Synthesis and characterization of low dimensional ZnS- and PbS-semiconductor particles on a montmorillonite template†

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Low dimensional metal sulfide particles have been prepared in the interlayers of montmorillonites via reactions of the metal ion-exchanged clay minerals in aqueous dispersions with gaseous hydrogen sulfide. The montmorillonites separated from the Wyoming (USA) and Jeľový Potok (Slovakia) bentonites were saturated with Pb$^{2+}$ or Zn$^{2+}$. In the final nanohybrids, the smectite mineral can be incorporated with metal sulfide pillars and/or nanoparticles. Properties of the prepared materials were investigated by various analytical techniques. The formation of metal sulfide nanoparticles in the interlayer galleries was indicated by X-ray diffraction and energy dispersive X-ray analysis. About 50% of Pb$^{2+}$ or Zn$^{2+}$ present in montmorillonite has formed metal sulfide semiconducting units. Infrared spectroscopy and thermogravimetric analysis were used for characterization of starting materials and products. Ultraviolet-visible absorption and photoluminescence spectroscopies confirmed that final composite systems acquired the optical properties of the incorporated quantum low dimensional systems exhibiting blue shift of the energy gap and higher oscillator strength excitonic peaks. Larger amounts of metal sulfide nanoparticles were formed in montmorillonite Jeľový Potok probably as a consequence of its higher cation exchange capacity.

1. Introduction

Expandable clay minerals such as smectites have extensive applications due to their swelling, adsorption and ion exchange properties and high surface areas.$^1$ The most commonly used clay mineral is montmorillonite (MMT), which has two siloxane tetrahedral sheets sandwiching an octahedral sheet with Al(III) as dominant central atoms. Due to the isomorphic substitutions, typically Mg(II) for Al(III) in the octahedra and Al(III) for Si(IV) in the tetrahedra, the layers are negatively charged. This is counterbalanced by hydrated exchangeable cations, such as Ca$^{2+}$ or Na$^+$, within the interlayer space and on the external surfaces. The intercalation process in these systems often proceeds via ion exchange and, in contrast with intercalation compounds of graphite, does not necessarily involve charge transfer between the guest and host species. One possibility to modify the surface and chemical properties of MMTs is by replacing the natural inorganic cations with other cations. This process may alter both the surface and pore structure of the minerals.$^2$ Surface modifications of clay minerals have received much attention because they can lead to new materials and new applications such as adsorbents of organic pollutants in soils, water and air, rheological control agents, paints, cosmetics, personal care products, refractory varnish, thixotropic fluids, etc.$^3$ The nature of the microenvironment between the aluminosilicate sheets regulates the topology of the intercalated molecules and affects possible supramolecular rearrangements or reactions that are usually not easily controlled in the solution phase.$^5$–$^7$

Layered silicates are also eminently suitable for the preparation of particles with a diameter of a few nanometres on the surface and in the interlamellar space in aqueous dispersions. Inorganic nanoparticles are most conveniently grown on the clay mineral surface by displacing the exchangeable cations with precursor transition metal cations and by subsequent reaction. The adsorption layer at the solid/liquid interface was employed earlier as a ‘nanophase reactor’ for the generation of nanocrystalline metal particles and for their stabilization in the presence of the clay mineral.$^8$ The nanoparticles can be grown attached to the surface in well controllable number and size between the silicate layers.

Semiconductor nanocrystals have attracted considerable attention in recent years because of their size- and shape-dependent optical and electronic properties as well as their potential for applications in nanodevices. Metal sulfides (MS) belong to the most important semiconductors and have potential applications in numerous areas including optoelectronics,$^9$ photocatalysis,$^{10}$ and thin-film electroluminescent devices.$^{11}$ Many reports appeared on attempts to control the size and morphology of metal sulfides including solvothermal routes,$^{12}$ thermal evaporation,$^{13}$ reverse micelle templates,$^{14}$ as well as intercalation...
in zeolites\textsuperscript{15} and mesoporous silica MCM-41.\textsuperscript{16} Layered systems could be potential hosts confining the growth of nanoparticles inside the interlamellar galleries; the reaction zone is sterically constrained by the layers,\textsuperscript{17} reminiscent of two-dimensional nanoreactors such as Langmuir–Blodgett (LB) films and self-assembled monolayers.\textsuperscript{18} One great advantage of these methods compared with lithographic fabrication is that regular nanoscale arrays of materials can be obtained with substantially reduced production costs.

