

Synthesis and Characterization of PMMA/ZnS Micro-Nanocomposite Spheres†

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In this study, PMMA/ZnS micro-nanocomposite spheres were successfully synthesized by precipitation method using self-made poly methyl methacrylate (PMMA) particles as the core template. The effects of different reaction conditions on the morphology and structure of the synthesized particles were studied and characterized by scanning electron microscope, X-ray diffraction and energy dispersive spectrometer. The results indicated that PMMA/ZnS micro-nanocomposite spheres were optimally prepared by pretreating at 50 °C for 6 h. The morphology and the amount of ZnS on the surface of the as-prepared spheres could be controlled by prolonging pretreatment time, reaction temperature, changing material ratio, *etc.*

Keywords: PMMA/ZnS micro-nanocomposite spheres, Precipitation method, Morphology, Crystals.

INTRODUCTION

Micro-nanocomposites with core/shell structures have attracted attention to scientists due to their unique properties in optical devices, sensors, molecular recognition and other fields^{1,2}. A key challenge to apply this type of novel micro-nanocomposites is developing abilities to control the morphology, size and property of the core/shell structures. Meanwhile, semiconductor nanoparticles have been actively investigated in the composite areas³. As a promising direct band gap II-VI semiconductor, ZnS plays an important role in photo-sensitive materials. Combining ZnS and organic polymer can provide the possibility to avoid agglomeration of ZnS nanocrystals and obtain compositions of functionalities⁴. The researches⁵⁻⁷ on the PMMA/ZnS composites were reported recently, *e.g.*, Agrawal *et al.*⁶ studied the thermal stability of PMMA/ZnS nanocomposites and have shown that the thermal stability of these nanocomposites was higher than other composites. Herein, a simple method of preparing the novel particles of PMMA/ZnS with PMMA microspheres as template were presented and the various factors on the novel particles' size, structure and morphology were studied.

EXPERIMENTAL

Synthesis of micro-nanocomposite spheres: Monodisperse PMMA microspheres with the size of 800 nm were

obtained by dispersion polymerization. Poly methyl methacrylate microspheres with carboxyl surface were modified by acrylic acid (AA) through soap-free emulsion polymerization⁸. PMMA/ZnS micro-nanocomposite spheres were prepared by precipitation method. Firstly, 0.2 g prepared PMMA microspheres were completely dispersed by ultrasonic oscillation in 100 mL of mixed solution of methanol and deionized water. Aqueous ammonia was added dropwise to adjust the pH 8-10 under stirring. Secondly, a certain amount of Zn(CH₃COO)₂ and Na₂S which dissolved in deionized water was added in the above solution, respectively. Then, the simple reaction was carried out for several hours at experiment temperature.

Characterization

The morphology of the sample was characterized through SEM (JSM-7500F, JEOL, Japan) at 15.0 kV. The structure of the products was ascertained by XRD (D8 Advance, BRUKER, Germany) at 40 kV and 40 mA with a CuK_α radiation source. The EDS X-Max (OXFORD, England) was used to collect the element types with the probe area 20 mm².

RESULTS AND DISCUSSION

Effect of pretreatment time: Fig. 1 showed the amount of ZnS aggregations formed on the surface of PMMA microspheres which pretreated by aqueous ammonia for three

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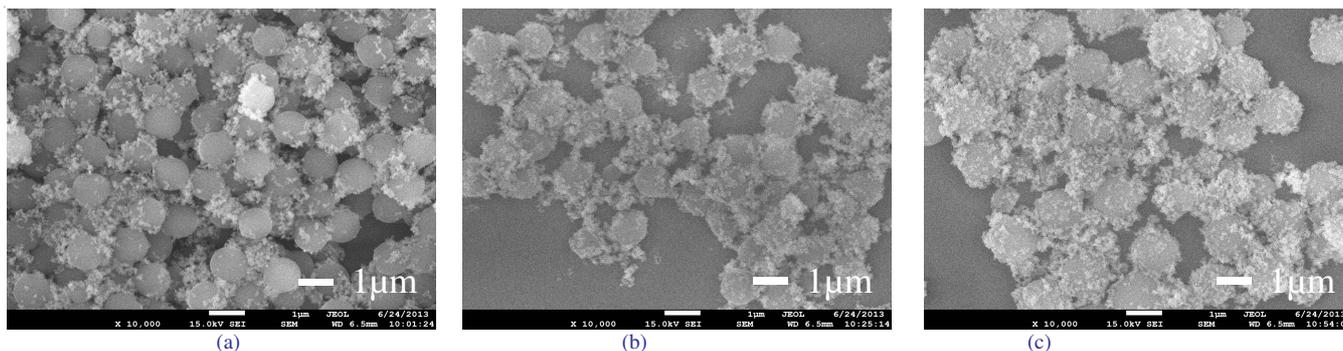


