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Theory for Morphology Engineering of Solid Compounds (ATMESC): Facts, Predictions and Experimental Evidences

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A theory for morphology engineering of solid compounds (ATMESC) that may cause a breakthrough in materials science and engineering is introduced. The ability of zinc oxide (ZnO), and expected similar behaviour of cuprous oxide (Cu_2O) and other binary compounds that exhibit (d^{10}) orbitals to experience morphology transition when react with phosphomolybdic acid (PMA), has initiated the idea of the ability of other solid chemical compounds to acquire polar surfaces to experience morphology transition under certain conditions. Facts, predictions and some experimental evidences are discussed which support the theory.

Abdelmohsen theory for morphology transition engineering (ATMTE) has paved the way towards a general theory that may govern the morphology transition of nearly all solid compounds under specific conditions [1]. The morphology transition of zinc oxide was explained physically by attributing the inducing of polarity to the repulsion force between electron clouds of surface ions and polyoxometalates anions (POMs anions) which induces relaxation of outer surface atoms [1,2]. The contribution of chemical etching was considered and supported by the ability of molybdates to form intermediate compounds like Zn-molybdates (ZM) or/and Zn phosphomolybdate (ZMP) (pigments) when react with zinc cations. Intermediate compound mechanism (ICM) was supposed which may involve dissolution and re-crystallization of zinc oxide to facilitate solid-state fusion [1-3].

From a point of view of a chemist, the concept of materials engineering [4] was expanded to include "controlling and designing the oriented structures of materials by rescaling their dimensions [5-7] or varying their external morphologies [8-10], favorably with functionalization [11-13], decoration [14-17], doping [18-21] or mixing [22,23] with other materials to attend the synergistic effect [24-26] which enhance their properties". There are two main methods used for nanofabrication; Top-down and bottom-up approaches. The bottom-up approach is recommended than the top-down approach, because the former can produce structures with homogenous chemical composition, and better short- and long-range ordering [1]. Figure 1 shows schematically the engineering of nanomaterials by different approaches.

The morphology evolution of zinc oxide (ZnO) from nanorods to hybrid nanoplatelets has initiated the idea of postulating a theory (ATMTE) that was expected to govern binary compounds especially those have similar physico-chemical properties to that of zinc oxide [1]. 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" [1]. ATMTE has expected similar behviour for all binary compounds that acquire (d^{10}) electronic configuration. This expectation still need more evidences as

some binary compounds that exhibit (d^{10}) like ZnS, and CdS have not responses to PMA at the same condition that was applied to ZnO to experience morphology transition [2]. We still believe in this prediction, and suppose that specific conditions like high PMA concentrations and high temperature may induce their surface polarity. More criticism was pointed towards ATMTE and their supposed mechanism [2]; for instance ATMTE has not predicted the morphology of engineered structures, has not mentioned the ability of $Zn(OH)_2$ to experience morphology transition, has not controlled thickness of nanoplatelets, and has not predicted the ability of phosphomolybdic acid to react with ZnO forming intermediate compounds like Zn-molybdates (ZM) or/and Zn-phosphomolybdate (ZMP). Moreover, they have not achieved complete morphology transition of the starting materials, and they have not sinter the final product that may enhance their physico-chemical properties [1]. Further progress in work lead to postulation of a series of morphology engineering rules (MERs) that manipulates the dimension and morphology of the engineered structures [2].

On the basis of all reported articles and a wide survey, we conclude that inducing surface polarity (creating dangling bonds) is the key factor for morphology transition engineering [1,2,27,28]. At specific conditions, this step is followed by stabilization process that can be achieved by fusion, reconstruction or adsorption of charged species [29-41]. Dangling bond can be defined as "An extremely reactive chemical bond that can be created chemically, physically or mechanically on the surface layer of solid compound" [27,42-49]. Atoms with few bonding partners acquire dangling bonds pointing outward and are known as immobilized atoms.