Semiconductor nanoparticles have attracted wide attention because of their special optical and electronic properties arising from the quantum confinement of electrons and large surface area. Nanoparticles of ZnS have been extensively studied due to their potential applications such as field-effect transistors, light emitting diodes, photocatalysts and biological sensors.\textsuperscript{19} PbS is an important semiconductor material with a narrow band gap (0.41 eV) and large exciton Bohr radius (18 nm).\textsuperscript{20} The strong quantum confinement effect exhibited by PbS nanoparticles has led to their potential application as IR detector.\textsuperscript{21} PbS nanoparticles have also been used in optical devices such as optical switches due to their nonlinear optical properties.\textsuperscript{22} SnS possesses nearly ideal solar control characteristics.\textsuperscript{23} Green CuS (covellose) shows a metal-like electrical conductivity down to the liquid-helium temperature.\textsuperscript{24}

Sulfide pillared clays can be produced by combining MMTs with metal sulfides; however, they have received only limited attention so far. These nanohybrids are promising materials for important industrial applications. Iron sulfide pillared clay successfully removes nickel and vanadium from heavy crude oil during demetallization,\textsuperscript{25} while a chromium sulfide-pillared clay is a suitable catalyst for thiophene hydrodesulfurization.\textsuperscript{26} Han \textit{et al.} reported recently straightforward wet-chemical routes for the preparation of nanohybrids of montmorillonite and CdS\textsuperscript{27} or other layered silicates and various metal sulfide species including cobalt, nickel, zinc and lead sulfides.\textsuperscript{28} The semiconducting properties of metal sulfides make these clay-sulfide hybrids promising visible-light photocatalysts for producing hydrogen from water, particularly as the photocatalytic performance of CdS in layered-composites is better than its performance alone.\textsuperscript{29} Consequently, further investigation of the properties of nanohybrids made from layered silicates and metal sulfide semiconductors is needed.

The aim of this work was synthesis of ZnS and PbS nanoparticles by gas–solid reaction in the confined interlayer gallery space of two montmorillonites and characterization of the resulting hybrid materials by a set of physico-chemical methods.

2. Experimental

Sodium chloride NaCl, zinc chloride ZnCl\textsubscript{2}, lead nitrate Pb(NO\textsubscript{3})\textsubscript{2} and sulfane H\textsubscript{2}S (cylinder), were all of analytical purity and supplied by Aldrich.

Materials

The montmorillonites were separated from two bentonites—from the deposit Ješový Potok (Slovak Republic) and from SWy-2, a Wyoming bentonite obtained from the Source Clay Minerals Repository of the Clay Minerals Society at Purdue University, IN (USA). The <2 μm fractions were separated by sedimentation in order to remove most of the accessory minerals. In the course of this process, the samples were repeatedly saturated with a NaCl solution to obtain Na\textsuperscript{+}-MMTs.

The metal cation-exchanged forms (M\textsuperscript{2+}-MMT) were prepared from the Na\textsuperscript{+} forms via multiple overnight saturation with 1 mol dm\textsuperscript{-3} ZnCl\textsubscript{2} or Pb(NO\textsubscript{3})\textsubscript{2} solutions. Excess salts were removed by washing with distilled water until a negative test for chlorides with silver nitrate solution or for nitrates by conductometric analysis. The M\textsuperscript{2+}-MMTs were dried at 60 C and ground to pass a 0.2 mm sieve.

The dried M\textsuperscript{2+}-MMT samples were re-dispersed in water for 24 h under stirring and the 1 wt.% clay dispersions were purged for one hour with H\textsubscript{2}S gas from the cylinder. The metal sulfide-montmorillonite (MS-MMT) nanohybrids were recovered by centrifugation, washed with deionized water, and dried at room temperature for 24 h. Thus prepared materials are denoted hereafter ZnS-SWy, PbS-SWy, ZnS-JP and PbS-JP to indicate the sulfide formed from metal ion precursors and the MMT used. For comparison, pure PbS and ZnS were also prepared by introducing H\textsubscript{2}S gas into the metal salts solutions.

Methods

X-Ray powder diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer using Cu K\textsubscript{α} (40 kV, 40 mA, λ = 1.54178 Å) radiation and a secondary beam graphite monochromator. Diffraction patterns were collected in the 2 to 80° range in steps of 0.02° 2θ and 2 s counting time per step.

