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One-pot monomer self-assembly route to PbS/poly(methyl methacrylate) core/shell nanocomposite thin coatings

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PbS/poly(methyl methacrylate) nanocomposites with a core/shell structure have been synthesised through a monomer self-assembly route. The sample has a 25 nm diameter PbS core in a 5 nm poly(methyl methacrylate) thin sheath. The PbS content in the nanocomposites is 57 wt%.

Introduction

Composite particles, often comprised of a solid core surrounded by a well-defined shell layer, are known to exhibit unique and enhanced characteristics over single-component colloids, making them attractive for use in a wide range of applications.[1] In this field, polymer-coated particles offer interesting prospects over a broad spectrum of applications, ranging from catalysis to additives and pigments, where they are exploited in the manufacture of cosmetics, inks and paints.[2] Therefore, methods for the construction of such materials with controlled precision have long been sought.

The synthetic routes that have been developed in order to produce polymer-coated particles fall into two main classes: polymerization at the particle surface or adsorption onto the particles.[2] More recent strategies used to coat particles with polymers include monomer adsorption onto particles followed by subsequent polymerization, heterocoagulation–polymerization and emulsion polymerization. However these methods show some limitations, such as formation of a continuous film on the larger colloids, limits on the type of particle type that can fit in the membrane supports used, or aggregation of particles.[3] Recently, an alternative and remarkably adaptable approach, termed the layer-by-layer (LbL) self-assembly technique, has been applied to the coating of colloids.[4] However, the biggest limitations of the LbL strategy are that it is time-consuming and cannot be applied to non-charged species.[5]

The micellar organization of block copolymers composed of blocks with different solubility properties is well known to occur when the block copolymer is placed into a selective solvent system at an appropriate concentration.[6] Variously ordered phase morphologies, such as lamellae, double gyroids, cylinders and spheres, have been found for diblock copolymers.[7] Thus there are many self-assembly strategies which have been designed to control the growth of nanocrystals. In contrast, considerably less attention has been paid to the controlled modification of nanoparticles *via* homopolymers. In designing a process to synthesise core/shell nanocomposites, we chose poly(methyl methacrylate) (PMMA), well known as an organic glass and which has merits of good weatherability, good impact strength, good mechanical and thermal properties and good fabricability, as the thin coating. More importantly, its monomer possesses hydrophobic non-polar methyl and hydrophilic polar carbonyl groups in the methyl ester, which lead to methyl methacrylate (MMA) being able to behave as a surfactant. In a heterogeneous aqueous/non-aqueous system, methyl methacrylate could form a micelle-like structure linked together by hydrophilic groups in the aqueous solution. The driving force for self-assembly of supramolecules with a hydrophilic core and a hydrophobic sheath structure comes primarily from the enthalpic contribution of hydrogen-bonding interactions.[8] The hydrophilic inorganic reagent is restricted within the core of the supramolecules, in which nucleation and growth of nanoparticles occur. The polymerization sequence leads to the formation of polymer coatings. Consequently PMMA can be used as a template to control the growth of nanocrystallites as block copolymers. The route which comes from this procedure has been named monomer self-assembly (MSA) .

The inorganic core selected here is PbS, which is extensively used in IR photodetectors[9] and electroluminescent devices such as light-emitting diodes.[10] Here PbS nanoparticles are observed for the first time encapsulated in PMMA nanocages.

Experimental

Analytically pure MMA (5 cm^3), saturated aqueous lead acetate (2 mmol) and 2,2′-azobisisobutyronitrile (AIBN) (0.05 g) were added to a Teflon-lined stainless steel autoclave (25 cm^3) that had been filled up to 90% of its capacity with carbon disulfide. The autoclave was maintained at 100 °C for 10 h, then cooled to room temperature naturally. The gel-like masses were separated by centrifugation. The black mushy mass at the bottom was marinated and washed with distilled water five times, then dried *in vivo*. The grey-black product was triturated for consequent characterization.

