Light emitting diodes based on blends of quasi-2D lead halide perovskites stabilized within mesoporous silica matrix

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The effective synthesis and embedding of semiconducting perovskite blends inside the pores of different mesoporous silica matrices is reported, as well as the implementation of these composites for the first time, as the single and active layer in light emitting diodes. The reported perovskites are blends of quasi-two dimensional hybrid organic-inorganic semiconductors based on lead halides. These blends have been synthesized within the pores of calcined or non-calcined MCM-41 hosts, of two different types, and were optically characterized with UV and PL spectroscopies, as well as structurally with XRD, BET, TEM and SEM techniques. Perovskites reside within the pores of the final dried samples, where degradation protection is provided from chemicals, including water. Moreover, the final white powder like composites exhibit naked-eye visible luminescence as well as electroluminescence under daylight.

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1. Introduction

The recently revived set of materials belonging to the broad class of low dimensional (LD) hybrid organic-inorganic semiconductors (HOIS), has been proved to be ideal for photovoltaic, light emitting diodes (LEDs) or other related device research, see for example [1,2] and refs. therein. HOIS, especially based on lead halides, exhibit useful quantum phenomena owed to native strong excitonic states, even at room temperature [3]. In particular, lead halide HOIS are more resistant to chemicals or oxidation comparable to all other perovskite halides, thus, have been widely used for basic research of materials with strong excitonic properties at room temperature. The PbX_2 lead halides (X = I, Br, Cl), which present excitonic states characterized by small binding energy and oscillator strength, are transformed to much more complex composite materials, after the use of intercalated organic amines that change the dimensionality of the inorganic PbX_2 network. HOIS are capable of spanning dimensionalities from three dimension (3D) to zero dimension (0D), including intermediate dimensionalities. Materials presenting dimensionality between one dimension (1D) and two dimension (2D) as well as between 2D and 3D, are designated as

quasi-1D and quasi-2D HOIS, respectively [4,5]. In the case of 2D and quasi-2D HOIS, the exciton's enhanced quantum and dielectric confinement leads to the increase of the excitonic binding energy by more than a factor of four, as well as to the increase of the respective excitonic oscillator strength [6].

A schematic representation of the quasi-2D semiconductors is shown in Fig. 1. In the left part of this figure, a 2D semiconducting network composed of corner sharing PbX_6 octahedra is alternated with 2D layers of the organic component. The general formula describing the crystalline compounds depicted is $(CH_3NH_3)_{n-1}(Z)_2Pb_nBr_{3n+1}$, where Z = phenethylamine-H. From left to right, the semiconducting inorganic layer's thickness increases in accordance to the n value. When n = 1, the layer is in its thinnest form, composing a 2D semiconductor, while in the case of n = ∞, the material is considered 3D, also known as perovskite. HOIS, synthesized with the same organic and inorganic components exhibit unique and distinct excitonic peaks, as well as unique energy band gaps for every given value of n. Mixing 2D with 3D HOIS yields to blends of 2D (n = 1), 3D (n = ∞) as well as all intermediate crystalline systems (n > 1) [7].

Phenomena and devices based on 3D [8], quasi-2D [9] or mixtures of 2D/3D, i.e. quasi-2D HOIS [7] have been well studied, however, there is always a range of conditions or treatments, such as heating or humidity, which impairs their functionality [10]. It has been shown that mixtures of 2D/3D HOIS are more stable than the

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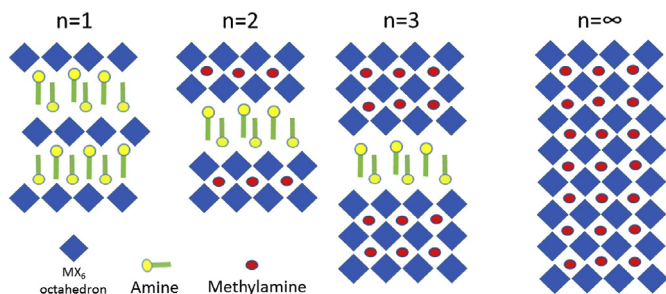 *E-mail address:* anastasia.vassil@gmail.com (A. Vassilakopoulou).

Fig. 1. Schematic structure for the crystalline $(CH_3NH_3)_{n-1}(Z)_2Pb_nX_{3n+1}$ LD HOIS, where Z is a long amine. The dimensionality of the semiconducting inorganic layer increases from left (2D, n = 1) to right (3D, n = ∞) as n = 1,2,3, …,∞.

single 3D or 2D HOIS, as LED active materials [7]. Efforts to include lead halide semiconducting units within inert matrices have already been made [11], as well as HOIS in the prospect of creating robust composites presenting properties attributed to the HOIS, alongside with the capability of sustaining these properties in time under various conditions, by virtue of the host matrix protection. An also interesting subject for research is the quantum confinement induced on the perovskite by the limited growth within the pores, assuming that the pores are completely filled; partial growth along the pore diameter or along the axis of the pore would induce further quantum effects.