The infrared spectra were measured on a Nicolet Magna 750 FTIR spectrometer (128 scans at 4 cm\textsuperscript{-1} resolution). For the measurements in the near IR region (NIR, 11000–4000 cm\textsuperscript{-1}) the samples were analyzed by a diffuse reflectance (DRIFT) accessory ‘Collector’ from Spectra-Tech without any sample dilution in KBr. In the middle IR region (MIR, 4000–400 cm\textsuperscript{-1}) the KBr pressed disk technique (1 mg of sample and 200 mg KBr) was used. For the far IR region (FIR, 500–50 cm\textsuperscript{-1}) the spectra were obtained from polyethylene (PE) pellets (10 mg of sample and 60 mg PE). All spectra manipulations were performed using the OMNIC software package (Thermo Electron Corp.). The positions of the absorptions appearing in the spectra as inflexions or shoulders were determined by the second derivative routine.

The thermogravimetric (TG) analyses were conducted from ambient temperature up to 900 °C on a T.A.I. SDT 2960 instrument (~20 mg sample mass, heating rate 10 °C min\textsuperscript{-1}, 90 cm\textsuperscript{3} min\textsuperscript{-1} air-flow).

Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu UV-2401PC two-beam spectrophotometer in the range of 200–800 nm, at a step of 0.5 nm, using a combination of deuterium and halogen lamps. The spectra were obtained from diffuse reflectance experiments of solid pressed pellets using the Kubelka-Monk relation. The spectra have also been confirmed to be the same as those obtained from thin film transmission measurements by rubbing the samples on quartz.
The photoluminescence (PL) spectra were obtained from pressed pellets mounted in a Jobin Yvon Fluorolog 3 spectrofluorometer FL-11 employing a xenon 450W lamp and a P928P photodetector. The slits were both set at 4 nm. The photoluminescence excitation and emission spectra were corrected through the instrument-supplied files, created from compounds with known quantum yields and an included Si photodetector. All UV-Vis and PL spectra were recorded at room temperature.

The morphology and microstructures of the prepared hybrids were determined by means of SEM (Zeiss, EVO 40) equipped with an energy dispersive X-ray spectrometer (EDS). The reported results are the average values of five different region surface measurements of each sample.

3. Results and discussion

X-Ray diffraction

XRD patterns of both Na+-MMTs are shown in Fig. ESI1;† they are of a typical shape for Na+-montmorillonites. No diffractions of accessory minerals appear in the trace of Na+-JP while quartz is clearly identified in the <2 µm fraction of Na+-SWy. Its strongest diffraction appears at 26.78° 2θ and several other quartz diffractions are present as well. This is in accordance with the previously published data on the presence of quartz also in fine fractions of SWy-2 bentonite.30,31 Higher relative intensities of montmorillonite 00l diffractions in comparison with the non-basal hk diffractions in the trace of Na+-SWy (Fig. ESI1†) suggest higher preferential orientation of the montmorillonite layers in SWy than in JP. Structural formulae of both MMTs were obtained from the chemical analyses after corrections for SiO₂ bound in quartz in Na+-SWy and the remaining magnesium in Na+-JP:

Na+-SWy: M⁺0.72(Si0.72Al0.28)(Al3.12Fe0.44Mg0.44)O20(OH)4

Na+-JP: M⁺0.88(Si0.89Al0.11)(Al2.96Fe0.27Mg0.77)O20(OH)4

where M is a monovalent exchangeable cation. They show higher tetrahedral but lower octahedral and total negative charge for SWy MMT.

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<th>Table 1 Basal spacings (d₀₀₁) of prepared materials</th>
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<td><strong>Zn²⁺-JP</strong></td>
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Fig. 1 shows XRD patterns of Zn²⁺-MMTs, ZnS and ZnS-MMT samples. All significant MMT diffractions appear in the patterns of SWy and JP, indicating that the structure of MMT layers is preserved. The relative intensity of the strongest quartz diffraction in SWy can be used as internal standard for comparison of the intensities of the MMT diffractions. This approach leads to the conclusion that the (001) diffraction in the Zn²⁺-SWy trace is more intense than in the ZnS-MMT pattern. This is not surprising; the MMT layers can arrange in a parallel way more easily if only hydrated Zn²⁺ cations are present in the mineral interlayers; d₀₀₁ = ~1.25 nm for the Zn²⁺-forms. All the d₀₀₁ spacings listed in Table 1 show that these values are very similar for both Zn²⁺ and Pb²⁺-forms. This is due to the similar sizes of these hydrated cations in the interlayers. Increased d₀₀₁ values of ~1.48–1.55 nm obtained for all the MS-MMTs suggest that the MS species occur in the interlayers of the samples. Both the shape and the intensity of this diffraction indicate that the interlayer distance is more variable in ZnS-SWy than in Zn²⁺-SWy. This is probably the consequence of heterogeneous occupation at the interlayer spaces due to ZnS, occurring in the form of nanoparticles or small pillars of variable size coexisting with unreacted hydrated Zn²⁺ cations within the clay mineral galleries. Very similar trends of changes of interlayer spacings from 1.24 nm to ~1.5 nm are observed for the Zn²⁺-JP and ZnS-JP; as well as for both Pb²⁺-MMT and PbS-MMT (Table 1). Weak and broad, but noticeable, diffractions of ZnS and PbS can be distinguished in the patterns of ZnS-JP and PbS-JP, respectively (Fig. 1 and 2).

