

Review Article

Naturally Self-Assembled Nanosystems and Their Templatized Structures for Photonic Applications

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Self-assembly has the advantage of fabricating structures of complex functionalities, from molecular levels to as big as macroscopic levels. Natural self-assembly involves self-aggregation of one or more materials (organic and/or inorganic) into desired structures while templated self-assembly involves interstitial space filling of diverse nature entities into self-assembled ordered/disordered templates (both from molecular to macro levels). These artificial and engineered new-generation materials offer many advantages over their individual counterparts. This paper reviews and explores the advantages of such naturally self-assembled hybrid molecular level systems and template-assisted macro-/microstructures targeting simple and low-cost device-oriented fabrication techniques, structural flexibility, and a wide range of photonic applications.

1. Introduction

Fabrication of nano/mesa photonic architectures from *top-down* technology involve precise growth techniques like molecular beam epitaxy (MBE), chemical vapor deposition (CVD) and also involve patterning techniques such as photolithography, particle beam lithography, scanning probe lithography, and nanoimprint lithography. While the above mentioned processes are laborious, time-consuming, and costly, the “*bottom-up*” technology based on *self-assembly* approach is the simplest, cost effective technique. Self-assembly is one of the most important “*molecular engineering*” strategies used in fabricating complex functional structures, from micro to the molecular levels, utilising the advantage of self-interaction of molecules. *Molecular self-assembly* is a strategy for nanofabrication that involves designer molecules and supramolecular entities so that molecules naturally aggregate into specific desired structures [1, 2]. This method reduces many difficult steps in nanofabrication, those involving atomic-level modifications of the structures. Moreover, molecular self-assembly tends to produce structures that are relatively defect-free and self-healing, because the target structures are selective with

thermodynamically stable assembly between the possible configurations. Several self-assembly methods have been developed in the recent past, such as phase-separation of copolymers, formation of pores in alumina, liquid crystals, zergels, and polymer spheres templating [3–5]. At molecular levels, one of the examples of self-assembly is the *intercalation strategy* wherein the organic entities are space-filled within naturally self-assembled crystalline inorganic semiconductor hosts, with an opportunity to produce a very special and tailor-made semiconductor, known as *inorganic-organic hybrids* [6–8]. In a macro level, mono dispersed mesa sized spherical colloids are self-assembled to form three-dimensionaly periodic lattices and are famously known as synthetic opals (3D photonic crystals) [9–17]. Another relatively easy and cost-effective methodology to produce nano to wavelength-scaled photonic structures with long-range order is through self-organized systems, which can be used to create periodic patterns, followed by material filling into the interstitial spaces through techniques like electrochemical deposition. This approach is called templated self-assembly. Overall, for large-scale production, the self-assembly and template assisted self-assembly techniques are better alternatives to *top-down* technology.

2. Naturally Self-Assembled Nanosystems

Though inorganic semiconductors are still a material of choice for high-performance semiconductor devices, in recent years organic semiconductors have attracted considerable interest for applications as active materials in low-cost semiconductor devices. For example, displays based on organic light-emitting diodes have already made their way into commercial products, and semiconductor devices like organic FETs have been demonstrated and are being rapidly improved [18–22]. Analogous to low-dimensional inorganic semiconductors are low-dimensional organic nanolayers, which are basically a self-assembly of organic molecules (e.g., *J*-aggregates) [23–25]. Significant advantages of these self-organized molecular nanostructures (*J*-aggregates) are the ultra-sharp absorption line widths with giant oscillator strengths, especially room-temperature performance. *J*-aggregates exhibit a very narrow and red-shifted electronic absorption band (*J* band) and strong fluorescence with a small Stokes shift. These characteristic optical properties, which are the origins of their expected functions, are explained by the interaction between the transition dipole moments [26, 27]. However, while organic semiconductors have obvious advantages, due to simple fabrication and high performance, the main draw-backs are a slow-optical response, lack of thermal/mechanical durability, and most importantly limited life span.

3. Naturally Self-Assembled Inorganic-Organic (IO) Hybrid Systems and Applications

Inorganic-organic (IO) hybrid nanostructures have recently emerged as highly-promising systems for applications as optoelectronic devices, opening up a new dimension to nanotechnology, as unique replacement to their inorganic and organic counterparts. These hybrid systems have great advantage to combine distinct properties of inorganic and organic components within a single-molecular material. The art of combining dissimilar components to yield improved materials is not actually new: ancient building construction material, adobe [28], was made from a mixture of clay (inorganic) and straw (organic). Another classical example is “blue Maya color” developed in around 900 A.D., is an IO-hybrid composite. In fact the *Maya blue* is an inorganic-organic hybrid composed of *palygorskite* clay and organic indigo dye $C_{16}H_{10}N_2O_2$ [29, 30]. The most characteristic beauty is its unusual stability; even after centuries of exposure to heat, humidity, and extreme atmospheric conditions, the color hardly faded.

Among various IO-hybrids, one of the most interesting and well-studied materials is a *perovskite* type hybrid [31]. These self-organized materials are derived from the general structure form of AMX_3 where A is an organic moiety, M is a divalent metal (such as Pb^{2+} , Sn^{2+} , Ge^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , and Eu^{2+}), and X is a halide (such as I, Br, and Cl). This simple 3D structure AMX_3 consists of corner-sharing MX_6 octahedra extended in three dimensions, where the “A” cations are located in the larger

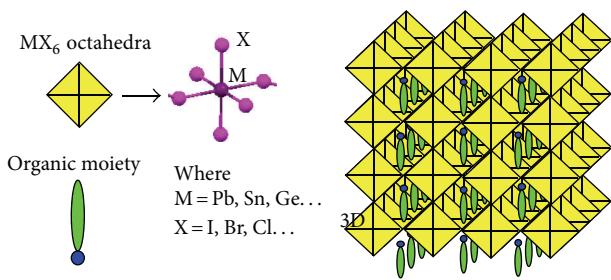


FIGURE 1: Schematic of MX_6 octahedra and the organic moiety of the basic AMX_3 perovskite unit cell and three-dimensional network formed by AMX_3 perovskite unit cells.

