Synthesis and characterization of PbI\textsubscript{2} semiconductor quantum wires within layered solids

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PbI\textsubscript{2} semiconductor quantum wires have been synthesized in the interlayer space of montmorillonite organic modified clays by simple intercalation reactions. The experimental results showed that the quantum wires have been retained within the lamellar space of layer silicates exhibiting a well-defined diameter and narrow length distribution. The synthetic procedure involves chemical reactions within the clay interlayer, which are achieved through a slow mass transport between the clay platelets via a low solubility path between two different lead iodide phases. The structure and properties of the hybrid composites have been studied by means of X-ray diffraction, energy dispersive spectroscopy, Transmission electron microscopy, optical absorption and photoluminescence experiments. The experimental techniques have verified that the resultant organo-clay-semiconductor composite contains within the clay platelets as nano sized low dimensional semiconductor species in the form of wires that exhibit well defined energy gap absorption peaks, which are blue shifted due to quantum confinement phenomena.

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1. Introduction

During the last 50 years semiconductors have been actively being pursued for basic research as well as for device applications. Lately, it has been found that aside of the naturally occurring three dimensional (3D) semiconductors there is the possibility of creating low dimensional (LD) semiconductors such as two dimensional (2D), one dimensional (1D) or zero dimensional (0D) systems, which in many specific cases are commonly referred to as quantum wells, wires and dots, respectively [1]. LD semiconductors have different properties with respect to the corresponding 3D systems, which in many cases are represented by outstanding physical, physicochemical or chemical properties. Most important properties for device applications are the shifting of the band gap energy to higher values, the increase of the excitonic binding energy and excitonic oscillator strength as the dimensionality of the semiconductor is decreased. These properties, which are all due to quantum mechanical manifestations of the electron, are inherently related to the size, shape and atomic structure of the LD systems and are important when the system size is smaller than the electron’s thermal de Broglie wavelength, usually of the size of a few tens of angstroms [2,3,4].

It has been possible to synthesize LD structures by natural methods, in contrast to the artificial methods, such as molecular beam epitaxy. These methods can be either direct chemical synthesis that lead to the crystallization of LD systems [5,6], such as the inorganic-organic hybrid semiconductors, or the incorporation into naturally occurring nanoporous materials of semiconducting systems, the latter being size restricted by the nanopores and in some cases interact with the nanopores walls. Such examples of porous materials can be zeolites [7,8,9], micelles [10,11,12,13], polymers [14] and molecular sieves [15,16] and mesoporous materials [16,17,18].

Chemically synthesized LD semiconductors can be accurately sized systems with well defined quantum properties, however, in most cases the resulting compounds, which have been fruitful for basic research of LD phenomena [5], suffer from two drawbacks. First, the LD objects are formed in a superlattice array separated by barrier material, usually organic, which is responsible for the quantum confinement phenomena preventing the accumulation of the LD objects, however, also prevent the extraction of a single LD component. Thus, the applicability of crystalline chemically synthesized LD objects is limited to devices where the whole superlattice can be incorporated, such as in, for example, photonic crystals [19]. Second, in cases of synthesized LD objects, and most usually in the case of chemically synthesized quantum dots, it is impossible, for many reaction paths, to create device useful monodisperse samples, thus limiting the applicability of such LD compounds, although in some cases controlled non-uniform sized assemblies are desired for novel phenomena study and applications [20, 21].

Incorporating nanoparticles within a host system can be achieved with either direct synthesis or by mechanical
incorporation. It is obvious that either of these methods, or when combined, can use the host empty regions (clay interlayer or porous), for controlling nanoparticle’s size, while at the same time using the matrix as a reactor for performing single or multi-component sample synthesis, the latter covering a variety of quantum phenomena, as for example, Forster energy exchange [22]. It must be stated, that periodic, thus exactly sized, multi functional systems are almost impossible to synthesize due to periodicity using hybrid the periodicity does not allow for such flexibility.

Therefore, a lot of effort has been placed, part of which is reported here, to synthesize low dimensional semiconducting objects within clay platelets, as this would not only be desired for the reasons already described, but also as such a composite would protect the low dimensional objects via the clay platelets. Existing published results, see for example [23,24], have mainly focused on chalcogenide systems, such as ZnS or CdS, and in all cases have incorporated quantum dot systems, organically capped or not. Until now, quantum wires have not yet been reported. Moreover, in contrast to similar methods, the materials reported here do not only have a specific functionality, but final product remains open to further functionalization, while at the same time the synthesis that is performed within the clay interlayer inherently connects the final properties of the nanosemiconductor to the organic molecules already introduced in the interlayer space to synthesize the organo-clay.