In summary, the XRD patterns of M²⁺-MMTs show 00l reflections of ~1.23–1.25 nm, similar to those reported in the literature for montmorillonites loaded with various metal cations. Formation of sulfides leads to a slight increase in d₀₀₁ spacing to ~1.5 nm, which is also comparable to the published
FTIR spectroscopy

Characterization of the initial samples. Fig. 3 presents the MIR spectra of both Na+-MMTs. The OH stretching bands (νOH) are observed at 3629 cm⁻¹ for Na+-JP and 3634 cm⁻¹ for Na+-SWy. The intense bands at 1034 (Na+-JP) and 1048 cm⁻¹ (Na+-SWy) are attributed to Si–O stretching vibrations of the tetrahedral sheets. The Al–O–Si and Si–O–Si bending bands appear near 525 and 467 cm⁻¹, respectively. A doublet at 799 and 780 cm⁻¹ confirms the presence of quartz in Na+-SWy, while a shoulder near 800 cm⁻¹ in the spectrum of Na+-JP corresponds to Si–O vibrations of amorphous silica.

The positions and the intensities of the OH bending bands (δOH) in the 950–820 cm⁻¹ region (inset in Fig. 3) reflect different chemistry of the octahedral sheets in these MMTs. The prevailing amount of Al in the octahedral positions of both montmorillonites is reflected in high intensity of the OH bending bands at 845 cm⁻¹/C0 and 847 cm⁻¹/C0 corresponding to Al(II) and substantial Mg(II) content in the octahedral sheets of Na+-JP. The spectrum of Na+-SWy shows similar intensities for δAlFeOH (886 cm⁻¹) and δAlMgOH (847 cm⁻¹) bands, i.e. Al(III) in the octahedral positions of Na+-SWy montmorillonite is substituted by similar amounts of Fe(III) and Mg (II). This is in excellent agreement with the calculated structural formulae (see above). The MIR spectra in the OH bending region reveal prevailing Mg(II) for Al(III) substitution in Na+-JP resulting in higher octahedral charge of this MMT.

Zn²⁺- and Pb²⁺-forms. The first step in synthesis of ZnS and PbS nanoparticles in the interlayer space of MMTs was preparation of their Zn²⁺- and Pb²⁺-forms. Exchange of Na+ with Zn²⁺ or Pb²⁺ cations, however, has no influence on the vibrations of OH and Si–O groups in the MIR spectra of both Na+-MMTs. The OH stretching bands (νOH) are observed at 3629 cm⁻¹ for Na+-JP and 3634 cm⁻¹ for Na+-SWy. The intense bands at 1034 (Na+-JP) and 1048 cm⁻¹ (Na+-SWy) are attributed to Si–O stretching vibrations of the tetrahedral sheets. The Al–O–Si and Si–O–Si bending bands appear near 525 and 467 cm⁻¹, respectively. A doublet at 799 and 780 cm⁻¹ confirms the presence of quartz in Na+-SWy, while a shoulder near 800 cm⁻¹ in the spectrum of Na+-JP corresponds to Si–O vibrations of amorphous silica.

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Fig. 3 MIR spectra of Na+-JP, Na+-SWy. Inset in figure: OH bending region.

Fig. 4 NIR spectra of Na+-, Pb²+-, and Zn²+-forms of JP montmorillonite.
structural OH and Si–O groups, visible in the MIR spectra, or vibrations of water molecules giving bands in the NIR region. However, changes in the MIR and NIR spectra are found neither for JP nor for SWy montmorillonite (spectra not shown). The bands present in the FIR spectra of smectites are related to the lattice and interlayer hydrated cations vibrations. However, that the bands in the FIR spectra of Na+ and Zn2+-forms of the JP and SWy samples (not shown) are in almost the same positions demonstrates that the effect of hydrated cations in smectites cannot be distinguished by FIR spectroscopy.

