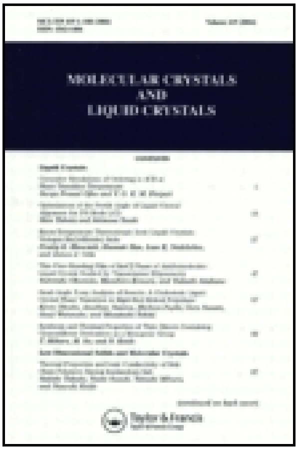

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# Preparation of Transition Metal and Semiconductor Nanocrystallites in the Interlayered Space of Clay Minerals

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# Preparation of Transition Metal and Semiconductor Nanocrystallites in the Interlayer Space of Clay Minerals

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Pd and CdS nanoparticles have been *in situ* generated in the adsorption layers of hexadecylammonium montmorillonite (HDAM) and hexadecylpyridinium montmorillonite (HDPM) clay organo-complexes. The clay intercalated Pd and CdS materials may find applications as catalysts and semiconductors, respectively. Information on the structure of clay intercalated nanoparticles have been obtained from X-ray diffraction and small angle X-ray scattering measurements.

Keywords: adsorption from solution, nanoparticles, clay organo-complexes, intercalation, X-ray diffraction, small angle X-ray scattering.

## INTRODUCTION

The synthesis and application of nanocrystalline materials including metals and semiconductors have received considerable attention in the past few years[1,2]. In addition to classical preparation methods [3,4], alternative techniques have been developed more recently[5,6]. The present study reports on a novel synthetic route for the generation of metal and semiconductor nanoparticles in the interlayer space of surfactant-modified montmorillonites (clay organo-complexes).

## EXPERIMENTAL

Hexadecylammonium montmorillonite (HDAM) and hexadecylpyridinium montmorillonite (HDPM) were prepared by cation-exchange reaction between Na-montmorillonite and the corresponding alkylammoniumbromides[6,7]. $Pd(OAc)_2$ and $Cd(OAc)_2$ precursors were ABCR chemicals. The solvents were distilled before use. $H_2S$ was prepared from FeS and HCl in a Kipp apparatus.

The adsorption excess isotherms of ethanol-toluene/HDAM and ethanol-cyclohexane/HDPM were determined at 298 K by the immersion method [8].

X-Ray diffraction (XRD) investigations were performed with a Philips 1820 diffractometer (Cu $K_\alpha$ radiation, $\lambda = 0.154$ nm).

Pd nanoparticles were prepared by the addition of $Pd(OAc)_2$ in toluene solution to HDAM suspended in an ethanol:toluene = 5:95 mixture[7].

CdS nanocrystallites were formed via addition of the ethanolic solutions of $Cd(OAc)_2$ to HDPM suspended in a liquid mixture of ethanol:cyclohexane = 5:95, followed by injection of the appropriate amounts of $H_2S$[6].

The metal contents of Pd-HDAM and CdS-HDPM samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) by a Jobin Yvon 24 sequential ICP-AES spectrometer.

Small Angle X-Ray Scattering (SAXS) measurements were effected with a compact Kratky Camera (Anton Paar) operated at 50 kV and 40 mA. The scattered X-ray intensities were analysed to obtain the $K_p$ Porod constants, $l_c$ correlation lengths and $R_G$ radii of gyration of the intercalated particles[9].

## RESULTS AND DISCUSSION

The liquid sorption and X-ray diffraction measurements on clay organo-complexes dispersed in binary liquid mixtures indicated that the chemical environment in the adsorption layer, suitable for the formation and growth of intercalated nanoparticles from the precursors, can be controlled by the nature and the composition of the dispersion medium. The 1st component of the binary liquid mixture should be preferentially adsorbed at the clay organocomplex/liquid interface and its concentration in the bulk solution should be kept as low as possible, whereas the 2nd component is expected to be present mainly in the bulk solution. In mole fraction terms, $x_1^s >> x_1$ and $x_1 << x_2 \cong 1$, where $x_i^s$ and $x_i$ refer to the adsorption layer and the bulk liquid phase, respectively. Furthermore, the precursors of either Pd or CdS particles should be predominantly present in the adsorption layer rich in component 1. In this way, particle fomation in the bulk solution is eliminated or minimized.

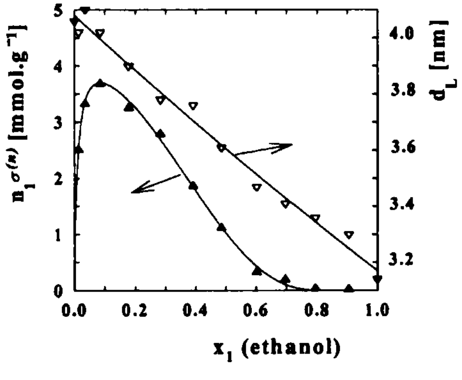

FIGURE 1 Adsorption excess isotherm and basal spacings in ethanol-toluene/HDAM suspension at 298 K.