Lead iodide is used as the starting semiconducting material, for which many types of low dimensional free standing and/or hybrid systems have been synthesized and characterized. Moreover, lead iodide can form hybrid organic inorganic LD structures that can have a variety of end applications, such as sensors [5] or lasers [25] or emitters [26] or thin film transistors [26] and is highly stable in ambient conditions as far as optoelectronic properties are concerned for large time periods [27]. PbI₂ is a direct band gap semiconductor with band gap at room temperature of 2.56 eV [28] at 1.6 K, while at 2.43 eV at room temperature [29], with an excitonic binding energy not readily unobservable as an isolated peak at room temperature [29], with an excitonic binding energy of 127 meV [69G in 23] or 30 meV [74L in 23] and, thus, not readily observable as an isolated peak at room temperature (RT) taking into account the weak excitonic oscillator strength. Upon formation of 2D, 1D or 0D systems, PbI₂ remains a direct band gap semiconductor and as the semiconductor’s dimensionality is reduced, the excitonic binding energy and oscillator strength are increased dramatically [5]. PbI₂ cannot be considered as a 3D semiconductor since its structure is layered-like (2H, 4H, etc) and thus any relation to deduce the size of a relevant LD object must be done with respect to a true 3D lead iodide network, as it will be mentioned further in the text.

In this research work, a new method is reported that incorporates lead iodide quantum wires, a material that has not been used for clay modification until now, within the interlayer space of organic modified clay with simple soft low temperature intercalation reactions. The resulting new hybrid semiconductors were characterized by a combination of analytical techniques such as powder X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), UV/Vis Optical absorption (UV) and Photoluminescence experiments (PL).

2. Experimental

Materials

Natural montmorillonite (Cloisite™ Na⁺) and commercial organically modified montmorillonites (Cloisite™ 10A and Cloisite™ 20A, referred as C10A and C20A from this point on, respectively) from Southern Clay Products, Inc. were used in this study as received. They are prepared from a Na-MMT with a cation exchange capacity (CEC) of 0.926 meq/g (Cloisite™-Na⁺) by modification with different proportions of dimethyl, dihydrogenated or benzyl, hydrogenated tallow ammonium chloride respectively (hydrogenated tallow is a blend of saturated alkyl groups with approximate composition: 65% C₁₈; 30% C₁₆; 5% C₁₄). The two dimensional visualizations for the organic molecules being intercalated into the clay are as follows:

![2D, 1D or 0D structures](image)

For comparison, a second natural montmorillonite from Wyoming (SWy-1) was used, obtained from the Source Clay Minerals Repository, University of Missouri, Columbia, with a cation-exchange capacity (CEC) of 76.4 meq / 100 g clay. The clay was fractionated to < 2 μm by gravity sedimentation and purified by standard methods in clay science [30].

Lead iodide microcrystals were prepared according to a similar procedure described by [31] from the chemical reaction of NaI with Pb(NO₃)₂ in water. The products of the reaction Pb(NO₃)₂ + 2NaI → PbI₂ + 2NaNO₃ appear as colloidal particles, dispersed in the water, which slowly form a yellow colour deposit on the bottom of the preparing vessel. The product was washed three times with water, centrifuged and re-dispersed in deionized water in order to obtain product free from NaNO₃. The semiconductor quantum dots –C10A product were obtained as follows: 500 mg of Cloisite™ 10A clay sample were dispersed in 50 ml of acetonitrile(AcN) at 60 °C. 200 mg of the PbI₂ yellowish microcrystals were then added to the clay suspension and the mixture was stirred for another 30 min. Finally, the mixture was left to slow cooling until it reached room temperature and it was further air-dried (hereafter named C10A±PbI₂(l) ). Another sample was also produced from 500 mg of Cloisite™ 10A clay sample and 500 mg of the PbI₂
microcrystals (C10A±Pbl₂(h)). The same procedure was followed for the preparation of clay-nanomaterial products using Cloisite™ 20A (C20A±Pbl₂), pure Cloisite™ Na⁺ (CNa±Pbl₂), pure sodium montmorillonite (SWy−1), (SWy−1±Pbl₂), or organically modified Cloisite™ Na⁺ with tetramethylammonium (CTMA±Pbl₂).