The samples were characterized by powder X-ray diffraction (PXRD) patterns employing a scanning rate of $0.05^\circ\ s^{-1}$ over a 2θ range from 10 to 70° using a D/max-IIIA X-ray diffractometer equipped with graphite monochromatised CuKα radiation (λ = 1.54056 Å). IR spectra were recorded in the range 4000–400 cm^{-1} with a Nicolet Model 759 Fourier Transform Infrared (FTIR) Spectrometer, using a KBr wafer. To determine the lead sulfide content in the PMMA matrix, a sample (0.010 g) was dissolved in hydrochloric acid (analytical reagent grade; 10^{-4} m^3). The lead ion content was determined by using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Electron microscopy studies were carried out with a Hitachi Model H-800 Transmission Electron Microscope with an accelerating voltage of 200 kV. Samples

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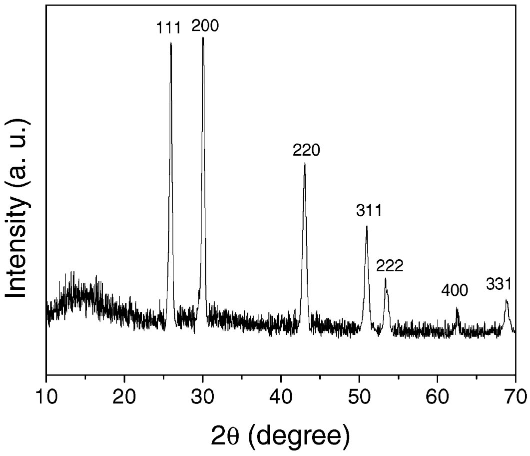

Fig. 1 XRD pattern of the product.

(the nanocomposites and pure PMMA) were prepared by adding distilled water and dispersing the amorphous particles in an ultrasonic bath. After ultrasonication, a drop of the suspension was placed on a microgrid and dried in air before observation. TEM images of the micellar-like system (prior to heating) were obtained by placing a drop of the micellar-like solution directly onto the microgrid and observing immediately.

Results and discussion

The XRD pattern of the product is shown in Fig. 1, in which all of the distinct diffraction peaks correspond to the (111), (200), (220), (311), (222), (400) and (331) reflections of PbS in its cubic phase (JCPDS Card File No. 5-592). The diameter of the lead sulfide, calculated from the half-width of the diffraction peaks using the Scherrer formula, is 35 nm. The broad upheaval around 2θ at 12–17° corresponds to the thin PMMA coating, which was confirmed by the IR spectra (Fig. 2) since that of the product is similar to the standard IR spectrum of PMMA and is totally different from that of MMA. There was no absorption peak arising from C=C. The strongest peak ($\nu_{C=O}$) at 1730 cm^{-1} and the characteristic peaks comprising two groups of double ν_{C-O} absorptions at 1240 and 1268 cm^{-1} and at 1150 and 2242.9 cm^{-1} of PMMA confirmed the polymerization of methyl methacrylate monomers under these conditions. Upon more careful examination, an extra peak was detected at 835 cm^{-1} by comparson with the PMMA absorptions. This peak was rather weak and poorly resolved due to the heavy Pb ion, and corresponds to the Pb–S bond.[11]

The lead ion content was determined using ICP-AES and the results indicated that the PbS content in the nanocomposites is 57 wt.%.

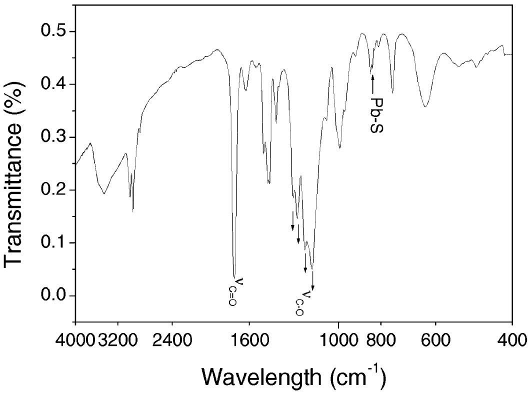

Fig. 2 IR spectrum of the product of Fig. 1.