On the other hand, mesoporous silica is the category of nano-structured materials being under intense study for potential uses in chemical catalysis [12], chromatographic separations, optoelectronics, biosensing and biolabeling [13]. Interest in mesoporous silica arises from its ordered pores structure, presenting diameter sizes of the order of 2–50 nm [14], as well as from its large surface area and high specific pore volume, which provide a stable and accessible surface for immobilizing a variety of functional molecules or small particles. Combining these two types of nano-structures, for example, incorporation of HOIS into porous silica matrices, could probably lead to novel nanocomposites with improved properties through synergetic effects.

Lately, research on the same subject has appeared, claiming that the entrapment of 3D perovskite nanoparticles within the pores of mesoporous matrices allows the encapsulation without the use of ligands for the electronic state passivation [15]. Simultaneously with this work, authors have reported the observation of quantum confinement effects of 3D lead halide perovskites within meso-porous matrices [16]. In our work, a simple method is presented to effectively synthesize and embed blends of quasi-2D HOIS within the ordered pores of mesoporous matrices of the MCM-41 family, where the excess of external to the pores perovskite has been washed away. Although the results of ref. [16] show quantum size effects as evident in the spectroscopic data of the composite materials, in this work the blends of quasi-2D HOIS entrapped within the mesopores are expected to show excitonic energy transfer effects besides the increased stability inherent in the quasi-2D low dimensional organic inorganic semiconductors. This MCM material family forms silica based mesoporous, which are transparent, yet their white powdered form is due to light scattering effects. In particular, the synthetic route, the process of the final materials, their structural and spectroscopic characterization as well as their application in LED devices, are presented. The active materials have been shown to reside within the pores while they do not appear to be affected by water or by time degradation. Finally, the reported synthesis here allows for the production of such high quality MCM-perovskite composites in a large scale which is desirable for many applications.

2. Materials and methods

Tetraethyl orthosilicate (TEOS), N-hexadecyl-trimethylammonium bromide (CTAB), aqueous ammonia solution wt.32%, absolute ethanol (Eth, 99%), gallium-indium eutectic (≥99.99% trace metals basis), phenethylamine (PhE, 99%), methylamine (Meth, 40% in water), indium tin oxide coated glass (square, surface resistivity 15–25 Ω/sq), hydrobromic acid (HBr, ACS reagent, 48%), acetonitrile (AcN, CHROMASOLV® Plus ≥99.9%), lead (II) bromide ($PbBr_2$, 99.999% trace metals basis), N,N'-dimethylformamide (DMF, 99.8%). All chemicals were obtained from Sigma-Aldrich and used without any further purification.

2.1. Synthesis of MCM-41

The spherical MCM-41 (sp.nc.ud) was prepared by the standard sol-gel technique using TEOS as the silica precursor and CTAB as the structure directing agent. In a typical synthesis, 0.85 g of CTAB were dissolved in 16 g deionized water, after 4.4 g ammonia and 20 g ethanol were added to the surfactant solution under stirring for 30 min. Then, 1.62 g of TEOS were added slowly in the solution. After 1 h of stirring, the white powder was filtered and washed with at least 50 ml of deionized water and 50 ml of methanol. The sample was dried for one day at 90 °C. Furthermore, part of the sample was calcined at 550 °C for 60 min in porcelain crucibles and presented the form of a white powder (sp.ca.ud).

For the synthesis of the non-spherical MCM-41 (ns.nc.ud), a primary water-ammonia-surfactant solution was placed in a poly-ethylene bottle of 420 g triple distilled water, 300 ml of 25% ammonia solution and 10.5 g of CTAB. Following vigorous stirring for 30 min, 54 ml of TEOS were added and the stirring was continued for a similar amount of time. The final solution was heated at 80 °C for four days and then the final product was rinsed with at least 50 ml of ethanol under vacuum. Drying of this sample was continued under low heating at 50 °C for two days. Part of this product was calcined at 500 °C for 60 min, in porcelain crucibles, presented the form of a white powder (ns.ca.ud).

The above four sets of porous materials were characterized for their porosity, while part of those was used for inserting various type of HOIS within their pores. Here, is provided the synthetic route of entrapment for only one type of HOIS, while in general, any type of HOIS cannot be simply inserted in the pores and reside only within the pores. The common problem of inserting HOIS in porous materials, is that their successful entrapment is dependent on their unit cell size, the solvent and the temperature used or on other physiochemical parameters attributed to the surfactant included in the mesoporous synthesis as template. However, here, successful cases of HOIS entrapment which led to active materials for single LED devices, are being reported.

2.2. Synthesis of HOIS

For the synthesis of the 3D perovskite (Meth-H)$PbBr_3$ (-H denotes amine's protonation), 5.4 mmol of $PbBr_2$ were dissolved in 3 ml of AcN with the addition of 3 ml of HBr, and stirred until an optically clear solution was obtained. 13.3 mmol of methylamine were dissolved by stirring in 3 ml of AcN with 0.910 g of HBr. These two solutions were slowly mixed and dried afterwards. Mixing 0.5 mmol of (Meth-H)$PbBr_3$ with 0.7 mg of the protonated phe-nethylamine (PhE.HCl) in 600 μl DMF, yielded solutions which provide composites of quasi-2D HOIS. This final dried material is abbreviated as HOIS1. The protonation of PhE in order to form PhE.HCl has been achieved by reacting equimolar quantities of PhE and HCl in acetonitrile, with subsequent drying of the solution at 60 °C.