Methods

X-ray powder diffraction data were collected on a D8 Advance Bruker diffractometer using Cu-Kα (40 kV, 40 mA, 1.54178 Å) radiation and a secondary beam graphite monochromator. Diffraction patterns were collected in the 2θ range from 2 to 80°, in steps of 0.02° and 2 s counting time per step.

UV-Vis absorption spectra were recorded on a Shimadzu UV-2401PC two-beam spectrophotometer in the range of 200-700 nm, at a step of 0.5 nm, using a combination of deuterium and halogen lamps as sources.

The PL spectra were obtained from solid pressed pellets mounted in a Jobin Yvon Fluorolog 3 spectrofluorometer FL-11 employing xenon 450 W lamp and a P928P photodetector. The slits were set at 4 nm. The photoluminescence excitation and emission spectra have been corrected through the instrument supplied files, created from compounds with known quantum yields and an included Si photodetector. All optical UV absorption and PL spectra were recorded at room temperature.

Energy-dispersive spectra were collected using a JEOL JSM-5600 scanning electron microscope (SEM) using a sample holder of the composition 39 %Zn - 61 %Cu. The Cu composition specified the Zn sample percentage, which was automatically subtracted from the measured data. The analysis results were the average of five different region surface measurements of each sample.

Transmission electron micrographs were obtained with a JEOL 120CX instrument equipped with a CeB₆ filament and operating at 120 kV. TEM samples were prepared by gently grinding the powders and casting on a holey carbon grid. The images are typical and representative of the samples under observation.

3. Results

X-ray diffraction measurements represent a powerful way to understand the changes in the interior of the clay microenvironment, since the interlayer distance can be estimated by measuring the d_{001} spacing. Fig. 1 shows the low angle powder XRD patterns of the pristine organophilic montmorillonites, i.e. the C10A (Cloisite™ 10A) and C20A (Cloisite™ 20A) materials and the tetramethylammonium-modified Cloisite™-Na⁺ (CTMA), before and after the intercalation with PbI₂ species.

It is obvious that the CTMA clay composite does not change upon treatment with lead iodide. However, the C10A and C20A clay – semiconductor composites show not only an increase of the d_{001} spacing but also a sharpening of the first diffraction peak.

Fig. 2 shows the powder X-ray diffraction patterns of C-Na (Cloisite™ Na⁺), C10A±Pbl₂(l), C10A±Pbl₂(h), CTMA±Pbl₂, SWy−1±Pbl₂ and polycrystalline PbI₂, in the range of large diffraction angles (2θ), between 10° and 90°.
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The XRD pattern for the pure Cloisite™-Na clay is depicted at the bottom of Fig. 2. No peaks are observed as in the other spectra, except for some small peaks at 20, 25, and 35. The XRD patterns for the clay – semiconductor composite in the cases of the SWy-1×PbI$_2$ and CTMA×PbI$_2$ composites reveal the existence of a pure lead iodide phase, the top spectra in Fig. 2. More specifically, the CTMA×PbI$_2$ has a few peaks different from the PbI$_2$ compound, which will be discussed later on.

In the same figure, it is observed that the product C10×PbI$_2$ at both high and low loadings with lead iodide show the same spectra, which have no resemblance to lead iodide. The spectra of C20A×PbI$_2$, not shown here, are also similar, all exhibiting small sharp peaks indicative of a new phase of PbI$_2$.

EDS measurements for the unloaded and PbI$_2$ loaded sample C10A are shown in the following Table 1, where Table 1a concerns the as prepared clay and Table 1b the PbI$_2$ treated clay.

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Table 1a

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<tr>
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<td>Pb</td>
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Table 1b

EDS measurements have shown that the ratio of I to Pb is 2.4, which clearly shows that the intercalated species are not related to PbI$_2$.

Fig. 3 shows the UV/Vis absorption spectra for some of the untreated and treated clay – semiconductor composites. Fig. 3a shows the absorption spectra for polycrystalline PbI$_2$, which shows absorption onset at c.a. 510 nm, with no distinguishable peaks at higher energies.