12-fold coordinated voids between the octahedra (Figure 1). These self-assembling inorganic-organic perovskites adopt an alternating framework of semiconducting inorganic sheets and organic layers. The increasing interest is because of the ability to derive low-dimensional crystals, which show unique crystal structure and physical and optical properties, from parent 3D networks of AMX_3 from simple and effective natural self-assembly [32–43]. These materials involve different types of interactions allowing the assembly of complex and highly-ordered structures with various bonding schemes. The chemical bonding involved in these IO-hybrid assembled systems are generally described as

- (i) covalent/ionic bonding within the inorganic network which favors the formation of sheets of corner-sharing metal halide octahedra,
- (ii) hydrogen/ionic bonding between the organic cations and the halogens in the inorganic sheets,
- (iii) various weak interactions like *Van der Waals* interactions between the organic R-groups.

Many structural, electrical, thermochromic, and magnetic studies were carried out from almost a decade, to explore the advantages of IO-hybrids over organic and inorganic counterparts [44–46]. These hybrids have an advantage of structural flexibility to choose suitable organic spacers (usually monofunctional or difunctional amines). The crystallographic orientation and the thickness of the perovskite sheets can be tailored as per the choice of appropriate organic cations. In other words, inorganic units can be self-organized into low-dimensional crystals of zero-(0D), one-(1D) and two-(2D) dimensional networks (Figure 2). In 0D networks, MX_6 octahedra are isolated and are surrounded with the organic spacers. In 1D networks, metal halides (MX_6 octahedra) are extended as a chain along one direction with corner/edge/face shared to form 1D hybrid. Similarly, inorganic network can be extended as layered sheets with corner shared MX_6 octahedra to form 2D networks. In 2D, inorganic and organic layers are stacked alternatively with orientation along a specific crystal direction.

During synthesis, the organic moieties, apart from controlling the dimensionality, can also alter the crystallographic orientation of the parent network. For example, based on the organic moiety interaction with metal halide network,

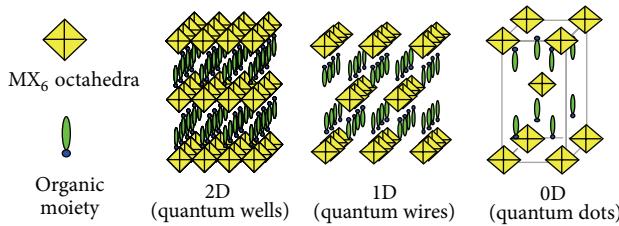


FIGURE 2: Schematic of 2D, 1D, and 0D IO-hybrid derived from parent AMX_3 type 3D IO-hybrid.

the resultant network can deviate from $\langle 100 \rangle$ oriented 2D network [47] to 1D dimensional $\langle 110 \rangle$ oriented hybrid structures also [48, 49]. Under special circumstances, based on organic moiety conformation, the metal halides may self-assemble into either edge sharing or face sharing of metal halide octahedra, forming various low dimensional inorganic halide networks of different orientations. Based on such different networks, these hybrids show marked variation in their structural and optical features [50–59].

Several studies were carried out in the recent past to prove the potential ability of IO-hybrids in photonic applications: electro-absorption and electroluminescence [60–64], photo-conductive devices, [65, 66], optical nonlinear devices [67, 68], stark effect [69] magneto-absorption, and spontaneous magnetization [70, 71]. Apart from linear optical studies, high-optical excitation effects such as ultrafast dynamics of excitons [50, 72], observation of higher-order excitons (biexciton and triexciton) [51, 52, 73–75], and even an attempt of biexciton lasing [76] were also reported. Photonic devices such as thin film transistors (TFTs), inorganic-organic field-effect transistors (IOFETs), inorganic-organic light emitting diodes (IOLEDs), and scintillators were also been successfully demonstrated [77–79].

4. Naturally Self-Assembled Two-Dimensional IO-Hybrid Systems

Among the several low-dimensional hybrids mentioned before, 2D hybrids are of special interest. The 2D ($\langle 100 \rangle$ oriented) hybrids are analogous to natural *multiple quantum wells* (MQWs), where inorganic and organic sheets (of molecular level sizes) are alternatively stacked. This is of special attraction because such natural MQWs are easily achieved from solution-processing techniques, without any involvement of laborious instrumentation like molecular beam epitaxy deposition. Various possible layered schemes of these MQWs are shown in Figure 3. Depending on respective inorganic and organic bandgaps, these MQWs can be classified [80] into Type I, II, or III (Figure 3).