Fig. 5 presents the spectra of Zn2+-JP and Zn2+-SWy with Al–O–Si and Si–O–Si bending bands at 522 and 466 cm⁻¹, respectively, and two bands near 337 and 197 cm⁻¹ assigned to lattice vibrations. The spectrum of ZnS with a strong broad band at 287 cm⁻¹ is presented as well. The interaction of exchangeable Zn²⁺ cations with H₂S is supposed to produce ZnS in the MMT interlayers and on outer mineral surfaces. However, no substantial difference between the Zn²⁺-SWy and ZnS-SWy spectra is observed (Fig. 5d and e). On the other hand, the FIR spectrum of ZnS-JP clearly shows a broad shoulder in the 330–200 cm⁻¹ region, which is probably due to the absorption of ZnS species originated upon H₂S treatment (Fig. 5c). A lower amount of exchangeable cations in SWy than in JP, compensating their layer charge, means that no ZnS features can be identified in the FIR spectrum of ZnS-SWy, contrary to ZnS-JP. However, in general, it is difficult to confirm unambiguously the formation of MS particles by IR spectroscopy.

Thermal analysis

Fig. 6 shows the thermogravimetric (TG) plots of PbS, Pb²⁺-JP and PbS-JP samples. Two remarkable steps appear on the TG curve of Pb²⁺-JP. The first mass loss of 11.5% in the range of 25–150 °C is attributed to the removal of adsorbed water. The second mass loss of 3% between 600 and 900 °C is assigned to the decomposition of structural O–H groups from the MMT layers.

The TG curve of pure PbS prepared in the same way as PbS-MMT (Fig. 6) shows 22% mass increase upon heating in the 200–400 °C range caused by oxidation of sulfide to sulfate. However, the trace of PbS-JP is very similar to that of Pb²⁺-JP, dominated by mass loss due to dehydration of montmorillonite. It shows no visible feature of PbS oxidation, probably because of a too low PbS content. Total mass losses upon heating from 25 to 900 °C of Pb²⁺-JP and PbS-JP are 16.5 and 19.4%, respectively. The DTG curves (not shown), exhibit two peaks due to sulfide oxidation of pure PbS at 190 and 320 °C with 4 and 16% mass gain, whereas only one peak appears at 215 °C for PbS-JP. Thermal behaviour of the nanohybrids has been slightly altered by the PbS intercalated into the MMT host, probably with some part of the PbS nanoparticles adsorbed on the outer surfaces.

UV-Vis and photoluminescence spectroscopy

Fig. 7 shows the UV-Vis diffuse reflectance spectra of ZnS (a) and ZnS-SWy (b) obtained from measurements after gently spreading the powder sample on a DR-holder covered with pure BaSO₄, for whose reference spectra had also been obtained. All optical measurements have been performed at room temperature at which, due to the low dimensionality character of the quantum systems, the blue shift was observable. Optical measurements reveal information about the nature of

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**Fig. 5** FIR spectra of ZnS (a), Zn²⁺-JP (b), ZnS-JP (c), Zn²⁺-SWy (d) and ZnS-SWy (e).

**Fig. 6** TG plots of PbS (a), Pb²⁺-JP (b) and PbS-JP (c).

**Fig. 7** Diffuse reflectance absorption spectra of ZnS (a) and ZnS-SWy (b).
the semiconductor nanoparticles, such as the energy gap \( E_g \), the type of the quantum confinement of the electron and hole, defect/trap centers, size, and the incorporation environment. In the latter case, the effects observed are dependent on energy transfer phenomena or alteration of the optical properties due to the dielectric constant of the surrounding medium. In this way it is possible to tune the dots and the host environment for specific properties or applications. Also, it has been possible to use a variety of precursor atoms such as Se or Cd in order to further tune the position of the energy gap and the related excitonic peaks. Thus, it is necessary to first optically characterize the semiconductor properties of the quantum dots within the inert matrix and second to compare the current optical properties to those of further research works altering the dot itself or the environment. Fig. 7b shows the absorption of the ZnS-SWy sample exhibiting an absorbance onset at about 337 nm, with no other peaks in the region from 340 nm to 800 nm except from a weak shoulder near 358 nm. Also, the spectrum in Fig. 7b exhibits a distinct peak at 246 nm. The two spectra ZnS and ZnS-SWy (Fig. 7) differ in the profile and the onset position which suggests that the two samples must differ with respect to the semiconductor particle size as the only species that are absorbing strongly can only be of the form \( \text{ZnS}_{x} \). The blue shift and increasing trend of the absorbance in the ZnS-MMT are comparable to the observed result of the CdS/montmorillonite\(^{36}\) and CdS/laponite clay,\(^37\) where a blue shift was exhibited on the absorption onset when the exchanged concentration of Cd was decreased. Also, the 3D ZnS spectrum, Fig. 7a, shows an absorbance onset at 384 nm and a strong shoulder at 422 nm, in agreement with ref. 38.

