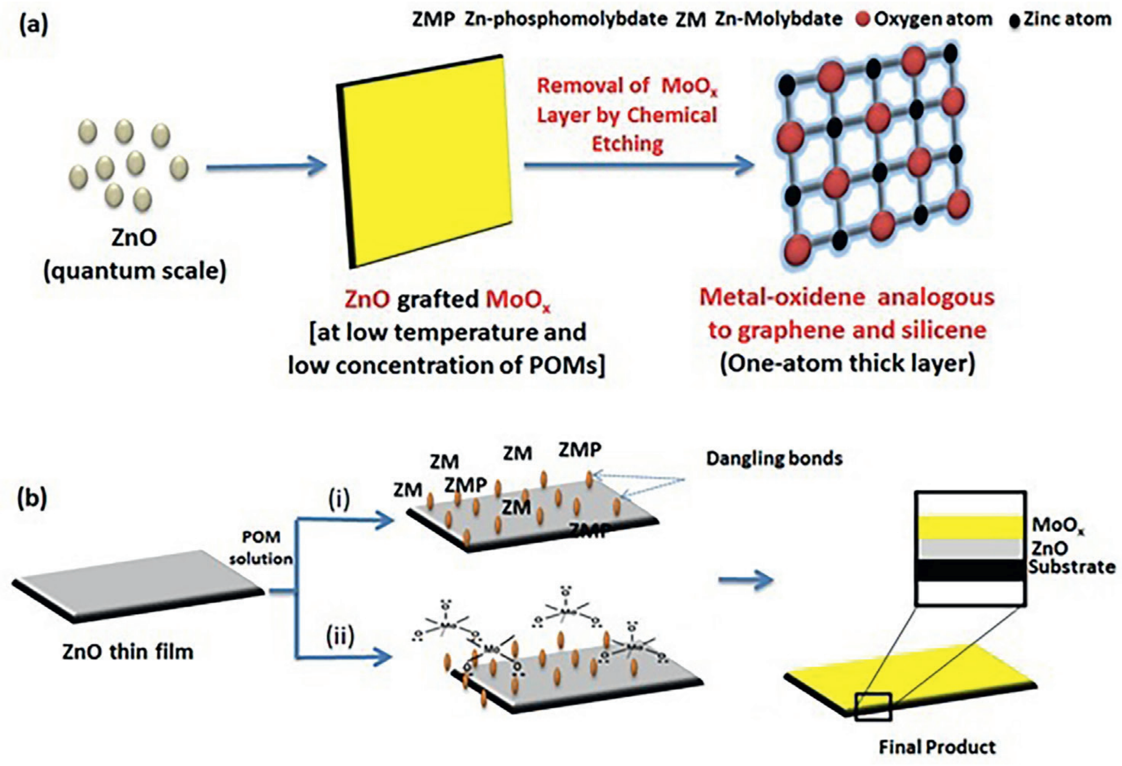

Figure 19.
(a) Schematic illustration for developing thin sheet of ZnO (Zn-oxidene) by chemical etching of MoO_x, and (b) developing thin film of MoO_x/ZnO top-down layers. Reproduced with permission [9] 2019, Springer Nature.

Other applications for pure ZnO are rubber industry, ceramic industry, medicine, food additive, pigment, UV absorber, coatings, corrosion prevention in nuclear reactors, methane reforming, and electronics [56].

7. Conclusion

These theories are expected to be the basis for reliable engineering of hybrid nanostructures with different dimensions and their functionality. This approach is expected to be the basis of a competitive fabrication approach to 1D, 2D and 3D hybrid nanostructures. These hybrid nanomaterials have potential use for energy, catalysis, biomedical and other applications. Additional experimental evidences are required to support these theories. Further work is required to manipulate the thickness of nanoplatelets/nanosheets, study catalytic properties of hybrid materials, and study morphology transition in the presence of carbonaceous materials (Graphene, CNTs, and CNPs) and their applications to alkali metal-ion batteries. In addition, more computational studies and experimental evidences are required to support our suggested mechanisms, theories, and the rules. Finally, we have intention to synthesis other ployoxometalates (POMs) and check their ability to engineer morphology transition of zinc oxides and other metal oxides or solid compounds to hybrid nanostructures.

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Conflict of interest

The authors declare no conflict of interest.

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