In Type I, the conduction band of the inorganic layer is generally below that of the organic layer, and the valence band is above that of the organic layer (Figure 3). Therefore, inorganic sheets act as “quantum wells” for both electrons and holes leading to Type I heterostructure. Similarly, if larger bandgap inorganic sheets are integrated with more complex, conjugated organic cations (with bandgap less than

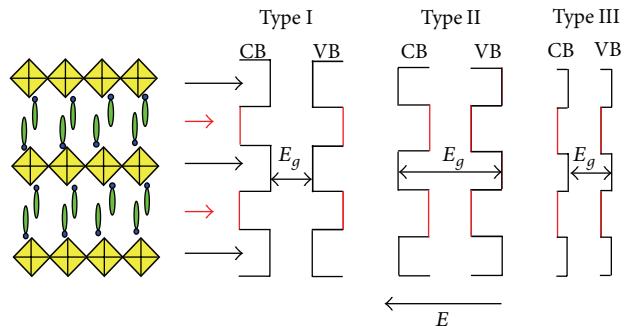


FIGURE 3: 2D IO-hybrid structure and several possible energy level schemes.

inorganic layer), the well and barrier layer roles can be reversed [77] forming Type II heterostructure (Figure 3). In special cases, by appropriate modifications of the chemistry of the organic and inorganic layers, the bandgaps for the organic and inorganic layers can also be offset, leading to Type III heterostructure, in which the wells for the electrons and holes are in different layers. The present study deals with the IO-hybrid system of R-PbI_4 (where R is organic), having Type I structure, where the inorganic (PbI network ~ 3 eV) bandgap is much less than the organic bandgap (4 to 6 eV), therefore, the electron-hole confinement is solely within inorganic network.

The most influencing factors in 2D IO-hybrids are (1) the choice of organic moiety, (2) how the organic moiety intercalates into the inorganic network (*vice versa*), thereby altering the structural rearrangement and the consequent energy band structure, (3) quantum confinement due to quantum-limit widths of the individual organic and inorganics, and (4) the dielectric contrast between the organic and inorganic sheets. Technically the last two are dependent on first two factors.

5. Structure and Fabrication Strategies of Naturally Self-Assembled IO-Hybrid Systems

5.1. Structure of Naturally Self-Assembled IO-Hybrids. Generic way of visualization of these IO-hybrids is intercalation of organic guest moieties into a parent crystalline host. Recent efforts in the crystal engineering resulted into the reduction of structures into 0, 1, 2, or 3- low-dimensional hybrid networks [32, 33, 77, 83–87]. The dimensionality of these IO-hybrids, based on the bridging of organic moiety between the MX one-dimensional planes, is critically dependent on (1) the choice of hydrogen bonding scheme between protonated amine terminal group(s) of organic moiety and the MX network and (2) the driving force, size, and shape of the organic molecule [80]. The simplest MX_4^{2-} network consists of corner-sharing metal halide octahedra oriented along $\langle 100 \rangle$ plane and, based on how the organic is

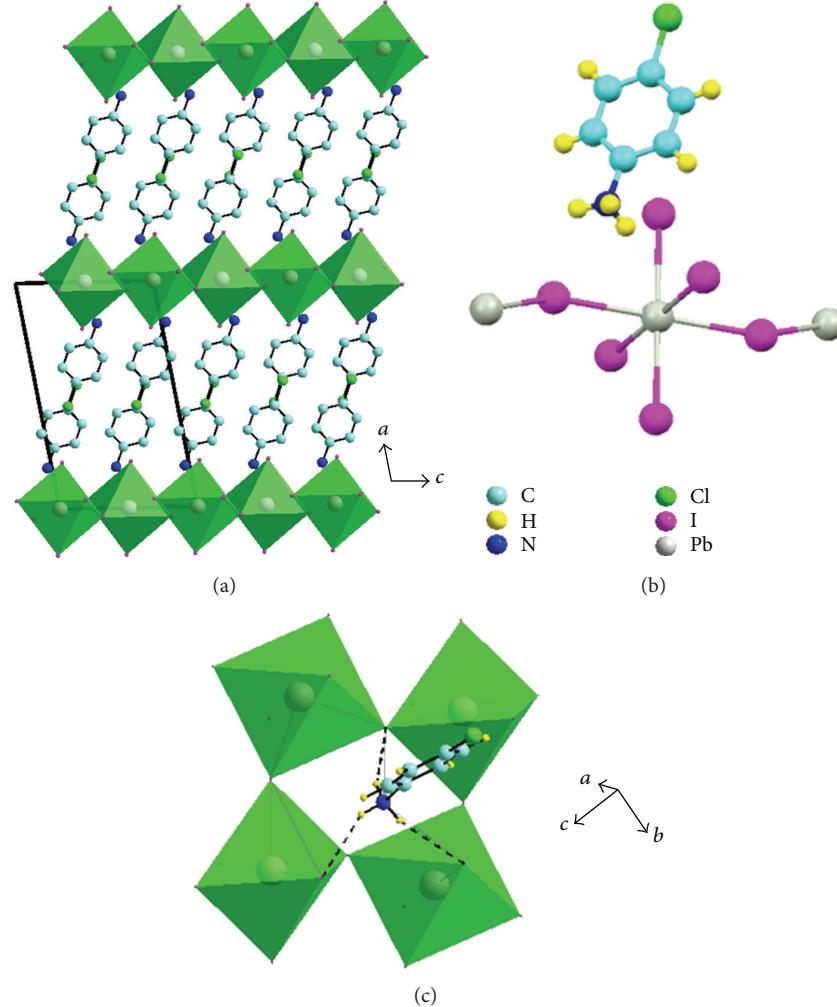


FIGURE 4: (a) Packing structure, (b) asymmetric unit, and (c) NH-I terminal halide configuration (equilateral triangle configuration) of CAPI [81].

intercalated into the parental network, intercalated structures of 0D, 1D, 2D, and 3D can be expected [32, 33, 48, 86, 88, 89].