The bare MMT shows extremely small light absorption ability above 300 nm, which is not shown here, and even in the case of small impurity amounts, they cannot be responsible for peaks or shoulders above 300 nm nor for the peak at 246 nm, at least with this absorption intensity. It is crucial to note that these spectra have been acquired through the Kubelka-Munk relation for thick samples and thus the thickness of the sample, especially of the MMT, plays no role in the final absorbance spectrum. It is rational that the sample contained some impurity such as ferric oxide and titania, but as these are in small quantities it is expected to have small contributions to the spectra and those should occur below 350 nm at lowered intensity peaks than the ones observed. The ZnS-SWy hybrid exhibits clearly, by comparing the noted onsets at 384 nm and 337 nm in Fig. 7, blue shift of the absorption compared to the 3D ZnS. It implies that smaller sized ZnS particles have been generated in the intergallery spaces of the clay host. The absence of a continuous absorption between the 384 nm and the 337 nm positions shows that most of the nanoparticles’ effective diameter is below a certain maximum size.

More specifically, the band gap of bulk ZnS, with no impurities, is \( \text{ca. 3.5 eV (354 nm) and 3.9 eV (317 nm)} \) for the cubic and hexagonal forms, respectively. Obviously, from comparing the XRD patterns of Fig. 2 with published powder XRD spectra, it is possible to see, as it has already been stated, that the first XRD peak at \( \text{ca. 28–29° } 20 \) that is being attributed to the nanoparticles that have formed within the mesoporous interlamellar space is identified to originate from the stable zinc blende form of ZnS, which has a band gap of 3.5 eV (354 nm) and most probably any other smaller species that is being formed is of the same symmetry. Therefore, in Fig. 7a, it is obvious that the main absorption from 354 nm and lower wavelengths is due to band gap absorption while any absorption at higher wavelengths above are due to impurities or defects that have been generated in the ZnS structure. The absorption shift in Fig. 7b to at least 337 nm denotes a blue shift of 176 meV at least for any semiconducting particles absorbing close to 337 nm. The peak at 240 nm can also be attributed to much smaller species of \( \text{ZnS}_{x} \) nanoparticles. It should be mentioned that small quantum dots do not necessarily have the 1:1 molar ratio. It is well known that metal chalogenides can form small clusters of the form \( \text{M}_{32}\text{S}_{14}\text{R}_{36}^{39} \) and thus the shoulders appearing near 300 nm or below in the spectrum of Fig. 7b could be due to different sizes of quantum dot species coexisting with small quantum wires. Also, Fig. 7b shows shoulders which are minor at 350 nm and are probably due to impurities of Zn, or S deficiencies since the molar ratio of \( \text{Zn:S} \) is not unity. In conclusion of the previous analysis of the spectra, it is expected that the nanoparticles absorbing at 337 nm, whose size as deduced by using the Brus equation\(^40\) is about 20 Å, are in the outer surfaces or at the edges of the clay platelets, while the nanoparticles that absorb at 246 nm, whose size is deduced by the same equation as \( \text{ca. 8 Å} \), have formed within the interlamellar space, not necessarily as spherical particles but with such an average size as to explain the blue shift from 354 nm to 246 nm and fitting in the same time within the platelets. In the calculation we have used electron and hole masses of 0.94\(m_0\) and 0.34\(m_0\), respectively (where \(m_0\) is the electron rest mass) and the dielectric constant of the ZnS material has been used as in ref. 16.

