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Synthesis and Characterization of Ag_2S Nanocrystals in Hyperbranched Polyurethane at Room Temperature

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Ag_2S nanoparticles in hyperbranched polyurethane matrix were prepared through the *in situ* reaction with thioacetamide as the sulfur source at room temperature. Transmission electron microscopic analysis revealed a uniform spherical shape for Ag_2S nanoparticles, with an average size of about 4–10 nm and a narrow size distribution. X-ray powder diffraction and UV–vis spectroscopy were also used to characterize the obtained nanoparticles © 2002 Elsevier Science (USA)

Key Words: **nanoparticle; hyperbranched; polyurethane; thioacetamide.**

INTRODUCTION

Synthesis and characterization of semiconductor nanoparticles have attained great consideration during the past decade owing to their unique size-dependent chemical and physical properties (1–3). Many synthetic methods, which normally include arrested precipitation in homogeneous solution and synthesis in confined reaction vessels such as reverse micelles (4, 5), have been elaborated for the preparation of relatively monodispersed nanoparticles.

Recently, the application of dendrimers has opened a new way of producing nanoparticles with small size and narrow size distribution because of their unique structure and properties (6, 7). Dendrimers usually take a spherical three-dimensional structure, which is very different from linear polymers adopting a random-coil structure, so dendrimers might provide reaction sites including their interior or periphery (8). Till now, many nanoparticles synthesized in dendrimers have been reported (9–11). For example, gold nanoparticles have been prepared by reduction of $HAuCl_4$ with UV irradiation in the presence of poly(amidoamine) dendrimers (9). However, the synthetic scheme of dendrimers which have a well defined and perfectly branching structure is usually complicated. As an alternative, hyperbranched polymers can be prepared by a much easier process. Although having a less perfect structure than dendrimers, hyperbranched polymers still maintain many of the architectural features found in their more perfectly defined dendritic counterparts and are supposed to exhibit properties resembling those of dendritic ones (12). It is surprising, however, that reports on the preparation of nanoparticles in hyperbranched polymers are still limited.

Silver sulfide semiconductor, as well as other silver chalcogenides, is a good prospective photoelectric and thermoelectric material, and has been intensively studied (13). Herein, we reported the preparation of Ag_2S nanoparticles in hyperbranched polyurethane (HP) with thioacetamide as the sulfur source at room temperature. It was worth noting that, thioacetamide was usually used as sulfur source in ultraviolet irradiation (14) or hydrothermal process (15), and to the best of our knowledge, we first used thioacetamide as sulfur source at room temperature without adjusting the pH value.

EXPERIMENTAL

All the reactants and solvents were analytical grade. HP was synthesized according to Ref. (16). In a typical preparation process, 0.1 g $AgNO_3$ was dissolved in the solution of 0.5 g HP dissolved in 20 mL *N*,*N*-dimethyl formamide (DMF) under vigorous stirring. Thioacetamide (50% excessive based on $AgNO_3$) was then introduced and the solution was stirred in dark for sulfuration reaction for 3 h. The obtained black viscous solution was stable and did not precipitate within 3 months. The resulting solution was cast on a glass substrate and dried at room temperature for 12 h, then at 30°C in vacuum for 12 h. The obtained film was then washed with deionized water to remove unreacted thioacetamide before characterized.

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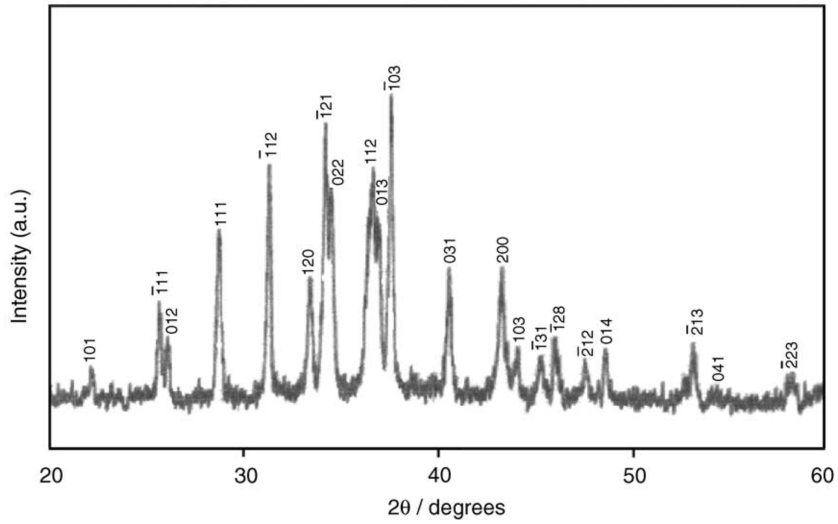

FIG. 1. XRD pattern of Ag_2S nanoparticles obtained in the presence of HP.