Dangling bond can be described as an immobilized free radical, as they are very similar to free radicals, except since they are immobilized in a solid, they are somewhat less reactive than free radicals [50]. Evidences to our theory are the ability of particles exhibiting dangling bonds to fuse with each other [1], they can react with any materials they are exposed to, such as water vapor, oxygen, hydrogen, charged species…etc. [51-56], in addition, they can reconstruct and terminate the surface when two neighboring dangling bonds bind together [57-63]. Moreover, atomically precise quantum states, self-directed growth of molecular nanostructures and atomic metal wires were successfully
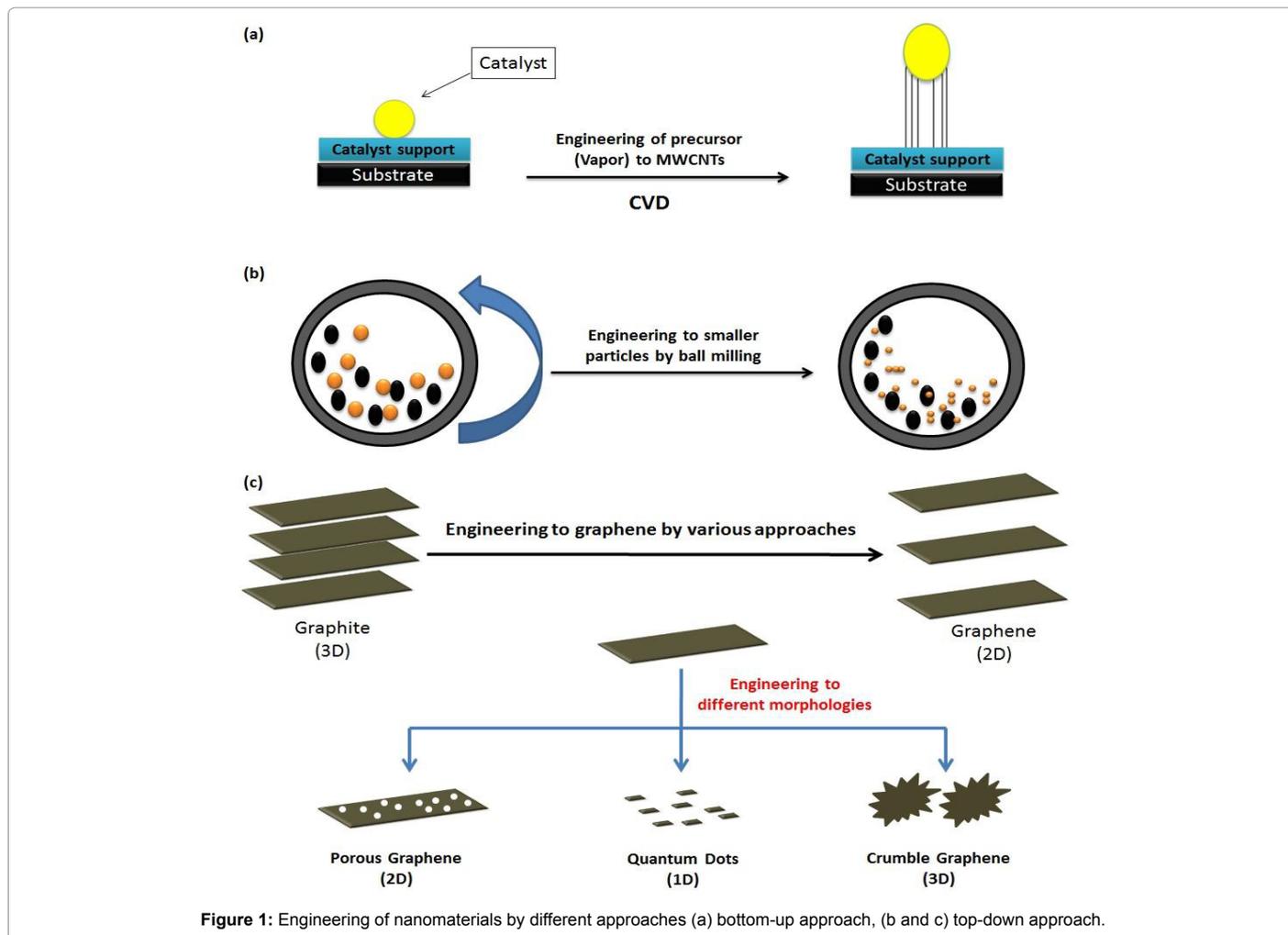
Figure 1: Engineering of nanomaterials by different approaches (a) bottom-up approach, (b and c) top-down approach.

fabricated on silicon using their dangling bonds [64-66]. Whatever the way by which the dangling bonds react, they tend to minimize the surface Gibbs free energy to attain stability [44,67,68].