In the two-dimensional R-MX₄ type hybrids, (MX₄)²⁻ octahedral network sheets are stacked up along <100> direction with alternate layers of organic moieties. The crystallographic information for one of the IO-hybrid (4-ClC₆H₄NH₃)₂PbI₄(CAPI) has been presented in Figure 4. CAPI IO-hybrid crystallizes in the monoclinic space group P2₁/c in which the asymmetric unit consists of half a (PbI₄)²⁻ anion and one (Cl-C₆H₄NH₃)⁺ cation. These structures comprises of well-ordered organic and inorganic layers, arranged alternately stacked along the *a*-direction with layers infinitely extended in the *bc* plane.

5.2. General View of Synthesis, Fabrication, and Implications. Many device applications demand simple and effective fabrication protocols specially the techniques to make highly uniform device-quality thin films. IO-hybrids are generally fabricated from conventional solution processing methods, and single crystals are harvested by slow evaporation

technique [90–94]. Though several synthesis recipes are available, a simpler, generalized, high product yield, and commercially viable process is as follows. Stoichiometric quantities of organic moiety and inorganic (PbI₂) were mixed with concentrated aqueous HI at 60°C. The resultant solution was allowed to rest at 60°C for an hour and then cooled slowly to room temperature without stirring. The precipitate, thus, obtained was filtered off and dried.

The general synthesis is as follows:



Single crystals of the respective compounds were harvested from slow evaporation process by dissolving the compound in a sparingly soluble solvent. However, the synthesis procedure slightly varies from its generic route depending on the nature of organic moiety.

From the application perspective, thin film processing demands to achieve easy and controlled thickness/morphology over large areas and most importantly highly oriented IO-hybrids. The applications of IO-hybrids will be

immense only if the fabrication parameters are precisely controlled. For the same reason, one has to develop methods of fabrication that can be carefully predicted and controlled for a predetermined technological application. Usual way of fabricating these thin films is from spin-coating of IO-hybrid solutions onto a desired substrate. Although other techniques like single- and double-source thermal vapor deposition, Langmuir Blodgett (LB) method, layer by layer deposition, spray pyrolysis, and low-temperature melting process had been employed to obtain films, it is always difficult to find empirical conditions and processes to obtain well-ordered thin films of these IO-hybrids [95–100]. Especially the applicability of thermal vapor deposition technique is limited due to stability and contamination issues and to balance organic and inorganic evaporation rates simultaneously. Recently, Rikukawa group [95] had developed layer-by-layer self-assembly method to fabricate ultra-thin films of bifunctional amino end-group based IO-hybrid. This method is based on alternate dipping of hydrophilic substrates in organic iodide and lead halides solutions followed by repeated washing to remove unreacted residuals, and this procedure was repeated several times to obtain required self-assembly films, up to 12 layers.

We have recently explored one of the much simpler, but efficient technique, so-called intercalation process to fabricate highly-ordered IO-hybrids over centimeter size lateral dimensions. In fact, the word *intercalation* in general refers to insertion of guest into self-assembled 2D/3D solids. Giesecking [101] and MacEwan [102] showed, for the first time, the ability of the formation of IO-hybrid by intercalation of organic cations into layered and charged inorganic hosts and further extended to neutral guesthosts by Bradley [103]. Owing to the intense interest in new nanocomposite functional hybrid materials for fundamental and device-oriented research, new *intercalation chemistry* has been established [104]. For 2D layered hybrids it is essential to focus on both new hybrids as well as highly ordered films, however, the later one has not been widely considered.

As mentioned before, the kinetics and layer formation during intercalation are critically dependent on the nature and shape of the guest moiety, concentration of guest molecules, thickness of parent films, intercalation time, and the solvent used [7]. The schematic of intercalation strategy of IO-hybrid for a high-quality thin film fabrication is demonstrated in Figure 5. When predeposited layered PbI_2 film is intercalated with presynthesized organic iodide, the structural network of PbI_2 and the conformation of organic chain are changed to form IO-hybrids. Uniform 2D IO-hybrids films can, thus, be fabricated by an appropriate choice of organic moieties. A brief description of the intercalation process is explained here by taking an example of the IO-hybrid 2(1-cyclohexenyl) ethylammonium tetraiodoplumbate ($(\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$, CHPI) [7]. The organic iodide, 2-(1-cyclohexenyl) ethylammonium iodide ($\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3\text{I}$) (CHI) is formed when 1 mL of 2-(1-cyclohexenyl) ethylamine was added to 2.1 mL of HI (47%). The obtained light yellow precipitate CHI eventually has been filtered and dried for further use. Similar is the method for other organic iodide synthesis. Suitable solvent (such as

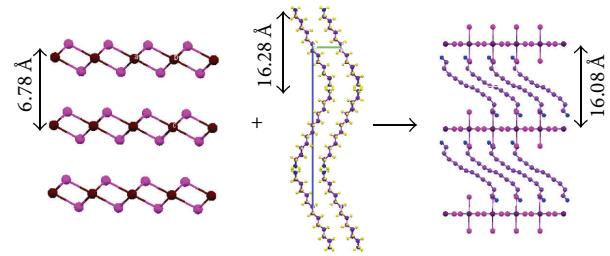


FIGURE 5: Schematic representation of intercalation process for 2D layered IO-hybrid thin films [7]. Essentially the intercalation method involves the intercalation of organic moiety into interstitial spaces of layered inorganic host to obtain desired inorganic-organic exfoliated layered hybrid.

toluene or a combination of toluene and isopropanol) is taken to dissolve organic iodide. Special care has to be taken on the solvent ratio so as to dissolve only the organic iodide but not PbI_2 or the resultant hybrid. Finally, the deposited PbI_2 thin films are dipped into organic iodide films, with a controlled speed and for specific time, to obtain desired IO-hybrid films. The resultant films, fabricated by the intercalation process, were smooth and uniform over a large area and had shown relatively well-stacked ($00l$ oriented) inorganic and organic monolayers [7] (Figure 6).