Fig. 1. SEM images of PMMA/ZnS micro-nanospheres at different pretreatment time of (a) 2 h, (b) 4 h and (c) 6 h

different time. With the pretreatment time prolonging, the interaction between ammonium ion and PMMA microspheres became fuller. On the one hand, the surface tension of PMMA microspheres can be reduced and the particles will disperse more uniformly and stably in the solution. On the other hand, the introduction of nitrogen contained ion on the surface of the core can improve the ability of microspheres ligand to metal ions. Zn^{2+} tended to bind on the core surface effectively and the shell structure could be constructed by ZnS aggregates through self-assembling.

Effect of reaction temperature: PMMA/ZnS micro-nanocomposite spheres were synthesized under different reaction temperature from 40 to 60 °C. The morphology of spheres was showed in Fig. 2. A portion of ZnS coated on the surface of the PMMA core, but the situation of the ZnS shell was uneven when the reaction temperature was 40 °C. When heated up to 50 °C, the core-shell structure was observed

clearly. ZnS aggregates were coated more closely and dispersed independent ZnS nanocrystals were very few. However, with increasing temperature, the size of ZnS crystals became larger and the surface of the spheres gone into rough.

Effect of the mass ratio of PMMA/Zn(CH₃COO)₂: The mass ratio of PMMA/Zn(CH₃COO)₂ was 2:1, 1:1 and 1:2, respectively. The morphology of spheres synthesized with different ratio was presented in Fig. 3. It was obvious in Fig. 3g that ZnS assembled uniformly as shell layer and preserved perfect shape, even though the addition of ZnAc₂ was the least. The microspheres in Fig. 3h were closely coated with massive ZnS aggregates. In Fig. 3i, the ZnS aggregates became larger with increasing the addition of Zn(CH₃COO)₂ and different from the others obviously. Finally, ZnS coated on the core surface as an indefinite form and tended to form mixed crystalline including α -ZnS hexagonal crystal and β -ZnS cubic crystal.

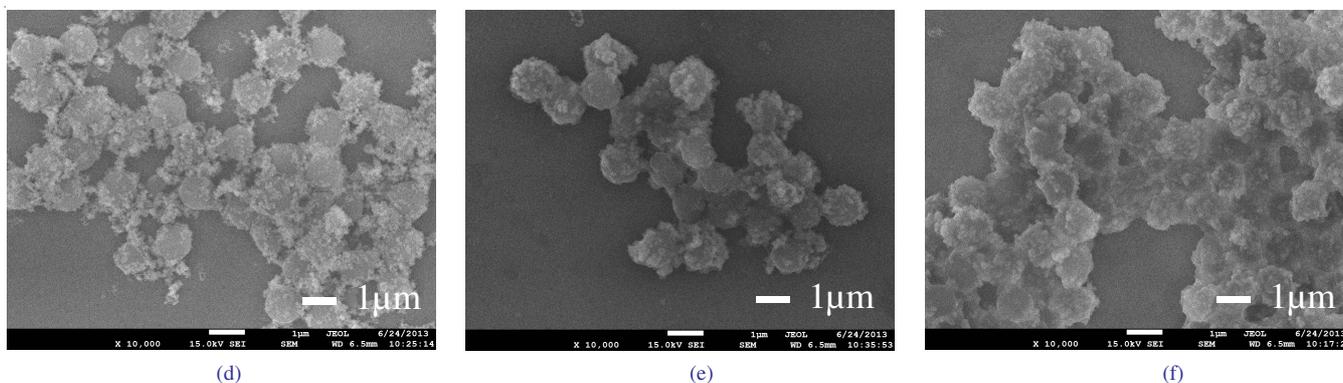


Fig. 2. SEM images of PMMA/ZnS micro-nanospheres with different reaction temperature of (d) 40 °C, (e) 50 °C and (f) 60 °C