For the generation of Pd nanoparticles, the 1st component of the liquid mixture was ethanol, which is a good solvent and a reducing agent of the precursor $Pd(OAc)_2$. The adsorption excess amount $n_1^{\sigma(n)}$ and the basal spacing $d_L$ for the system ethanol-toluene/HDAM are plotted against $x_1$ in Figure 1.

The thickness and the composition of the adsorption layer can be calculated from a combination of XRD data with the adsorption isotherm. For example, a quantitative analysis of the functions in Figure 1 yielded $x_1^s = 0.5$ at $x_1 = 0.07$ with $d_L = 4$ nm[7]. Under these conditions, the selective sorption of ethanol in the adsorption layer of the swollen organoclay ensured that $Pd^{2+}$ reduction occured exclusively in the interlamellar space of HDAM.

A similar observation was made for the formation of CdS in HDPM. The lowest ethanol concentration ($x_1 = 0.05$) afforded the highest $Cd^{2+}$ concentration in the interlamellar space of HDPM, as shown in Figure 2. In this case, CdS formation was restricted to the interlamellar space.

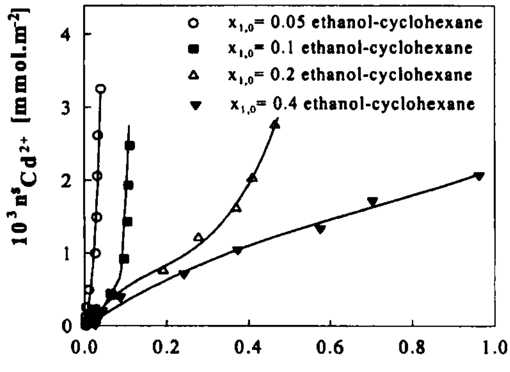

FIGURE 2 The adsorbed amount of $Cd^{2+}$ as a function of $Cd^{2+}$ concentration in the bulk phase.

The mechanism of the formation of CdS nanoparticles in the adsorption layer of HDPM is illustrated in schematic Figure 3.

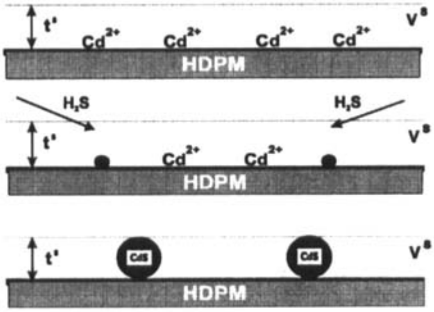

FIGURE 3. Generation of CdS nanoparticles in the interfacial layer of HDPM, in a mixture of ethanol:cyclohexane = 5:95.

Tables 1 and 2 summarize the characteristic data obtained for Pd/HDAM and CdS/HDPM. For both materials, nanoparticle formation took place in the interlamellar space without any appreciable aggregation in the bulk liquid phase. The structure of Pd/HDAM and CdS/HDPM is stabilized by adhesion forces which prevent leaching out of the intercalated particles.

TABLE 1 Characterization of Pd/HDAM samples

| Pd wt (%) | $K_p$ (cps.nm$^{-3}$) | $l_c$ (nm) | $d_{TEM}$ (nm) |
|---|---|---|---|
| 2.5 | 4.8 | 6.59 | 3.5 |
| 3.9 | 19.6 | 7.09 | 6.3 |
| 7.1 | 24.0 | 7.25 | 10.4 |
| 10.9 | 31.9 | 7.30 | 12.8 |

TABLE 2 Characterization of CdS/HDPM samples

| CdS wt (%) | $d_L$ (nm) | $R_G$ (nm) | $d_{SAXS}$ (nm) |
|---|---|---|---|
| - | 4.21 | - | - |
| 0.092 | 4.14 | 8.0 | 20.6 |
| 0.92 | 3.85 | 9.0 | 23.2 |
| 9.2 | 3.98 | 10.4 | 26.8 |

The analysis of the XRD and SAXS data led us to the conclusion that a regular intercalation of the particles is unlikely to occur. We propose that the Pd and CdS nanocrystallites occupy clay particle defect sites. Intercalated Pd and CdS may find applications as catalysts and semiconductors, respectively. However, the method of preparation presented in this work can be extended to different sorts of clays and nanocrystallites.

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