Creating dangling bonds can take place by various ways. Firstly, we suppose chemical etching by etching-agents [69-71] like acids (e.g. phosphomolybdic acids (PMA) and reduced PMA) [1]. PMA has been used successfully to induce the polarity of ZnO and it is expected to induce the polarity of $(Zn(OH)_2)$ which has Surface chemistry similar to that of ZnO. POMs are expected to induce the polarity of other zinc compounds, besides other metal oxides. Chemical reagents may induce the surface polarity physically as in case of zinc oxide (ZnO) when react with PMA [1]. This case also involves reaction of etching-agents with solid forming intermediate compounds (ZM and/or ZMP) as shown in Figure 2 [2]. Electronegativity may play role in the ability of metal oxides to acquire polar surfaces chemically [1]. Moreover, organic layers that are used for functionalization and passivation of Si surfaces create dangling bonds at intermediate step of reaction [72,73]. To sum up, morphology transition by chemical inducing of polarity was successfully used for engineering 1D, 2D and 3D nanostructures and ultra-thin sheets (~30 nm) at room temperature and low concentration of PMA [1,2]. Secondly, it's a fact that; the simplest way to introduce dangling bonds physically is to create a vacancy as in case of semiconductors. For instance, pure covalent materials can acquire dangling bonds on their surfaces by removal of the central atom [27].

This leads to rupture of four covalent bonds, i.e. the creation of four dangling bonds as shown schematically in Figure 3b. It is supposed that surface bombardment by particles/ions may be used for this reason. Imaginary set-up for physical inducing of polarity is shown in Figure 3a.