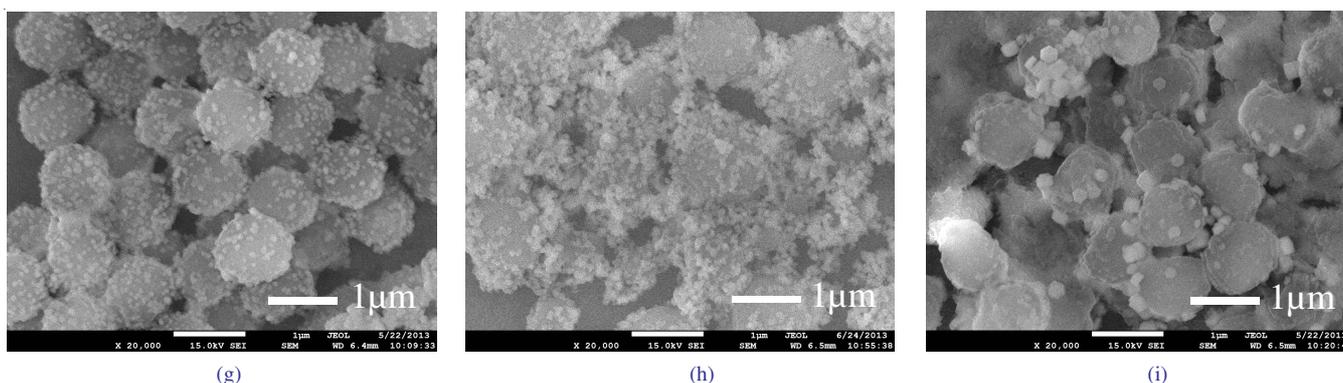


Fig. 3. SEM images of the samples with different mass ratio of PMMA/Zn(CH₃COO)₂

Effects of carboxyl groups: The surfaces of PMMA microspheres were functionalized by aqueous ammonia and introducing the rich carboxyl groups into the surfaces of microspheres. When the modified microspheres pretreated with aqueous ammonia, the carboxyl groups on surface of PMMA microspheres and nitrogen atoms ligands tended to come into being bidentate ligands through synergistic effect. The novel structure enhanced surface adsorption capacity, selective coordination ability and other effects, which made Zn^{2+} concentrated easily on the surface of the microsphere.

Elemental analysis: The elemental analysis of PMMA/ZnS micro-nanosphere samples were determined by EDS, as shown in Fig. 4. EDS analysis collected mainly information of four elements C, O, S, Zn. The elements of C and O due to the PMMA core layer, S and Zn belong to the ZnS aggregates of the shell layer.

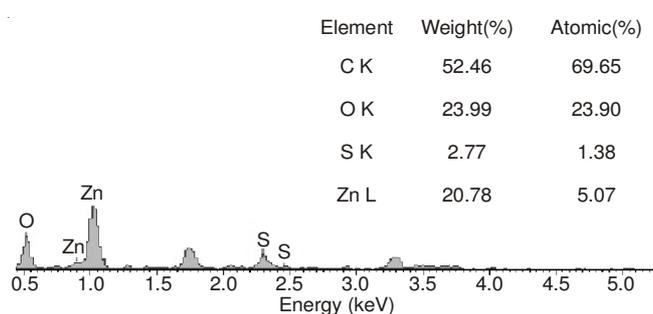


Fig. 4. EDS spectrum of PMMA/ZnS micro-nanospheres

Nanostructure analysis: XRD pattern of PMMA/ZnS micro-nanosphere was shown in Fig. 5. The presence of three intense peaks at angles 28.5, 47.9 and 56.5° corresponding to (111), (220) and (311) planes of ZnS crystals. The XRD data confirmed that the prepared ZnS aggregates belong to the structure of cubic sphalerite and the ZnS crystals had nano size. A broad peak at the diffraction angle around 13° was the characteristic diffraction peak of PMMA. Meanwhile, three diffraction peaks of the ZnS had a certain phenomenon of broadening, due to the material's characteristics of the quantum size effect, intimated that the ZnS shell was composed of small nanocrystals. The consistence of XRD phase analysis and EDS analysis results indicated that ZnS crystals with cubic structure constituted the shell layer.

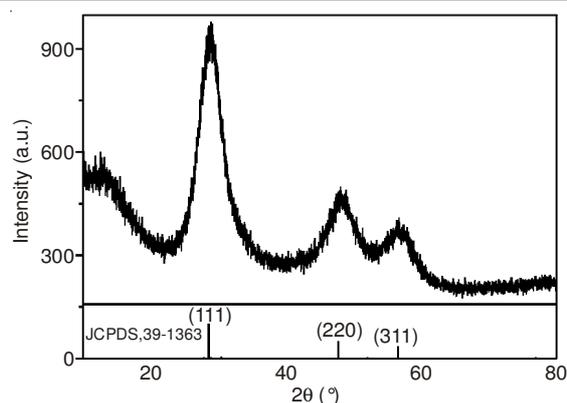


Fig. 5. XRD pattern of PMMA/ZnS micro-nanospheres

Conclusion

Pretreatment time and soluble salts added ratio had the greatest impact on the morphology of the products. Prolonging pretreatment time with aqueous ammonia can bring about complete formation of core/shell structure. The variable quantity of added zinc acetate affected the crystal structure of ZnS aggregates and some of ZnS crystals with hexagonal structure appeared when the $Zn(CH_3COO)_2$ was added with increased quantity.

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