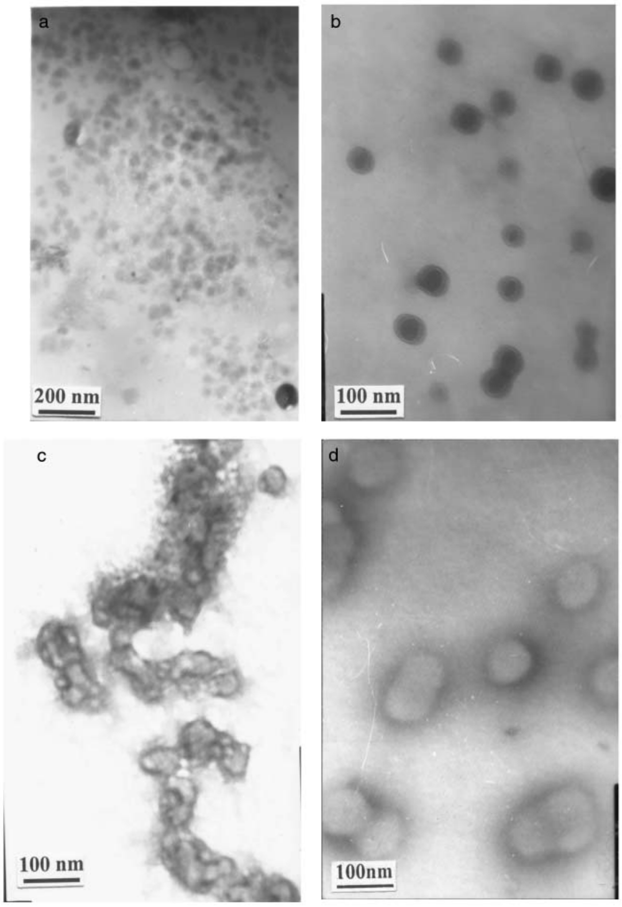

Fig. 3 (a) TEM photograph of the product of Fig. 1 with lower magnification, (b) TEM photograph of the product of Fig. 1 with higher magnification, (c) TEM image of MMA with micellar-like structure, (d) TEM image of PMMA hollow sphere.

Typical TEM images of the prepared nanocomposites are illustrated in Fig. 3(a,b). At lower magnification [Fig. 3(a)] we can see that the nanocomposites are spherical. A histogram (Fig. 4) of the size distribution of nanocomposites based on this photograph shows a distribution of particle sizes ranging from 24 to 35 nm. The average particle size calculated was 30 nm with a standard deviation of 2. Further examination of the TEM photograph with larger magnification [Fig. 3(b)] shows that the projections of the nanocomposites are two homocentric circles, indicating that the nanocomposites must be

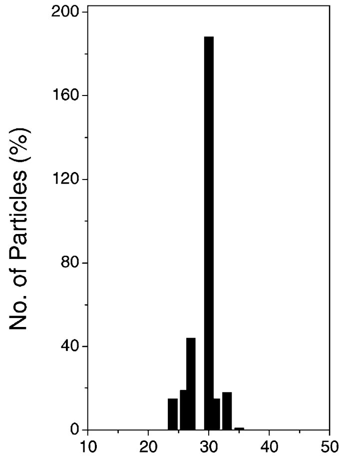

Fig. 4 Histogram of the size distribution of nanocomposites based on Fig. 3(a).

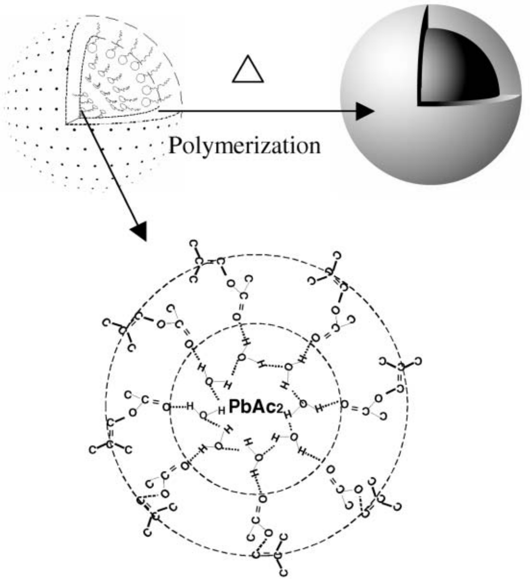

Fig. 5 Schematic representation of the product formation.

two homocentric spheres. The diameter of the PbS core in the sample is 25 nm in a 5 nm PMMA thin sheath, which is consistent with the XRD result. As predicted, the sample has a core/shell structure. In contrast, a similar system but without $Pb(MeCO_2)_2$ and CS_2 has been determined by TEM Fig. 3(c,d) which shows the images for a micellar-like system (prior to heating) and pure PMMA obtained by heating the above system at 100 °C for 10 h, respectively. From Fig. 3(c,d) one can see that the MMA monomers exhibit a micellar-like structure with a diameter of 30 nm, while PMMA exhibits a hollow sphere structure of diameter 90 nm. The larger cavity of PMMA may be caused by the expansion of PMMA while dispersing in distilled water. This results indicate the successful formation and stability of the micellar-like structure of MMA under such conditions.