Fig. 3b shows the absorption of the untreated organo-clay C10A, which shows peak only at c.a. 250 nm. Similarly, Fig. 3c shows the spectra of the CTMA×PbI$_2$ clay, which again exhibits the organo-clay peak at 250 nm as well as a small weak peak at 365 nm, as well as a small, almost undetectable, shoulder at 510 nm. Fig. 3d and 3e show the absorption spectra for the low and high content loaded treated organo-clay. In the last two cases distinct peaks at 390 nm and 400 nm appear, and in parallel the organo-clay peak at 250 nm has been broadened. For the high loading treatment the absorption peak at 250 nm appears to be much broader masking the whole region 270 nm-370 nm retaining the detectable peak at 400 nm. Similar results have been obtained for the C20A treated clay. Both treated clays C10A×PbI$_2$-(h) and C10A×PbI$_2$-(l) have also both a small shoulder at 510 nm, which is much smaller than in the case of the CTMA×PbI$_2$ treated clay.

The photoluminescence experiments have shown no detectable luminescence for all possible excitations other than the luminescence of the organic molecules within the clay interlayer.

TEM images of the C10A×PbI$_2$-(l) are being shown in Fig. 4. The lower left corner of the image on the left has been zoomed as it probably corresponds to a region with rather uniform thickness. It can be seen that the clay platelets have an average distance of 37 Å. More specifically, the black lines that are being displayed have a thickness between 8 Å and 12 Å (the clay sheet has...
the thickness 9.7 Å) and an average length of 140 Å. The black lines are probably the edge of the platelets, which appear easily due to the high contrast of the intercalated species of lead iodide.

On the other hand, the insertion of PbI$_2$ species in the interlayer of C10A montmorillonite expanded even more the distance between the layers (Fig. 1). In this case, the (001) diffraction peak appears at the higher spacing of 37 Å, which corresponds to an intersheet separation of 27.4 Å, confirming the remarkable binding capacity of C10A organo-clay for PbI$_2$ moieties. This distance suggests that the insertion of PbI$_2$ species into the C10A organo-clay interlayer ($d_{001} = 21$ Å) highly expands the distance between the layers, induced an increase in the basal spacing to 16 Å. Similarly, as in the case of organo-clay C20A, higher order reflections (00ℓ) are observed. In conclusion, XRD data show that most probably in the case of C10A larger lead iodide species, Pb$_3$I$_4$, have been incorporated within the interlayer. As it will be discussed further, these have clearly improved the regularity of the C10A:PbI$_2$ system, while showing no resemblance to the XRD spectra of PbI$_2$.

From Fig. 2, as it is shown, the large angle diffraction patterns of CTMA:PbI$_2$, SWy-1a:PbI$_2$ exhibit the characteristic reflections of PbI$_2$, suggesting that large size crystals of lead iodide semiconductor have formed on the external clay surfaces, but not lying in the interlayer space of the phyllomorphous material, in accordance to the data of Fig. 1, since the interlayer spacing has not increased to host another species. On the contrary, no XRD detectable PbI$_2$ diffraction peaks have been observed in the patterns of C10A:PbI$_2$-(l) and C10A:PbI$_2$-(h), whereas a large amount of PbI$_2$ microcrystal was used. At this point, before discussing the optical absorption spectra, it should be noted that the XRD peaks of the CTMA:PbI$_2$ are slightly different from those of the PbI$_2$ compound and these variations will be explained as been attributed to nano sized layer-like Pb$_3$I$_4$ phases that have been attached on the outer surfaces of the clay platelets, which lack 3D periodicity and thus give rise to reflections that would ordinarily be absent in PbI$_2$.

Optical absorption is an useful tool in understanding the nano sized semiconductor objects as the absorption is size dependent, thus allowing direct size estimation and calculation. Fig. 3 shows the optical absorption spectra of the as prepared organo-clay, the composite systems loaded with nanosemiconductors as well as the spectra of PbI$_2$. In Fig. 3a we can observe from the onset of absorption that lead iodide has an energy gap of at least 2.38 eV, which is in agreement with the bibliographic data. It is important to note that the other spectra with PbI$_2$, i.e. Fig. 3c, 3d and 3e, have no direct resemblance to Fig. 3a indicating that there is no bulk PbI$_2$ in the clay-semiconductor composites.

In Fig. 3b it can be observed that the C10A organo-clay exhibits no absorption in the range of 300 to 600 nm, while the absorption at c.a. 260 nm is due to the organic molecules that have been intercalated into it, mainly due to the benzene ring.