Fig. 8 shows the photoluminescence (PL) and photoluminescence excitation spectra (PLE) for the MS-MMT samples. The samples of MS do not show any appreciable photoluminescence. In general, PL spectra of quantum dots (QD) portray more complex phenomena than those of higher dimensionality LD semiconductor structures. Photoluminescence at room temperature provides here extra evidence about

![Fig. 8](image-url)
the energy gap and its shift with respect to the 3D compound, and the energy levels within the semiconductor energy gap. Especially, PLE spectra can confirm the nature of the emission peaks, which all extend to provide information about the atomic structure, the formation or absence of defect-free quantum dots, as well as providing basic characterization of the emission properties for applications of the QD. PL/PLE spectra also include details from possible metal ions and clarify effects that are due to the clay matrix luminescence. In particular, Fig. 8b shows that the emission spectrum of the ZnS compound, excited at 240 nm, shows a broad peak centered at 380 nm, whose extent is from 350 to 450 nm. The mechanism for the PL at this wavelength is clearly related to the band gap of ZnS at 3.5 eV, i.e. 354 nm, convoluted with defect states, all giving PL at lower than the band gap energies. On the other hand, the similar PL spectrum (Fig. 8a) of the MS-MMT sample, i.e. the clay loaded with quantum semiconducting nanoparticles, appears to have two different distinct peaks centered at 344 nm and 380 nm, while a small shoulder appears at 300 nm. It is obvious that the existence of nanoparticles within the clay is responsible for the peak at 344 nm, showing that the blue shift of luminescence is at least 340 meV, i.e. shifted from 380 nm in the 3D case to 344 nm in the 0D case. In both cases of the 3D and 0D samples, there is a Stokes shift between the PL and the absorption peaks, at least for the larger particles, which is comparable in value but depends strongly on the specific choice of wavelength onsets as the spectra at room temperature are rather broad. The mechanism of the Stokes shift is suggested to be related to the defects in the ZnS structure rather than impurities or otherwise since in both cases the Stokes shift is comparable.

A point which still needs to be clarified is the luminescence of the MS-MMT sample at 380 nm, which probably shows that a fraction of the ZnS nanoparticles is large enough, thus exhibiting luminescence at 380 nm. This fraction is obviously quite small as it does not show peaks nor strong shoulders in the UV absorption spectra. This fraction is probably related to the set of particles at the edges of the clay platelets. Possibly, the MS-MMT 380 nm peak is due to some other impurity state that only coincides with the 3D PL peak. Further, time resolved experiments could shed light on this problem, which could also explain the small shoulder in the MS-MMT PL spectrum at 420 nm. The PL of the smaller nanoparticles, which absorb at 246 nm, could be observed at either the shoulder of Fig. 8a at 300 nm, or it is emitting light via energy transfer mechanisms to larger nanoparticles and thus at lower energies. Actually the same mechanism of energy transfer, usually Förster type, could explain the strong luminescence of the MS-MMT sample at 380 nm, where all the energy is being channeled to the lower energy excited states until being emitted with the band centered at 380 nm.

The PLE spectra, as observed by the emission at 500 nm, illustrate that the 3D sample in Fig. 8c shows a peak at 360 nm after a trough at ca. 350 nm, while a similar spectrum of the nanohybrid material in Fig. 8d shows the same peak at 350 nm and the trough at ca. 330 nm. The peak at 360 nm does not coincide with the band gap of the 3D ZnS and is rather 10 nm Stokes shifted. Thus, it is quite probable that the ZnS has impurity states that are existent in the nanohybrid complex system and could be responsible for the Stokes shifting of the luminescence peak from its named band gap value and could also explain the fact that the UV absorption spectra shows shoulders at lower energies from the observed band gaps. Finally, the troughs of the PLE spectra are comparable to the UV absorption defined band gap energies and show that the PLE spectra are indeed similar to the UV absorption spectra at low wavelengths.

Similar UV absorption and luminescence spectra have been obtained for Pb loaded clays, showing blue shifts of at least 300 meV. It is rather easy to tune the final optical properties of a composite clay semiconductor material using mixed Pb/Zn loaded clay as it has been done in the case of some organic-inorganic hybrid compounds based on metal halide units.31

Microscopy and EDX

The morphology and microstructures of the pristine MS-MMT hybrids were examined by SEM and EDX analyses. Fig. 9a shows a low magnification SEM image of the ZnS-SWy, exhibiting granular morphology of flocs (grains) accompanied by a “river-like network” of non-crystalline composite materials. This morphology change may result from the coagulation process, in which the surface charge of MMT was compensated for by hydrated Zn2+ cations and protons. Hydrophilic surface of MMT became partly hydrophobic due to the presence of the sulfide nanoclusters. Upon treating Zn2+-MMT with H2S, the amount of disorder leaf-like layers increased, i.e. the ordered structure of MMT had been

![SEM images (a) and EDX pattern (b) of ZnS-SWy hybrid.](image-url)
changed and led to the formation of isolated agglomerates (domains) with a size of 20 μm, as demonstrated in Fig. 9a.