In our experiment, CS_2 is both the hydrophobic solvent of the monomer and the sulfur source of the PbS. The water in the saturated aqueous $Pb(MeCO_2)_2$ and the hydrophobic CS_2 make up the heterogeneous system in which the MMA monomers form a micelle-like structure. As shown schematically in Fig. 5, the cavity of the supramolecular monomer nanocage is hydrophilic and the shell is hydrophobic. Lead acetate was retained in the hydrophilic cavity.

Here the solvothermal method is necessary for the formation of the core/shell structure. Under such violent solvothermal conditions, methyl methacrylate forms a most stable micelle-like spherical structure with the hydrophilic cavity and the hydrophobic shell providing the lowest surface energy. In addition, the reaction of $Pb(MeCO_2)_2$ with CS_2 occurs so quickly that it is initiated completely within the hydrophilic cavity rather than within the interspace of the polymer chain as observed under conditions of mild γ-irradiation.[12]

Conclusion

PbS/PMMA nanocomposites with a core/shell structure have been synthesised for the first time through an MSA route. A major feature of this procedure is the coating of nanoparticles so that they do not cause aggregation, which is a common phenomenon of nanostructured materials with extremely small dimensions and high surface energy. The MSA route offers new alternatives for the controlled synthesis of novel, stable and functional core-shell-type materials. Its simplicity and universal nature, combined with the high quality of the thin coatings, open broad perspectives for this technique in both research and industry.

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References

1 (*a*) R. A. Caruso, A. Susha and F. Caruso, *Chem. Mater.*, 2001, **13**, 400; (*b*) S. J. Oldenburg, R. D. Averitt, S. L. Westcott and N. J. Halas, *Chem. Phys. Lett.*, 1998, **288**, 243.
2 C. H. M. Hofman-Caris, *New J. Chem.*, 1994, **18**, 1087.
3 (*a*) F. Caruso, *Adv. Mater. (Weinheim, Ger.)*, 2001, **13**, 11; (*b*) R. H. Ottewill, A. B. Schofield, J. A. Waters and N. S. J. Williams, *Colloid Polym. Sci.*, 1997, **275**, 274.
4 (*a*) G. Decher, *Science*, 1997, **277**, 1232; (*b*) F. Caruso, *Chem. Eur. J.*, 2000, **6**, 413.
5 H. Y. Huang, E. E. Remsen, T. Kowalewski and K. L. Wooley, *J. Am. Chem. Soc.*, 1999, **121**, 3805.
6 (*a*) K. B. Thurmond II, T. Kowalewski and K. L. Wooley, *J. Am. Chem. Soc.*, 1996, **118**, 7239; (*b*) A. Qin, M. Tian, C. Ramireddy, S. E. Webber, P. Munk and Z. Tuzar, *Macromolecules*, 1994, **27**, 120.
7 L. Zhu, B. H. Calhoun, Q. Ge, R. P. Quirk and S. Z. D. Cheng, *Macromolecules*, 2001, **34**, 1244.
8 Y. Xie, Z. P. Qiao, M. Chen. Y. J. Zhu and Y. T. Qian, *Adv. Mater. (Weinheim, Ger.)*, 1999, **11**, 1512.
9 V. Subramanian, K. R. Murali, N. Rangarajan and A. S. Lakshmanan, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1994, **2274**, 219.
10 R. S. Kane, R. E. Cohen and R. Silbey, *Chem. Mater.*, 1996, **8**, 1919.
11 C. Ricolleau, M. Gandais, T. Gacoin and J.-P. Boilot, *J. Crystal Growth*, 1996, **16**, 769.
12 Y. Xie, Z. P. Qiao, M. Chen. Y. J. Zhu and Y. T. Qian, *Nanostruct. Mater.*, 1999, **11**, 1165.

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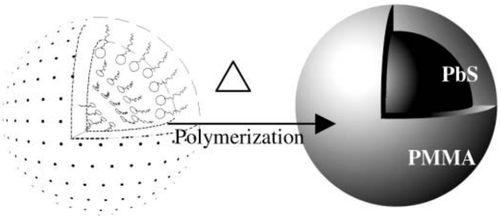

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