Fig. 3c shows that spectrum of the tetramethylammonium organo-clay, for which effort has been taken to load with lead iodide species, under exfoliation in acetonitrile. It is readily seen that the spectrum contains no peaks in the region of 300 to 600 nm.

4. Discussion

In more detail, as shown in Fig. 1, the low angles XRD patterns of CTMA and CTMA=PbI$_2$ montmorillonites do not show any differences, suggesting that the interlayer space retains its dimensions and no intercalation of lead iodide phase has occurred, as it is the only species that is available, also proved by the EDS spectra discussed further. Therefore, the organophilic character of tetramethylammonium does not favour the insertion of lead iodide nanospecies in the clay galleries, which is also supported by the UV-Vis spectra, as discussed later. This is expected, since, units of Pb$_3$I$_4$ are negatively charged and thus cannot be exchanged with TMA cations. However, as it will be evident later, nano sized PbI$_2$ species have been attached on the external surfaces or on the edge sites of the clay mineral or within random space of various platelets but the spacing of the plates has not changed.

In contrary, as again depicted in the spectra of Fig. 1, the effort for the intercalation of C20A with PbI$_2$ nanoparticles, gave an XRD pattern with a $d_{001}$ basal spacing value of 28 Å; this indicates an interlayer separation of 18.4 Å ($\Delta = 28-9.6 = 18.4$ Å, where 9.6 Å is the thickness of a clay layer). This $d_{001}$ spacing is higher compared to the pristine organo-clay C20A ($d_{001} = 23$ Å and $\Delta = 13.4$ Å) indicating that the insertion of PbI$_2$ species into the organo-clay interlayer caused an increase in the distance between the layers equal to 5 Å. In addition, the presence of higher order reflections (00ℓ) in the pattern of C20A:PbI$_2$ indicates layer insertion of PbI$_2$ species and a high degree of lamination (clay layers are stacked in perfect registry) of the organo-clay–PbI$_2$ system.
other than two weak peaks at c.a. 360 nm and at 500 nm. The peak at 360 nm is due to the small PbI$_2$ species that have formed within the AcN solution and have been deposited randomly on the outer surface of the CTMA (clay with TMA cations). This is in agreement with previous works [25,32,33], which show, that in various solvents in which PbI$_2$ possess low solubility, various PbI$_2$ soluble species can exist, having magic dimensions (magic numbers). More specifically, it has been shown that the species forming specifically in pure AcN have dimensions of c.a. 28 Å with peak at ca 364 nm, which is not due to I$_2$ species, as it has been shown by [27]. These small nanoparticles have been formed by the dissolution of PbI$_2$ in the AcN that was used to exfoliate the clay plates, however, these species could not form any structure nor intercalate within the interlayer space of CTMA. Thus, optical absorption detects only these that have remained on the outer surface of the clay platelets.

The second peak at 510 nm is very weak and is due to lead iodide that has again probably remained on the plates and has formed micrometer size particles. In [33] it has been mentioned that the dried solid products of PbI$_2$ dissolutions in AcN are rod-like micrometer-sized lead iodide. It is quite possible that parts of the lead iodide species that have formed in AcN solution can, in fact, remain as nanosized species with peak at 360 nm outside the platelets, while a small portion of these can form micrometer sized crystals that have peak at 510 nm, remaining again on the outer surfaces of the clay.

Fig. 3d shows the absorption spectrum of an organo-clay-nanosemiconductor composite, C10=PtI$_2$-(l), with peak at 390 nm which clearly is attributed to absorption peak of lead iodide nano formed semiconductor. The peak is not only due to the energy gap ($E_g$) absorption onset but also due to the excitons, which in LD objects can be well distinguished from the energy gap due to increase of binding energy. The blue shift of the nanosemiconductor within the clay is approximately 700 meV with respect to the energy gap absorption peak of PbI$_2$. It must be noted that the blue shift from the energy gap of a 3D Pb-I compound (MeNH$_3$PbI$_3$ \([\text{5}]\)) is 1500 meV. In the case of Fig. 3e, the spectrum of C10=PtI$_2$-(l) shows a peak at 400 nm, due to the fact that larger LD species have been formed with respect to the C10=PtI$_2$-(l). Despite, the large increase of the interlayer spacing, a small percentage of lead iodide has formed outside the platelets and thus gives rise to small shoulders at c.a. 510 nm, which are very quite hard to observe in the spectra and do not appear at all in the related XRD spectra.

