

Nanocomposite materials based on natural phyllosomorphous or/and synthetic mesostructured porous solids

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ABSTRACT:

We report in the present Ph.D. Thesis the synthesis and study of new nanocomposite materials based on natural or synthetic porous materials. The research was focused in the composition of low-dimensional (LD) semiconductor species and hybrid sorption materials. The new materials that were developed, presented enhanced or even new properties regarding equivalent three-dimensional (3D) semiconductor systems or initial porous materials. Low-dimensional structures of various semiconductor systems such as ZnS, PbI₂ and GaN were composed in the interior of the pores of MCM-41 material or in the interlayer space of organomodified or not clays. More specific a new method for the importation of ZnS nanosized particles inside the pores of MCM-41 was used by insertion of Zn²⁺ cations with melt-exchange reactions and later reaction with H₂S. The synthesis of zero-dimensional (0D) Pb_xI_y quantum dots (QD's) in the interlayer space of hectorite clay was also studied, with those QD's being organized in two-dimensional (2D) quantum layers with hexamethyldiamine addition independently from the concentration and the synthesis route. Moreover one-dimensional (1D) Pb_xI_y quantum wires were synthesized in the interlayer space of montmorillonite organomodified clays creating hybrid semiconductor systems. Low-dimensional GaN species were also developed at low temperatures in the interior of MCM-41 pores with two different methodologies. In the first of them the insertion of the GaN species inside the pores was achieved with the insertion of Ga³⁺ cations by ion-exchange reactions and later reaction with NH₃ at temperatures 150-450°C lower regarding already known methods, while in the

second the composition was achieved at 365°C with use of a precursor. An intense blue shift of the energy gap was observed in all semiconductor systems while excitonic peaks were also observed in the optical spectra.

The synthesis of the substance N(2-Aminoethyl)dithiocarbamate (AEDTC) was carried out for the growth of new hybrid sorption materials. The molecule has a (-CS₂) group that binds strongly heavy metals and in addition has a small enough size so that it doesn't fill the MCM-41 pores decreasing his specific surface area or prevents the insertion of heavy metals in the interlayer space of clays. The AEDTC molecules were later inserted in the MCM-41 pores and in the interlayer space of montmorillonite clay. In the case of MCM-41, the new hybrid materials showed enhanced sorption abilities for various heavy metals up to 237% at physiologic pH values (pH = 7) regarding their initial materials. However the hybrid materials showed no improvement in binding Cd²⁺. This as it was predicted from the theoretical Surface Complexation Model (SCM) and the probable mechanism of the metal binding on the materials is owed in stereochemical hindrance from the hydrated Cd²⁺ cations. These results were confirmed by competitive adsorptions of heavy metals and EPR measurements. In the case of montmorillonite, the final hybrid materials showed also enhanced sorption abilities for various heavy metals up to 434% at physiologic pH values (pH = 7) regarding their initial materials. This improvement is comparatively bigger than this reported of analogous materials in recent published works.

The final new nanocomposite materials at both the low-dimensional semiconductor systems and the hybrid sorption materials showed new optical or enhanced sorption abilities in correspondence, while simultaneously they maintained the porous character of their initial materials. These results are encouraging for the use of these materials in analogous applications as well as for further study of those or growth of other materials with analogous properties.