Dangling bonds can be also induced by light as in case of amorphous silica [74-80]. Moreover, physical etching of other solid compounds rather than covalent compounds may create dangling bonds on their surfaces. We suppose that some charged species like (O^{2-}) or molecules can bind nanoparticles together which cause fusion and morphology transition as shown in Figure 3c [65]. Furthermore, ability of engineering quantum layers (atomic wires) [66] that may be followed by engineering of multi-atomic layers may support the validity of this theory (ATMESC) as shown in Figure 3c.

Thirdly, breaking large particles mechanically creates particles with polar surface. In other words, solid compounds under mechanical force experience bond cleavage which leads to smaller particles with polar surfaces [28,81-89]. Ball milling of metal oxides (e.g. ZnO) is expected to induce the surface polarity as shown in Figure 4. Inert atmosphere condition is supposed in case of solid compounds that are etched physically or mechanically to avoid reconstruction [57-59] or adsorption of charged species [51,52]. This approach may be used for minimizing size before applying chemical or physical treatment to induce polarity (e.g., milling commercial ZnO (microscale) before
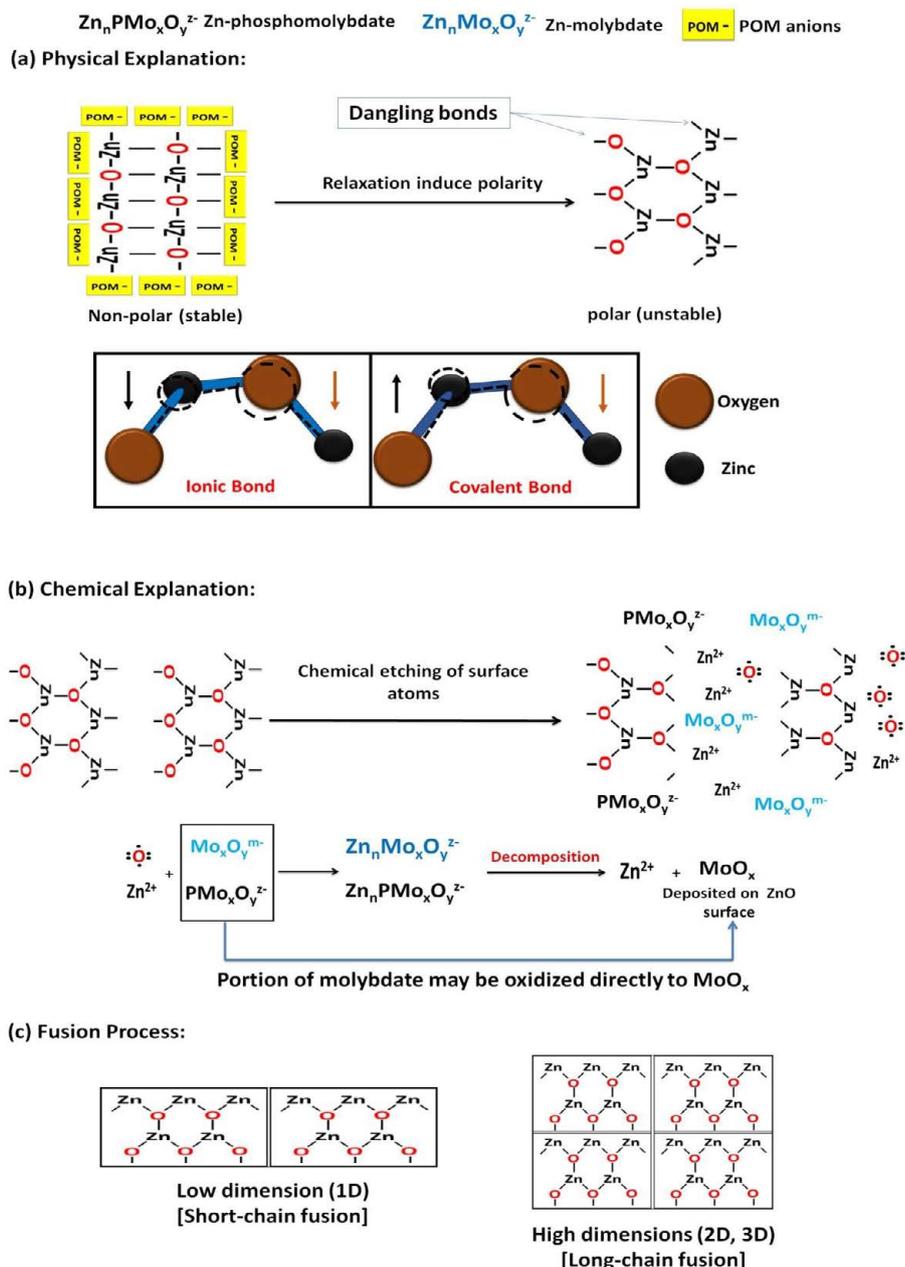
Figure 2: Creating dangling bonds (inducing surface polarity) chemically for zinc oxide; (a) physical explanation, (b) chemical explanation, and (c) fusion process.