Fig. 9b shows the EDX spectrum of the Zn\(^{2+}\)-JP after H\(_2\)S treatment indicating that Zn and S are present in the final hybrid systems and the S:Zn molar ratio is ≈0.6, further confirming that ZnS has been formed. Analyses from various spots of the sample prove that the ZnS nanoparticles have homogeneously grown on the layers of MMT; no heterogeneity of the MS particles distribution has been found by this method.

It is also worth mentioning how the samples change their appearance after the H\(_2\)S treatment. Although Zn\(^{2+}\)-JP (brick yellow) and Zn\(^{2+}\)-SWy (white) hardly change colour after H\(_2\)S adsorption, they become slightly lighter, and Pb\(^{2+}\)-MMTs undergo rapid colour changes from white or yellow to dark brown to black. This supports the hypothesis that brown Pb\(_x\)S\(_y\) is formed first and then transformed to black PbS.

The amount of Zn\(^{2+}\) and Pb\(^{2+}\) cations present in the MMT was compared with the number of moles of H\(_2\)S adsorbed on the sample obtained from the EDX data. The results are collected in Table 2. The molar ratios between the sulfur and the metal (nS:nM) are, for all MS-MMTs, less than 1, suggesting partial saturation (chemical reaction) of metals ions with hydrogen sulfide. The probable reason for partial sulfidation might be the limited accessibility of the clay interlayers loaded with Zn\(^{2+}\) and Pb\(^{2+}\) cations. Due to aggregation of clay layers in the dispersion, part of the clay layers might not be accessible for H\(_2\)S. Moreover, hydrated metal cations being exposed to H\(_2\)S on the particle surfaces react preferentially followed by those in the interlayers, possibly resulting in filling of micropores and formation of large metal sulfide clusters. Due to steric hindrance of the formed sulfide nanoparticles, H\(_2\)S cannot reach the remaining unreacted metal cations to form more MS and these cations became unavailable for ion exchange, as is confirmed by unchanged M\(^{2+}\) content (EDX data) before and after the reaction with H\(_2\)S.

The results described above allow proposal of the mechanism for H\(_2\)S immobilization on metal-doped MMT based on acid–base reactions. In the first step, H\(_2\)S is adsorbed on the sample surface through reaction of hydrated M\(^{n+}\) acting as a Lewis acid toward the base HS\(^-\) and H\(^+\) with H\(_2\)O composing the other acid–base pair:

\[
\text{M}^{n+} + \text{H}_2\text{O}_{\text{m}}^\text{m} + \text{H}_2\text{S} \rightarrow \text{MS}_{\text{n}(\text{n}/2)} + \text{H}_2\text{O}_{\text{m} - 2} + 2 \text{H}_2\text{O}^+ 
\]

The H\(_2\)O\(^+\) formed during this first step causes pH decrease and probably contributes to the following flocculation of clay dispersion observed for all MS-MMTs. However, the reaction of M\(^{n+}\) with H\(_2\)S is very rapid and the formed nanoparticles become immobilized within the clay galleries and is sufficiently stable at decreased pH. The more basic surface of JP MMT due to the larger structural magnesium content may shift the reaction equilibrium by buffering of H\(_3\)O\(^+\) by-products.

4. Conclusions

A simple route for synthesizing nanoclusters (agglomerates) of metal sulfides on montmorillonite surface is reported. The synthesis includes effective ion exchange reaction with precursors (Zn\(^{2+}\), Pb\(^{2+}\)) and subsequent reaction of clay dispersion with gaseous hydrogen sulfide. Various physicochemical properties of prepared MS-MMT nanohybrids were characterized. A complex effort was made toward identification of MS species; however, only XRD data clearly demonstrated presence of a new MS phase in the galleries of MMT while EDX confirmed sulfur in the solid phase. The extent of the formation MS was ≈50% of the total M\(^{2+}\) present in the clay.

Effort has been made toward understanding the optical properties with the basic bulk semiconductor parameters. The final hybrid system has both porous and semiconducting properties, making it suitable for novel applications demanding high surface area and active optical states, which are due to low dimensional semiconductors with fast transition rates, surface character and high oscillator strength excitonic character. The latter can be tuned by means of extra surface passivation or doping of the MS active semiconductor or by tuning the chemical composition with Se, Zn, Cu, Mn. These high surface area materials are promising for chemical sensors and electroactive materials.

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