6. Room-Temperature Optical Exciton Features

Exciton absorption/emission features in these low-dimensional IO-hybrids, especially in 2D hybrids, are significantly enhanced as compared to the 3D counterpart, due to the low-dimensionality. In the PbI based 2D IO-hybrids, electrons are excited from the valence band (VB), consisting of a mixture of Pb (6s) and I (5p) states, to the conduction band (CB), derived mainly from the Pb (6p) states, leaving holes in the VB. An electron and hole pair up to form an exciton via coulomb interaction, and the resulted excitons produce photoluminescence by radiative recombination [105, 106]. The enhancement of exciton features in 2D systems is a well-known phenomenon because of the spatial electron and hole confinement in a very thin and deep quantum wells and, hence, multiples the exciton binding energy, enabling *quantum confinement effect*. Apart from the usual quantum confinement in these natural MQWs, the excitons binding energies are further enhanced due to large contrast in dielectric constants of organic and inorganic layers. Such large binding energy enhancement, leading to strong room-temperature exciton features, often is referred as *dielectric confinement effects* [107, 108]. Ishihara et al. [105] in 1989, reported for the first time the exciton binding energy of $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$ (C10PI), which is 370 meV and is much higher than that of bulk PbI_2 , (~30 meV) [106]. This was well-accounted from *dielectric confinement* assumption, where the dielectric difference between “well” and “barrier” induces strong columbic interaction between an electron and a hole

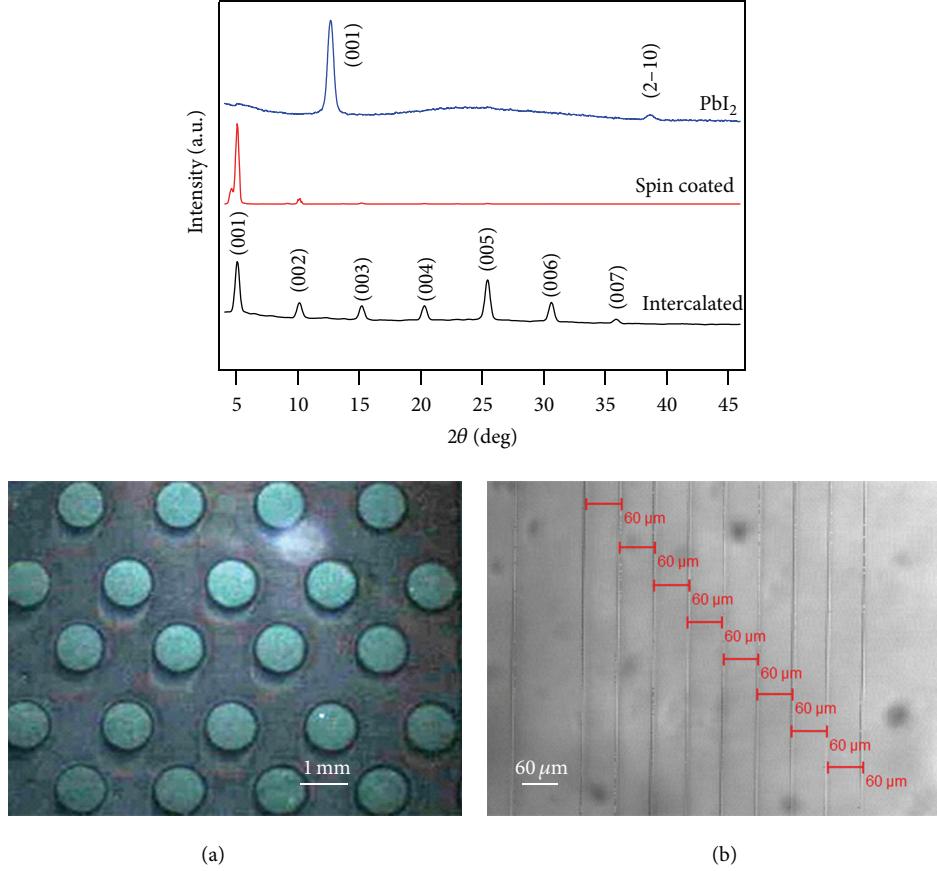


FIGURE 6: X-ray diffraction patterns of pure PbI_2 film, spin-coated CHPI (from synthesized CHPI), and intercalated CHPI films (for 10 seconds) [7]. Bottom microscopic reflection images represent the obtained periodic photonic structures using top-down technology: (a) patterned structures from direct deposition of materials from templates using intercalation technique and (b) femtosecond laser written structures on CHPI thin films.

and as a consequence the binding energy of the exciton is 12 times larger than that of PbI_2 [84, 105, 107–109].

For example, in CAPI (Figure 4), the inorganic and organic layer thicknesses are estimated to be 6 Å and 10 Å. This layered structure resembles MQWs, where inorganic layer has a bandgap of ~3 eV forming “well,” and organic layer has a bandgap ~6 eV forming “barrier.” Figure 7 shows the typical photoluminescence (PL) and absorption spectra of CAPI thin film.

