Fabrication of excitonic luminescent inorganic–organic hybrid nano- and microcrystals

I. Saikumar,[a] Shahab Ahmad,[a] J.J. Baumberg[b] and G. Vijaya Prakash[a,*]

[a]*Nanophotonics Lab, Department of Physics, Indian Institute of Technology Delhi, New Delhi 110 016, India*
[b]*Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK*

Inorganic–organic (IO) hybrid nano- and microcrystals are fabricated by a low-cost, environmentally friendly and easily scaled-up route. Lead(II) iodide (PbI_2) nano/microcrystals are obtained by solvothermal techniques and subsequent IO hybrid ($(C_{12}H_{25}NH_3)_2PbI_4$) crystals are produced by intercalation of the organic moiety. The hexagonally shaped crystals obtained range in size from 20 nm to $\sim$7 μm. Sequential stacking of inorganic/organic layers in these IO hybrid crystals results in strong room-temperature exciton photoluminescence, wherein the excitons are confined within the inorganic sheets.
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The optical properties of soft materials have attracted attention for a number of years due to their potential applications in optoelectronic devices. An increasing number of studies focus on hybrid inorganic–organic (IO) materials [1], due to the possibility of combining the diverse properties of inorganic (high mobility, electrical pumping, band engineering) and organic (low-cost technology, high luminescence quantum yields, room temperature) performance. In this context, IO hybrids of chemical formula $(R-NH_3)_2MX_4$, where R is an organic moiety, M is a divalent metal (Pb^{2+}, Sn^{2+}, Cu^{2+}, Cd^{2+}, etc.) and X is I^-, Cl^- or Br^-, represent a natural hybrid IO system. These perovskite-type structures possess structural flexibility that can be tailored by substituting different halides [2,3] as well as various organic moieties [4]. Tremendous interest has been shown both for fundamental studies and for applications in optoelectronics and photonics [2–5].

A recent successful approach to fabricate device-compatible IO hybrids is based on inserting appropriately sized organic guest moieties into the empty spaces within a crystalline host. Layered semiconductor compounds (e.g. PbI_2, SnI_2) exhibit anisotropic confinement along different crystallographic axes [6]. Lead iodide (PbI_2) has a structural repeat unit of hexagonally closed-packed I–Pb–I molecular layers which are separated by a gap of 6.78 Å with the layers stacked perpendicularly along the c-axis [7–9]. Compared to conventional synthesis, the intercalation of organic moieties into PbI_2 to obtain the desired IO hybrids ($(R-NH_3)_2PbI_4$) is relatively easy and yields well-ordered centimeter-sized films [10]. The kinetics of inorganic and organic layer formation typically depends on the nature and shape of the guest moiety, the concentration of guest molecules and the solvent used [10]. The organic moiety conformation results in variations in the sequence of stacking layers along the layer normal to the hexagonal c-axis [11]. Due to the presence of alternate layered arrangements of Pb–I and organic networks, these IO hybrids exhibit remarkably strongly bonded excitons ($E_b \sim 200$ meV) which are even observable at room temperature. This is due to the effects of dielectric mismatch and quantum confinement in the semiconductor layers that hold the electronic carriers [12]. As a consequence, these IO hybrids are considered to be "natural" inorganic–organic multiple quantum wells (IO-MQWs) which show strong and narrow absorption and photoluminescence at room temperature.

Conventional synthesis of these IO hybrids includes sol–gel processing methods for thin film formation [10,13,14] and single-crystal harvesting methods [13,15–18]. However, such IO-MQWs are difficult to fabricate directly into nano- and microscale structures.

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* Corresponding author. Tel.: +91 (11) 2659 1326; fax: +91 (11) 2658 1114; e-mail: prakash@physics.iitd.ac.in

Growth of highly anisotropic inorganic low-dimensional structures, by controlling the size and morphology through a single-step process and at relatively low temperatures, is a formidable task but is highly desirable for many new types of optoelectronic devices.

In this paper we demonstrate a novel and simple methodology for the fabrication of highly anisotropic and efficiently luminescent IO hybrids into nano/micro-scale crystals. This method follows a two-step process: first, preparation of PbI₂ nano/microcrystals by a solvo-thermal method [6]; and then their complete conversion into IO hybrids via a newly developed intercalation process using pre-synthesized organic moieties [10]. The structural, morphological and optical properties of these strongly emissive IO hybrid nano/microcrystals show the success of this approach.

PbI₂ nano/microcrystals were synthesized at room temperature using an aqueous solution of potassium iodide (KI) and lead nitrate (Pb(NO₃)₂) in methanol, ethanol and acetonitrile solvents [6]. 5 ml of 0.01 M aqueous solution of lead nitrate was added to 100 ml of the solvent of interest. Into this solution, under vigorous ultrasonic homogenization, 5 ml of 0.05 M aqueous KI was added. The sudden appearance of a yellow colour by the addition of KI is the first evidence of the formation of PbI₂ crystallites. The PbI₂ crystals thus formed were collected carefully and dried at 60 °C. The crystal growth and size are critically dependent on concentrations of the constituents, the use of different host solvents, separation time and temperature. While the obtained crystals are of various nano/micron dimensions, nanosized crystals are directly obtained from the supernatant solutions and used for analysis.

