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Copper sulfide nanoparticles are prepared *in situ* using a 3D organic layered crystal of tetrahalos of bis(n-alkylammonium) as template by its reaction with H_2S gas. Under suitable reaction conditions, these quantum dots may be organized automatically to an ordered pattern.

Keywords semiconductor nanoparticle; template; layered crystal

INTRODUCTION

Chemists are contributing increasingly to the synthesis and characteriza-tion of advanced materials with desired mechanical, optical, electro-optical and magnetic properties. Among them, *in situ* generation and assembling of nanoparticles within or at the interfaces of templates is at present under vigorous investigation to attain control over their size and shape and to arrange them in ordered or structured systems. [1-3]

In this report, we introduce a novel and interesting approach using a

3D layered crystal of copper tetrahalos of bis(n-alkylammonium) (Abbr. C_nCuCl, n =10, 12, 14, 16 and 18) as template to prepare semiconductor nanoparticles *in situ* by a gas-solid reaction. Under suitable reaction conditions, they may be organized automatically to an ordered pattern.

EXPERIMENTAL

Chemicals and samples preparation are the same as described previously.[4-5] The sulfides are produced by exposing the templates to H_2S gas at room temperature. UV-visible spectra are measured by a HP-8453 diode array spectrophotometer. The formed nanoparticles are observed by TEM in a JEOL 1200 EXII electron microscope.

RESULTS AND DISCUSSION

Within the crystal used, the nearly separate inorganic $CuCl_4^{2-}$ sheets are sandwiched between two hydrocarbon layers and the separation of these sheets is determined by the width of the alkylammonium bilayer. These layered compounds provide appropriate matrices for the preparation of nanoparticles of chalco-genides by *in situ* reaction with H_2S.

The generation of the copper sulfide nanoparticles is confirmed by UV-visible spectra and TEM images. Two distinct exciton absorption bands for thin films of crystalline C_nCuCl (Figure 1A) gradually disappear during reaction with H_2S gas. After completion of reaction, the spectra exhibit only monotonously increasing extinction in the UV side (Figure 1B), similar to that of a copper sulfide particulate film.[6] Comparing the absorption onsets in Figure 1B with those reported by Engelken *et al.*[7], we tentatively assign the spectra to copper sulfide,

Cu_xS, with x between 1.6 and 1.8. The apparent blue-shifted absorption onset (from ~1000 to 700 nm), if interpreted as a size quantization effect. suggests the presence of nanoscale particles in the 3D organic crystal.

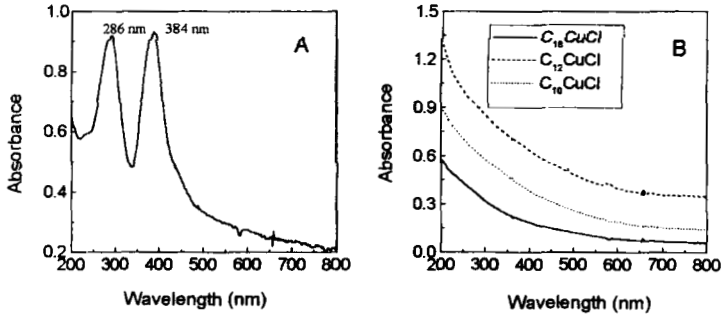

FIGURE1 UV-vis spectra for (A) crystal film of $C_{10}CuCl$ and (B)three crystal films after reaction with H_2S.

TEM exhibits more direct evidence of the particle formation. Figure 2A shows spherical Cu_xS nanoparticles formed *in situ* in the thin $C_{10}CuCl$ film, corresponding to particle mean diameters of 4.6 ± 1.4 nm.

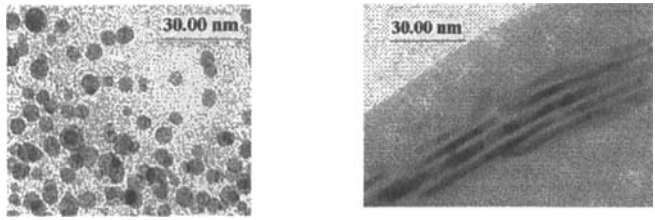

FIGURE 2 TEM images for Cu_xS particles formed in the thin $C_{10}CuCl$ film.

FT-IR and X-ray diffraction (XRD) results indicate that the particle formation does not influence much the overall structure of the organic

molecules in the layered crystal, though local deformations are unavoidable. The Bragg peaks are kept with only little position shift due to the increase by several angstroms of the lattice spacing after reaction.

We have also observed that these particles can be self-assembled to ordered arrays. In one of the TEM images obtained from particles extracted from crystal after reaction, we find nanowires formed in some regions of grid (Figure 2B). The dimensions of them, estimated from the image, range from 2.2~3.2 nm in diameter and 60~74 nm long.

It is plausible that the H_2S penetrates preferentially alone the layers in the alkylammonium crystal, retaining the full structure of alkyl-ammonium chloride as confirmed by FT-IR measurements. Similarly, the motion of the copper ions is expected to proceed laterally. Such motion in the limited 2D inorganic space makes formed particles probable to be arranged into linear organized arrays.

Therefore, it can be expected, from a more detailed mechanism study of such reaction, we can better control the assembly of the particles to construct novel nanostructured material.

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