The room-temperature absorption of CAPI shows two principal absorptions: a broad absorption at ~400 nm and a strong narrow peak at ~480 nm (Figure 7 (black)). While the former is attributed to the charge-transfer transition between the organic and inorganic layers, the narrow absorption peak at about 480 nm is attributed to the lowest exciton within the inorganic layers [84, 105, 110]. CAPI thin films show strong room-temperature photoluminescence (PL) at ~485 nm upon UV excitation (Figure 7 (red)). The PL spectrum of CAPI has narrow line shape with spectral width ~15 nm. The oscillator strength of exciton absorption peak obtained for the hybrid CAPI thin film (of thickness 100 nm)

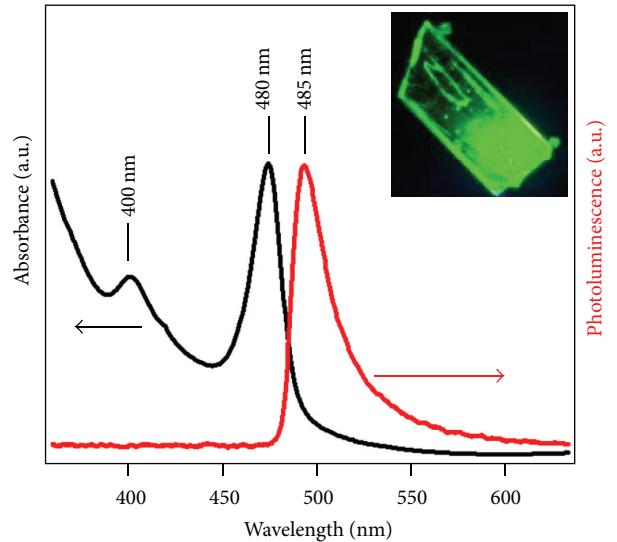


FIGURE 7: Absorption and PL spectra of the 2D layered IO-hybrid, CAPI, thin film [81]. Inset shows typical single crystal PL microscope image.

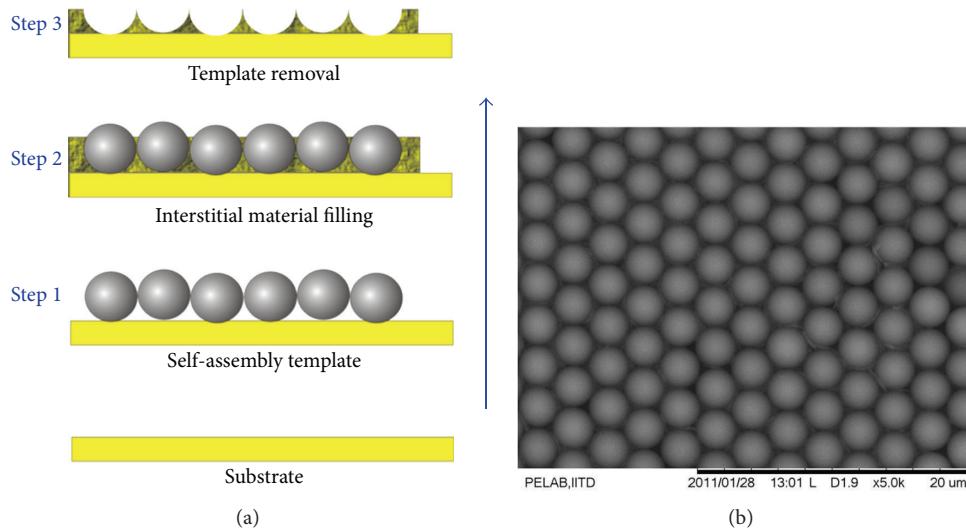


FIGURE 8: (a) Schematic representation of self-assembly template assisted fabrication of photonic structures and (b) polymer microsphere templates.

is $f = 6.5 \times 10^{15} \text{ cm}^{-2}$. Since, for the film thickness of 100nm, there are ~ 70 quantum wells, the oscillator strength per quantum-well $f_{\text{qw}} = 9.2 \times 10^{13} \text{ cm}^{-2}$. This value is an order of magnitude higher than the conventional inorganic quantum wells such as InGaAs structure [111].

Despite some understanding on the dependence of exciton energies of 2D layered IO-hybrids on various parameters like the inorganic *well* width and organic *barrier* separation, the dielectric contrast and the inorganic layer geometrical arrangement, quantitative calculations of exciton binding energies remain out of reach. A systematic correlation between the exciton energies and a specific structural feature has recently been established and discussed [110, 112]. However, the structural features are strongly dependent on several factors such as (1) disorder or conformation of the organic moiety, (2) crystal packing, (3) arrangement of inorganic layers, and (4) position of tagging of ammonium group in organic moiety to the PBI network. As a consequence the optical excitons features are also strongly dependent on the studied IO-hybrid thin films based on organic moiety conformation, solvent used, temperature, and the film thickness [110, 113–115]. Special control over thickness of the IO-hybrid film is critical for device oriented 3D structure fabrication, to avoid the exciton deformation and defect related emission/absorption features.

7. Tempered Self-Assembled Microstructures

Carving useful materials itself into the nano to micron-sized structures using simple bottom-up technology is economically viable. This new approach is based on the natural self-assembly of templates and subsequently space filling the voids either by precipitation via chemical routes or by the electrochemical reduction of materials (Figure 8). Therefore, nano-/microstructuring using templates such as artificial polymer opals and liquid crystal is a whole new

class of research. These micro-/nanostructures have potential applications such as tunable plasmonic bandgaps [116], novel types of liquid crystal displays [117], and nanolaser cavities [118]. These macroporous materials are already available in the market as surface enhanced Raman scattering (SERS) devices [119]. Despite the fact that the methodology offers highly ordered structures with very large single-crystalline domains, it has so far been restricted only to metals.