To obtain IO hybrid nano/microcrystals of dodecyl-lammonium tetraiodo plumbate, $(C_{12}H_{25}NH_3)_2PbI_4$ (hereafter C12PI), pre-synthesized organic iodide solutions of $C_{12}H_{25}NH_3I$ (hereafter C12I) in toluene (40 mg/5 ml) are used in an intercalation process as explained in an earlier communication [10]. We also demonstrate the approach using another organic iodide $C_6H_9C_2H_4NH_3I$ (hereafter CHI) to obtain IO hybrid crystals of 2(1-cyclohexenyl) ethylammonium tetraiodo plumbate $((C_6H_5C_2H_4NH_3)_2PbI_4)$ (hereafter CHPI) for comparison.

The prepared PbI₂ nano/microcrystals were characterized by thin-film/powder X-ray diffraction (XRD) in for the 2θ range from 10° to 60° to determine the phase purity and crystallinity. XRD pattern of nano/micro-crystals of PbI₂ prepared in various solvents (methanol, acetonitrile and ethanol) are shown in Figure 1(i). All the peaks in the XRD pattern indicate the pure hexagonal structure (JCPDS Card No. 79-0803) with space group $P\text{-}3m1(164)$. The strong diffraction peaks of PbI₂ nano/microcrystals in Figure 1(i) indicate high crystallinity and a layered structure with plane separation $d = 6.78$ Å along the c-axis.

The unit cell parameters ($a = b$ and c) of the prepared PbI₂ nano/microcrystals are found to be 4.544 and 6.937 Å (methanol), 4.507 and 6.974 Å (acetonitrile) and 4.575 and 7.083 Å (ethanol), respectively, which are highly compatible with reported data ($a = b = 4.557$ Å, $c = 6.979$ Å) [19]. Furthermore, relative broadening occurred in the observed XRD peaks for the PbI₂
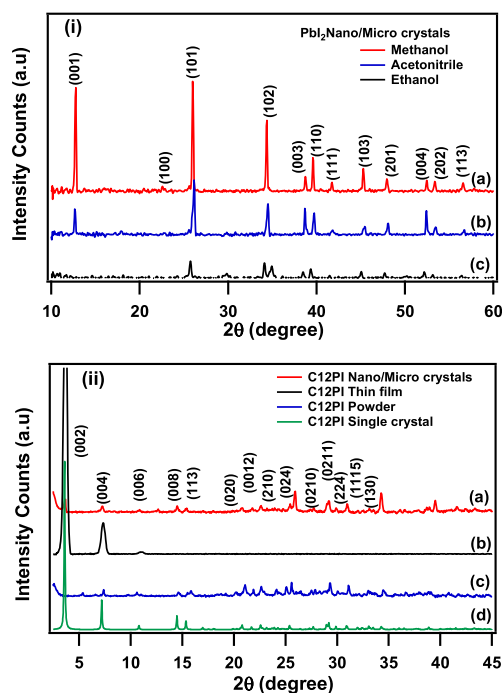

Figure 1. (i) XRD patterns of PbI₂ nano/microcrystals prepared from (a) methanol, (b) acetonitrile and (c) ethanol. (ii) XRD patterns of C12PI as (a) intercalated nano/microcrystals (PbI₂ prepared in methanol), (b) thin films, (c) powder and (d) simulated C12PI XRD patterns from single-crystal XRD analysis.

crystals (Fig. 1(i)c) synthesized in ethanol compared to methanol and acetonitrile. The peak related to [0 0 1] is also absent in PbI₂ crystals prepared in ethanol, though the reason for this is unclear at present. The PbI₂ crystals thus prepared were used to prepare IO hybrid crystals using this intercalation process [10]. Figure 1(ii)a shows that after intercalation with C12I there is a complete conversion of PbI₂ crystals (Fig. 1(i)a) into the desired C12PI. Due to this intercalation, the spacing between Pb–I layers is substantially increased, as seen from the shift in the diffraction peaks to low angles. The strong [0 0 2] reflection of C12PI crystals corresponds to an interlayer distance of 24.08 Å separating the inorganic sheets [20], which is in accordance with the spacing (24.91 Å) obtained from single-crystal XRD analysis [16]. The comparison is shown (Fig. 1(ii)) between the XRD patterns of conventionally fabricated C12PI thin films, powder and single-crystal XRD data [10]. In the XRD pattern of C12PI powder, the missing [0 0 2] peak indicates the lack of a layered arrangement, whereas [0 0 l] reflections are prominent in thin film, which suggests that the alternating organic/inorganic layers stack perpendicular to the substrate surface.

SEM images reveal the hexagonal shape of the PbI₂ crystals extracted by filtration from methanol (Fig. 2a), acetonitrile (Fig. 2b) and ethanol [21], with average diameter of 5, 4 and 1.5 μm respectively, with meagre variation in average thickness (400 ± 100 nm). The hexagonal shape of these crystals is assumed to be due to the strong interaction between the Pb(II) and I₂ molecules in the solvothermal system [6], which controls the