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In Situ Fabrication of ZnS Semiconductor Nanoparticles in Layered Organic-inorganic Solid Template

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Abstract: Ordered ZnS semiconductor nanoparticles were *in situ* synthesized in metal halide perovskite organic/inorganic layered hybrids $(C_nH_{2n+1}NH_3)_2ZnCl_4$ (n=10 and 12) by reaction of their spin-casting films with H_2S gas. Transmission electron microscopy, UV-vis spectroscopy and small-angle X-ray diffraction were used to characterize the morphology and the structure of formed nanoparticles. Obtained results indicate an effective way to incorporate functional inorganic nanoparticles into structured organic matrices.

Keywords: Layered solid template, *in situ* fabrication, ZnS, nanoparticles.

Semiconductor nanoparticles have been widely investigated because of their size-dependent electronic and optical properties and their potential applications in electronic and optoelectronic devices[1~3]. Among them, much research interest has been stimulated for ZnS due to its commercial use as phosphor and electroluminescent devices[1, 2]. Many aqueous synthesis routes have been adopted to fabricate ZnS nanoparticles[1, 4] while there are also a few attempts to produce ZnS nanoparticles from solid template, like Langmuir-Blodgett films of metal alkanoates[5]. In this paper, we report the *in situ* preparation of layer-distributed ZnS nanoparticles by using metal halide organic-inorganic perovskites as templates. The rigid perovskite structure will be self-assembled after spin-casting and the layered structure will be kept after the formation of semiconductor nanoparticles. Such a nanoparticle-doped perovskite structure forms a stable exciton with large binding energy and may exhibit attractive properties owing to their low-dimensional semicon-ductor structures[6].

The $(C_nH_{2n+1}NH_3)_2ZnCl_4$ crystals (n=10 and 12, which can be abbreviated as $C_{10}ZnCl$ and $C_{12}ZnCl$ respectively) were synthesized in the same way as previous work[7]. ZnS nanoparticles were *in situ* fabricated inside $C_{10}ZnCl$ and $C_{12}ZnCl$ crystals by the reaction of their spin-casting films with H_2S gas. The nanoparticles morphology was observed by transmission electron microscopy (TEM) (JEM-100 CXⅡ, accelerating voltage =100 kV). Samples for TEM measurements were prepared according to ref.7.

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A drop of the ethanol solution of C_nZnCl was placed in a holey carbon film supported by a 300 mesh copper grid. After the evaporation of the solvent, the sample-covered grid was exposed to H_2S gas to form the sulfide. UV-visible absorption spectra were recorded by a HP 8453A diode array spectrophotometer. The small-angle X-ray diffraction (SAXD) patterns were measured using a Rigaku D/Max-γ X-ray diffractometer (CuKα λ = 0.154 nm).

The TEM images of ZnS semiconductor nanoparticles were shown in **Figure 1**. Spherical or disc-like nanoparticles with average diameters of 50 nm in $C_{10}ZnCl$ and 60 nm in $C_{12}ZnCl$ were formed. They were linked to each other in some way. A little larger nanoparticles formed in $C_{12}ZnCl$ can be attributed to more rigid and compact structure of $C_{12}ZnCl$ due to its long alkyl chains[7]. During the reaction process, more compact packing resulted in slower rates for the diffuse of H_2S molecules along inorganic layer and nucleation of particles, which made the formed particles larger in $C_{12}ZnCl$ compared to $C_{10}ZnCl$.

Figure 1 TEM images of ZnS nanoparticles formed in $C_{10}ZnCl$ (A) and in $C_{12}ZnCl$ (B)perovskite templates

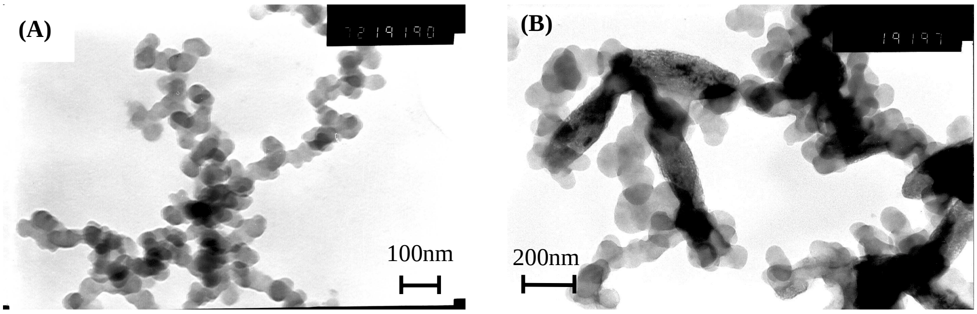

Figure 2 UV-visible absorption spectra of $C_{10}ZnCl$ spin-casting film before and after reaction with H_2S