However, fabrication of self-assembled semiconductor photonic structures is still scarce, particularly understanding the chemistry for interstitial filling and deposition for semiconductors and adequate interconnectivity between the pores [120–123]. Electrochemical deposition is one of the low-cost deposition techniques which is an optimal bottom up technique for complete interstitial space filling of desired material through various types of templates. Over the years, conducting thin films (Ag, Au, etc.) were deposited on various semiconducting and conducting substrates utilizing this technique, but the deposition of semiconductors, organic materials, and polymers have always been a formidable task, due to low-conductivity issues. Constant research work on electrodeposition finally emerged out to be more useful than expected when deposition of semiconductors and several organic materials had been possible. However, structural and optoelectronic properties of semiconductors are critically affected by the preparation conditions such as fabrication method, types of substrates, thickness, and annealing conditions. Nevertheless, it is necessary to optimize the fabrication conditions and postprocessing methods for desired applications.

Here the template assisted method to fabricate periodic structures from 50 nm to as big as 20 micron is exemplified. After having optimized electrodeposition conditions, such as electrolyte recipe, surface quality, structural, and optical properties, we have extensively investigated to fabricate 2D and 3D periodic and quasiperiodic nano/micro-structure

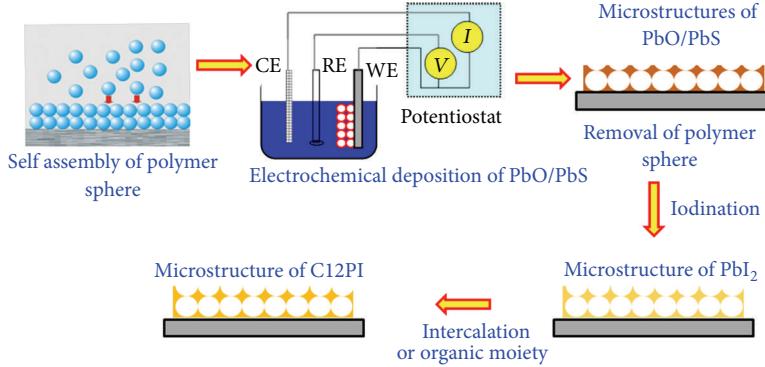


FIGURE 9: Schematic representation of carving naturally self-assembled hybrid systems into 2D/3D microstructures from template self-assembly method.

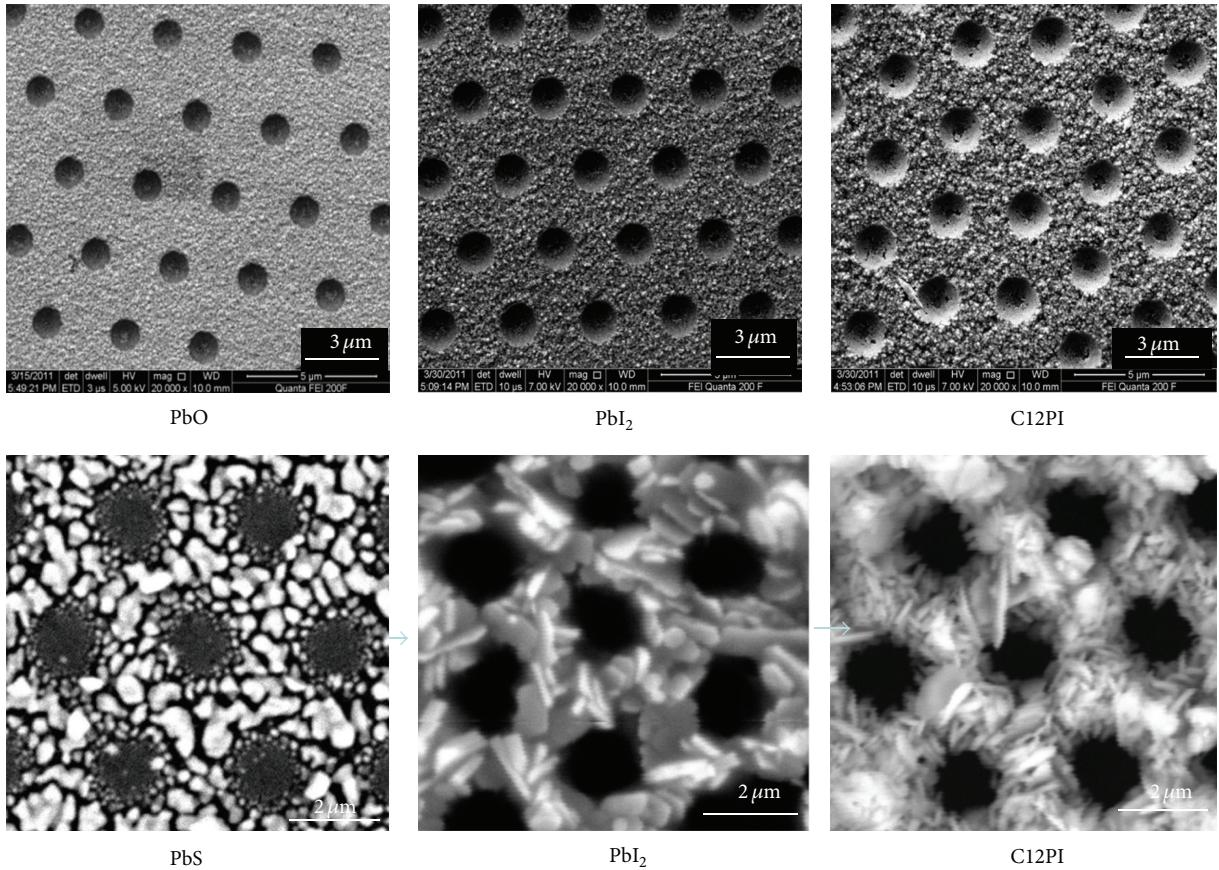


FIGURE 10: Scanning electron microscope images of template-assisted PbO, PbI₂, PbS, and C12PI microstructures [82].

from template-assisted growth techniques [11, 12, 17, 82]. During this investigation, several composite semiconductors such as CdSe, CdTe, ZnO, PbO, PbS, and PbI₂ are successfully fabricated and their optoelectronic properties are thoroughly investigated. We further demonstrated micron-scale 2D periodic highly emitting IO-hybrid structures, using template-assisted electrochemical growth followed by three-step processing, which can be easily extended to wave-length scale and nanoscale structures.