In interpreting the spectra of the C10=PtI$_2$-(h) and C10=PtI$_2$-(l) systems, the facts that the interlayer distances appear the same for both the low and the high loaded samples, the existence of well defined peaks at 390 nm and 400 nm, as well as the similarity of the optical absorption peak widths imply certain important results.

First, the synthesized quantum objects within the clay have uniform size distributions and that their average sizes are dependent on the starting PbI$_2$ loading. If this was not true then well resolved UV/Vis peaks would not have been observed but rather wide peaks would have existed. If the interlayer stacking distance was different for the high and low samples then the intercalated nanobjects would have different sizes or would have coordinated randomly along with the organic molecules within the clay interlayer, which does not happen and on the contrary, the organo-clay composite becomes highly organized both in the high and low samples. Had the latter case been true, all such effects would have led to not well-defined, similar and sharp absorption peaks corresponding to irregular size distributions.

If it is taken into account that the formation mechanism of the nanoobjects must be such that upon higher loading (larger sizes) the distribution of sizes remains the same (similar absorption peak widths between the high and low), which in conjunction with the similar interlayer distances between the two differently loaded samples, imply that the growth takes place parallel to the plates, following an atomic model that permits an equilibration to a particular size as the solvent is being removed and the clay plates start stacking.

If the nano-objects were to grow perpendicular to the clay platelets it would have been very hard to transform the various grown species, which would not have necessarily the same thickness, from one type to another, which however seems to be the case since the ordering of the clays seems to be high. Also, the growth been perpendicular to the clay plates, which already include organic moieties, this would have occurred in a random manner inducing random sized interlayer spacing and of course the ordering would not be as good in the treated clay samples.

Moreover, since the XRD spectra of both the high and low PbI$_2$ loaded samples reveal the same stacking it is only logical to assume that the species that have been formed within the interlayer cannot be quantum dots, or else the spacing would have increased by significant length at twice the loading.

It has been shown that PbI$_2$ in AcN forms small nanoparticles, lateral size of the order of 28 Å and thickness of c.a. 7 Å, which have an absorption peak at c.a. 360 nm. Therefore is rather hard to expect that these magic number nanophases will be stacked together throughout the interlayer clay space, since magic number for z stacking of such nanophases has not been reported, nor it is easy to vision an atomic mechanism of regular growth within the clay interlayer that is active during the “opening” of the clay in the organic solvent.

Also, since AcN produces upon evaporation micrometer sized, rod-like PbI$_2$ crystals [33], it is reasonable to accept that the asymmetry in the lead iodide rod growth starts at the atomic level, and thus it is reasonable to accept that 1D objects have been integrated into the clay.

Thus, with all the arguments and all the relevant data based on the existing forms of LD PbI$_2$ systems that have been published, it is plausible to assume that either 2D or 1D objects have been formed by growth parallel to the clay platelets, with most improbable case being the 2D. In conclusion, from simple arguments, it seems plausible that quantum wires have formed with the clay interlayer space.
1D objects growing parallel to the clay platelets are the simplest system that allows the transfer of mass from one wire to another, thus producing nano-objects of more or less the same length as envisioned from the UV/Vis spectra. As the 1D nano-objects are being formed inside the clay interlayer, atoms can move from the ends of each nanowire hopping to different wires thus giving rise to a narrow size distribution of sizes, since by symmetry arguments there is no reason that one strand should be larger than another, except for arguments that are related to the formation energy of a specific length of quantum wire and the total amount of dislocation a wire can bear, since it is being supported by the organic moieties which are not periodically space within the clay interlayer.

As it is known [5], lead iodide LD compounds are usually formed by octahedra that form LD networks with particular connectivity (edge, face, corner). In the possibility that lead iodide corner sharing octahedrons 2D layers have been formed within the organic material in the interlayer space, then the absorption spectrum would have shown intense single excitonic peak at about 510 nm [5,34] and $E_g$ of 2.84 eV, or 436 nm. Thus, we can conclude that such a 2D system has not formed. Even if 2D species, comparable in size to the Bohr radius, had formed the excitonic peak would be very intense.

The case of quantum wires being formed and the interpretation of the optical spectra in this context is more complex, since the reported systems of hybrid organic-inorganic lead iodide quantum wires consist of corner sharing or face sharing octahedral.