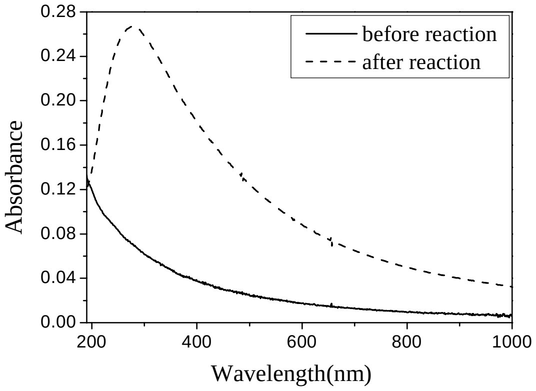

Figure 3 SAXD of $ZnCl_2$-based layered perovskite ($C_{12}ZnCl$) spin-casting film before and after the reaction with H_2S

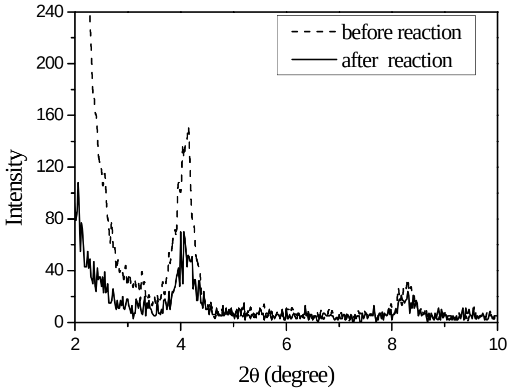

Figure 2 shows the UV-vis spectra of the thin films of $C_{10}ZnCl$ recorded before and after its reaction with H_2S gas. Compared to the regular smooth curve before reaction, a sharp absorption peak at 279 nm appeared in the spectra for the reacted film. The 61 nm blue-shift of the absorption peak comparing to that of bulk ZnS, further confirmed the formation of ZnS particles[4].

In **Figure 3**, small-angle X-ray diffraction patterns before and after reaction were compared for the film of $C_{12}ZnCl$. We can see that the layered template structure was kept after the reaction, with little change in the interlamellar spacing. But the intensity of the peak was reduced after reaction, which indicated the deteriorated order and local defects in the layered hybrid[8]. Based on SAXD measurements and considering the smaller interlayer space of our templates, we supposed that disc-like nanoparticles were formed and distributed between the organic amine layers, similar to the situation having been confirmed in alkanoate multilayers [9].

In conclusion, we have exhibited an effective way of incorporating functional inorganic nanoparticles into structured organic matrices through a gas-solid reaction. Such inorganic/organic hybrid materials should be of potential applications in the area of optoelectronic devices.

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References

1. N. I. Kovtyukhova, E. V. Buzaneva, C. C. Waraksa, B. R. Martin, T. E. Mallouk, *Chem. Mater.*, **2000**, *12*, 383.
2. K. Sooklal, B. S. Collum, S. M. Angel, C. J. Murphy, *J. Phys. Chem.*, **1996**, *100*, 4551.
3. A. Samokhvalov, M. Berfeld, M. Lahav, R. Naaman, E. Rabani, *J. Phys. Chem.* B, **2000**, *104* (36), 8631.
4. J. Nanda, S. Sapra, D. D. Sarma, *Chem. Mater*., **2000**, *12*, 1018.

5. L. L. Sveshnikova, S. M. Repinsky, A. K. Gutakovskv, A. G. Milekhin, L. D. Pokrovsky, *Chemistry for Sustainable Development*, **2000**, *8*, 73.
6. M. Era, S. Oka, *Thin Solid Films*, **2000**, *376*, 232.
7. W. Wang, X. Chen, S. Efrima, *Chem. Mater.*, **1999**, *11*, 1883.
8. L. Konopny, M. Berfeld, R. Popovitz-Biro, I. Weissbuch, L. Leiserowitz, M. Lahav, *Adv. Mater.*, 2001, *13* (8), 580.
9. M. Berfeld, A. Samokhvalov, R. Naaman, M. Lahav, *Adv. Mater.*, 2001, *13* (8), 584.

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