The systematic procedure has been explained in the schematic diagram (Figure 9). Essentially the electrodeposited PbO/PbS microstructures (Figure 10) are iodinated to obtain PbI₂ microstructures, then the presynthesized organic iodide is intercalated into PbI₂ to obtain desired IO-hybrid microstructures. During the process, the thickness of IO-hybrid film has to be fixed and such thickness optimization is required because these type of IO-hybrids are sensitive to thickness induced stacking imperfections, which directly

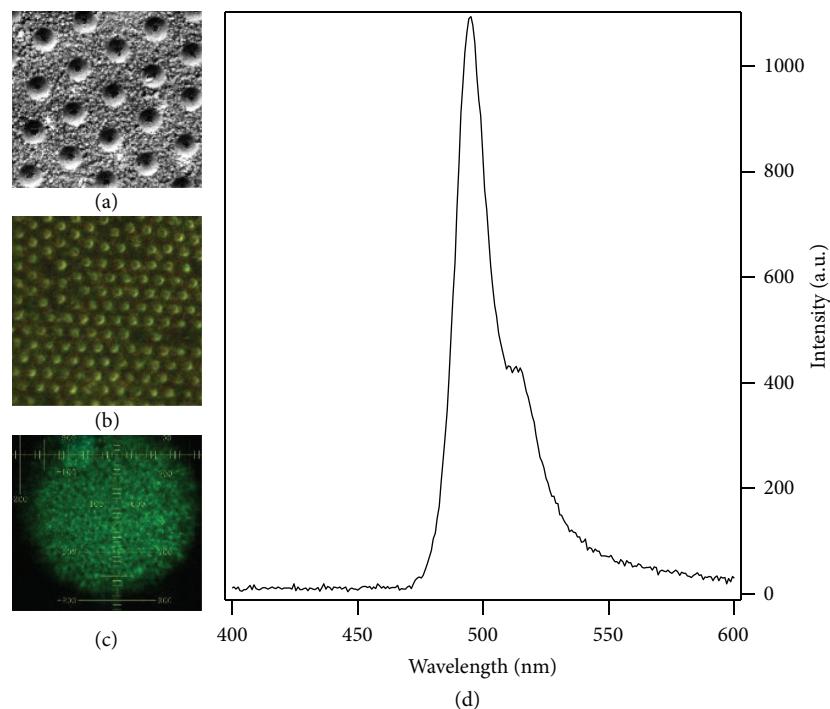


FIGURE 11: (a) SEM, (b) dark field microscope, and (c) PL microscope images ($\lambda_{\text{ex}} \sim 410 \text{ nm}$), (d) corresponding to the PL spectra from the fabricated C12PI microstructures [82].

results into rapid change in their exciton-related emission/absorption behavior. The thickness-dependent disorder produce uneven crystalline planes, and as a consequence, the shift in the exciton PL peak and/or broad defect emission were observed [81, 113].

The fabricated IO-hybrid microstructures (Figures 10 and 11) are uniform over large areas and are highly luminescent. In general, the fabrication of 3D structures from infiltration methods, using conventionally synthesized hybrids is difficult due to surface morphology issues [81]. In contrast to that, the hybrid structures fabricated from this novel method pave the way for new directions in the fabrication of different photonic structures of IO-hybrids. As a hybrid nanosystem, low-dimensional IO-hybrid systems have shown potential applications and those applications were reviewed in previous sections. Photonic structures of these nano systems could further improve the optical properties and hence would find device applications in the area of optoelectronics.

8. Conclusions

Fabrication, structural and optical exciton features of naturally self-assembled low-dimensional IO-hybrid nano systems were discussed. While the fabrication of these self-assembled systems are usually from solution chemistry techniques, a novel device-compatible thin film fabrication from very inexpensive method, that is, intercalation, was reviewed. Finally, the designing and fabrication of optoelectronic-compatible photonic architectures from these IO-hybrids, especially from template-assisted method, have been clearly discussed.

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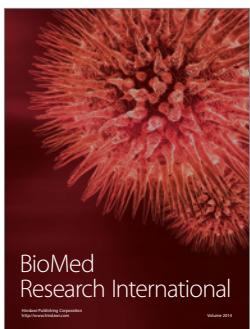
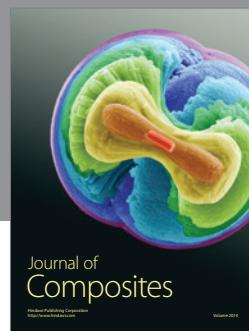
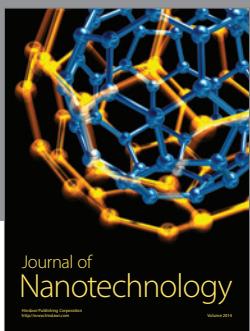
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