If there were infinite 1D corner sharing octahedral chains being formed then an intense excitonic peak would have appeared at 460 nm [34,35] by virtue of the encapsulation of the quantum wire within an organic matrix, with energy gap at about 3.1 eV, or 400 nm. Thus, if one dimensional chains of PbI$_2$, have formed, however, missing the appearance of the excitonic peak, then this implies that the exciton confinement is not very good, probably due to the proximity of the clay platelets (high dielectric constant) to the quantum wires [34]. It is possible however, since the energy gaps agree at the 400 nm to have this type of quantum wires. It must be mentioned that the peaks at 390 nm and 400 nm of the clay-semiconductor composites correspond to excitonic peaks while the energy gaps should occur at a little higher energies. The possibility of having corner sharing octahedral chains but with smaller length than then Bohr radius cannot hold because the infinite chains have already energy gap at 400 nm, and thus smaller wires should show absorption onsets at smaller wavelengths.

In the case of another type of quantum wire having formed, it is useful to consider the EDS measurements which have revealed a stoichiometric ratio of I to Pb of 2.4. This value does not correspond to neither the classical corner sharing octahedral 1D systems, which would have ratio I/Pb 3 or 5, neither to 2D systems with ratio I/Pb 2, 4, 3.5, for all these see [5]. Due to the EDS stoichiometry results, it is rather impossible to understand the results in the form of isolated standard type chains of PbI$_2$ or PbI$_3$ since these do not satisfy the EDS stoichiometric ratios, except if these wires are not exact copies of the hybrid organic-inorganic systems.

However, there have been reports of one dimensional and two dimensional compounds of the form M$_x$Pb$_y$I$_z$, see for example [36,37]. The structure in [36] is 1D forming asymmetric cylinders, while the structure in [37] is 2D by forming bilayers of edge and corner sharing octahedra. The case of this 2D system is ruled as invalid since such a system would portray excitonic peak and energy gap at higher wavelengths than the single layered 2D system [5]. Thus, it is expected that quantum wires of the latter type have formed, with I/Pb stoichiometric ratio of 2.5, slightly deficient in I, which could be due to the nature of the organic moieties to attract lead due to complexation.

In order to have quantum wires of the form having I/Pb ratio as close as to 2.5, there should be created a chain of PbI$_{6-x}$ octahedra. Therefore, it is reasonable to assume that part of the organic molecules of the untreated CloisiteTM have rotated to accommodate the chains providing the necessary charges on the inorganic wires, and these rotated molecules are attracted to the ones holding the plates together via Van der Waals forces.

Finally, it is interesting to note that the optical absorption spectra of PbI$_3$ chains have been observed experimentally before and the results agree with those presented here, as well as to the data for PbI$_4$ chains as far as $E_g$ is concerned. More specifically, such chains have been reported [38] to have absorption spectra that start from 2.0 eV (620 nm) and show peak at c.a. 3.1 eV (400 nm). In fact, the authors report that the light in the energy region from 2-3 eV is absorbed for light polarization perpendicular to the infinite chains, where the peak at 400 nm has been attributed to the free exciton in the PbI$_2$ wires, as it is observed for light polarization parallel to the quantum wires. In all cases, 1D chains of lead iodide with diameter of the Angstrom scale have energy gaps at c.a. 3.1 eV.

5. Conclusions

Montmorillonite clays have been modified by inclusion within their interlayer of well formed and sized semiconductor objects, namely quantum wires of Angstrom diameter. The experiments can verify the inclusion of such quantum wires, giving the composite that has only been subjected to soft chemical reactions at room temperature unique properties, with the open possibility of further functionalization. We can safely conclude that in our case the nano semiconductor objects are lead iodide quantum wires, which agree with other published results on the optical absorption spectra and these are embedded into an organic matrix which shifts the excitonic peak to slightly lower energies. Also, from the absorption spectra we see that no energy transfer takes place between the quantum wires and the surrounding organic molecules. Also, the complete loss of luminescence, where PbI$_2$ in its LD forms and hybrid LD forms is highly luminescent, is pointing to the direction of quantum wires that may have defects, such as deficient in iodine, or are bound to organic molecules that suppress all singlet fluorescence. Such a
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quenching could also take place from AcN molecules that may still be present in the clay and act as quenchers and these problems are part of future research on these materials.

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