immersing in PMA solution to induce morphology transition) [1,2]. Milling can be used directly for morphology transition without further treatment, by dividing bulk particles to small structures [82,84].

After inducing the polarity of solid compounds, we suppose treating them in a certain medium for attaining stability by different ways (e.g., solution as a medium in presence of external cations, anions, chemical reagent to induce fusion process) [1,2]. Solid compounds with active sites like ZnO may catalyze deposition of molybdenum oxides over their surfaces, if they dispersed in POMs solution [1,2]. Other medium may be suggested that may keep dangling bonds without passivation. In-situ TEM analysis for these experiments is suggested to investigate the fusion of nanoparticles [90,91]. Properties of the dangling bonds may govern the feasibility of morphology transition

process [92-94]. Under specific conditions, physical and mechanical treatment is enough for inducing morphology transition, i.e., we do not need further treatment as mentioned above. For instance, physical treatment of solid compounds by bombardment with highly energetic particles/rays is expected to cause ions redistribution which may cause morphology transition. In case of mechanical treatment, high-energy ball milling cause also cations redistribution as reported here [95]. In addition, ZnO nanowires were engineered by ball milling and annealing methods [96].

Herein, on the basis of a theory for morphology transition engineering Theory (ATMTE) [1], suggestions, experimental studies and scientific facts; we introduce a new theory that may be applied to most of solid compounds; Abdelmohsen Theory for Morphology
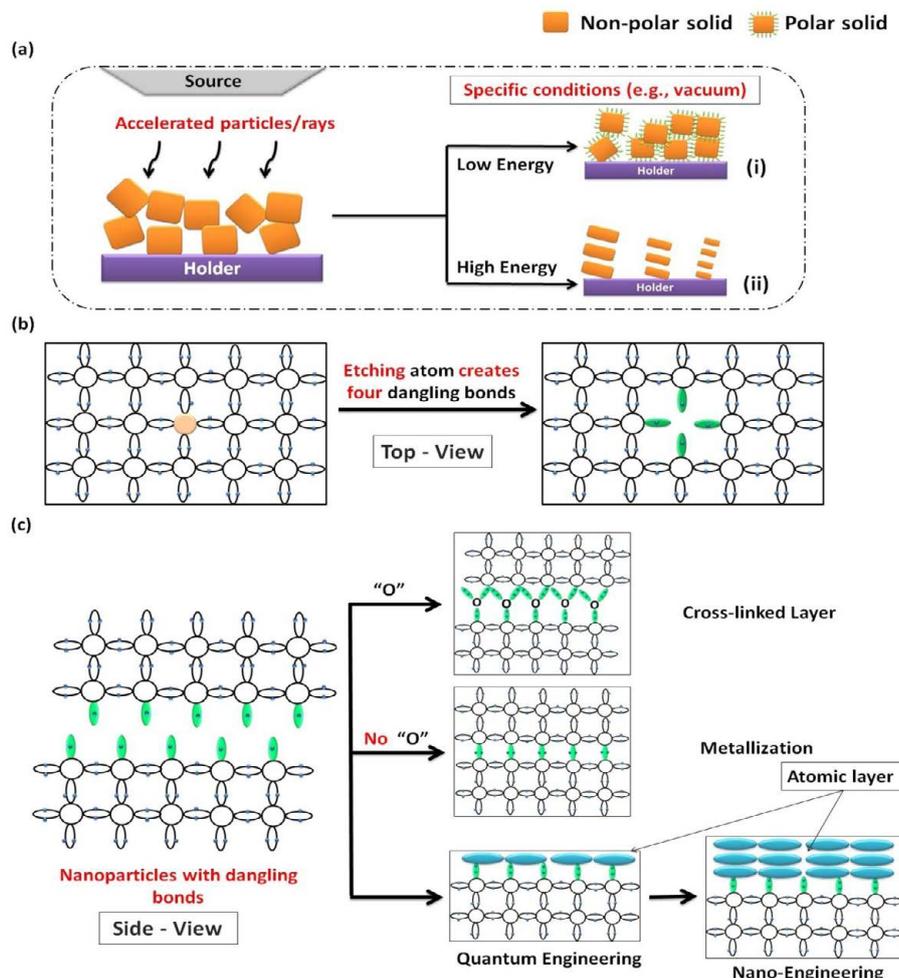
Figure 3: Shows (a) experimental set-up for physical creation of dangling bonds, (b) top-view for etching surface atom of semiconductor (e.g. Silicon) to create four dangling bonds, and (c) supposed engineering processes for semiconductor nanoparticles by fabricating atomic wires on surface.

Engineering of Solid Compounds (ATMESC): which states 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, compounds and composites) with a possibility to manipulate the engineered morphologies, and surface catalytic activity depending on the morphology engineering rules (MERs)*".

In order to simplify the idea, Figure 5a illustrates schematically the growth mechanism of nanoparticles by bottom-up approach [97,98]; starting by mixing the reactants under specific conditions, passing by nucleation of seeds to the formation of the active unstable state (AUS) (polar state) in which the particles still keep growth by binding their dangling bonds to other species. Particles may reconstruct to terminate growth in preferred orientation according to specific conditions and rules [1,99]. The final solid product will have terminated surfaces (no dangling bonds). The idea is to allow these solid compounds to acquire the surface properties of active unstable state (AUS). By this way, they will have the ability to fuse to each other, reconstruct to preferred morphologies, or adsorb charged species as shown in Figure 5b. Immersing polar particles in ionic solution e.g., ZnO polar particles in $ZnSO_4$ or $ZnCl_2$ solution may have influence on the morphology of engineered structures as external cations will contribute to morphology engineering.

It is supposed that, there will be selection criteria for the materials to acquire dangling bonds by each suggested methods, such as size, and chemical composition. Hybrid and pure nanostructures (1D, 2D, and 3D) of ZnO that were engineered by chemical method is expected to have potential use in catalysis, energy, biomedical and other applications; especially few and one-atom thick layer structures (Zn-oxidene) [1,2,100]. Moreover, many papers have been reported about morphology evolution and surface decoration and their effect on the physio-chemical properties of materials [101,102]. In addition, carbonaceous materials like graphene and carbon nanotubes may follow this theory (ATMESC) [82,103-105]. Progress in scientific research will facilitate the way to introduce more evidences for this theory. This theory is expected to be criticized, or corrected like most theories that have been suggested before [106,107].

Conclusions

The possibility for inducing surface polarity of solid compounds by various ways (chemically, physically, and mechanically) was introduced.
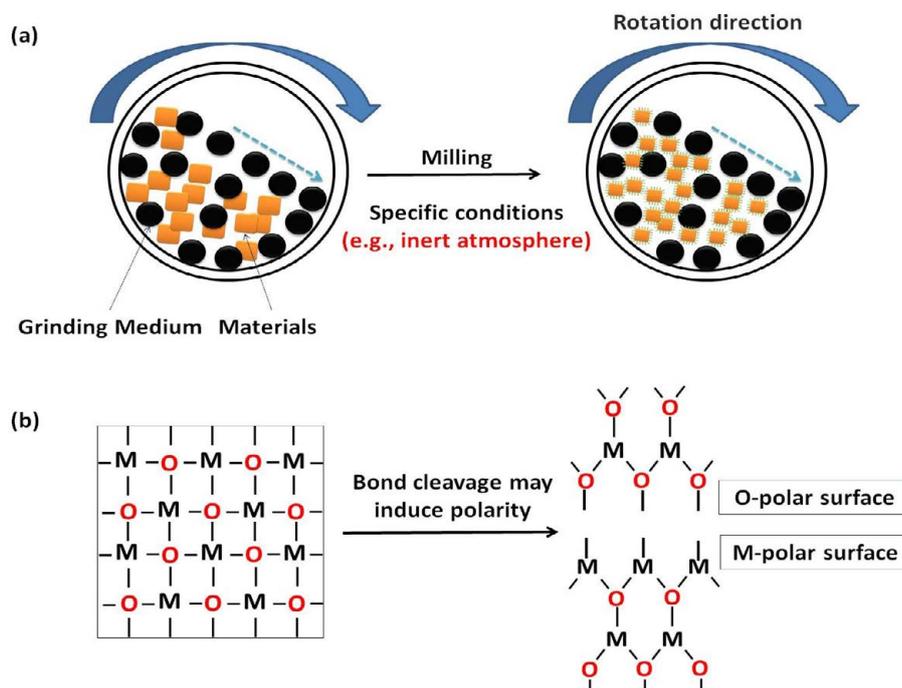
Figure 4: Shows (a) mechanical creation of dangling bonds (inducing polarity) by ball milling in inert atmosphere, and (b) bond cleavage of metal oxides particle (e.g. ZnO).
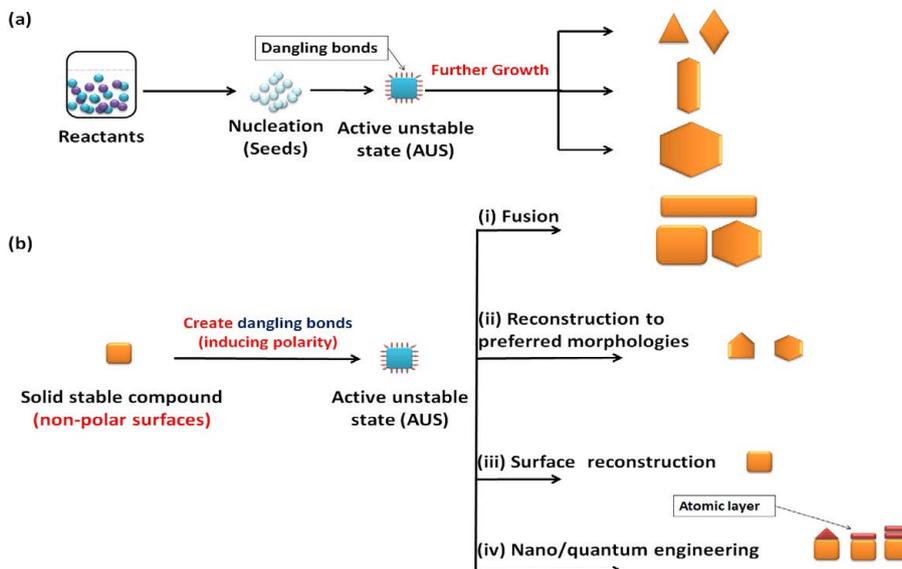

Figure 5: Shows (a) supposed growth mechanism of various nanostructures (metal oxides) in solution, and (b) inducing the polarity of solid stable compound.

This suggestion supports the theory (ATMESC) which paves the way to manipulate pure and doped (1D, 2D, and 3D) nanostructures that have potential applications in nearly all fields of science. This theory is expected to cause breakthrough in materials science and engineering if more experimental evidences are introduced. In addition, it will be used for explaining the morphology evolution phenomenons for nearly all solid compounds.

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