The X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $4^\circ\,min^{-1}$ in the 2θ range of 20–60° using a Rigaku D/max γAX-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). Average particle sizes of Ag_2S nanoparticles obtained were determined from several negative films (approximately 100 particles) taken using a transmission electron microscope (Hitachi S-530). The samples were prepared by mounting a drop of the resulting solution on carbon-coated Cu grids and allowed to dry in air. Ultraviolet–visible (UV–vis) spectra were measured on a Perkin-Elmer Lambda 20 UV–vis spectrophotometer.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 showed the typical XRD patterns of the obtained samples. All the diffraction peaks could be indexed to β-Ag_2S phase with cell constants $a_0 = 4.3$ Å, $b_0 = 6.9$ Å, $c_0 = 7.9$ Å. The values were close to those in the JCPDS card (card No. 14-72). The average crystalline size, which was determined from the half-width of the diffraction using the Debye–Scherrer equation, was approximately 6 nm.

TEM Analysis

Figure 2 (a) showed the transmission electron microscope (TEM) micrograph of the Ag_2S nanoparticles obtained in HP. The β-Ag_2S particles in HP consisted of uniform spherical particles, with sizes of about 4–10 nm, which was consistent with XRD results, indicating that almost no aggregation of Ag_2S particles happened. Furthermore, as could be seen from the particle size distribution graph (Fig. 3), the diameter of more than 65% particles was in the range of 4–8 nm, indicating the

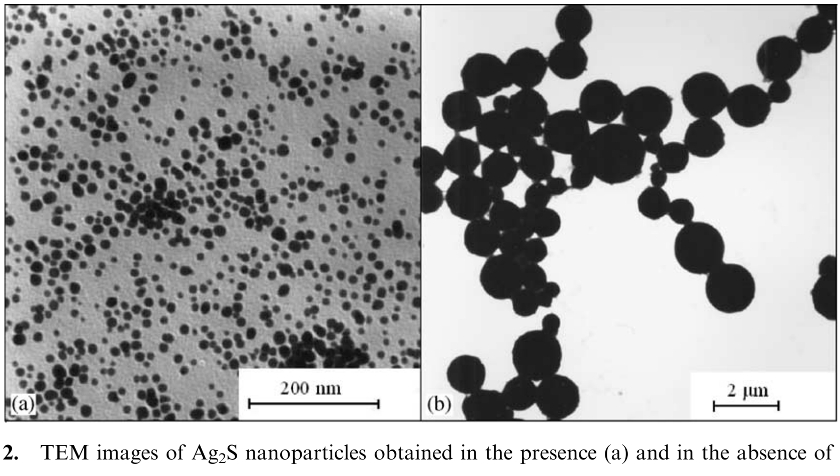

FIG. 2. TEM images of Ag_2S nanoparticles obtained in the presence (a) and in the absence of HP (b).

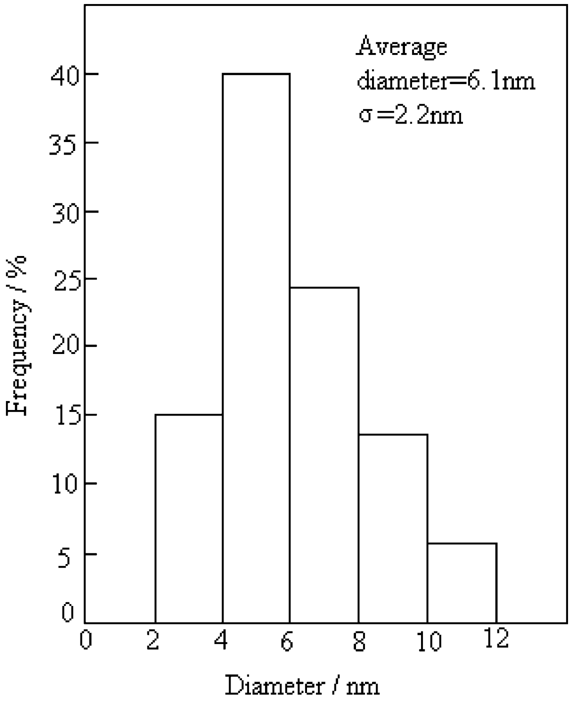

FIG. 3. Particle size distribution of Ag_2S nanoparticles obtained in the presence of HP.

monodispersion of the HP-capped Ag_2S nanoparticles. Notably, the Ag_2S particles obtained in HP had a rather small size and narrow size distribution compared with those obtained in the absence of HP (Fig. 2 (b)). Thus, it was conceivable that HP operated as a very effective protective colloid for the preparation of Ag_2S nanoparticles.

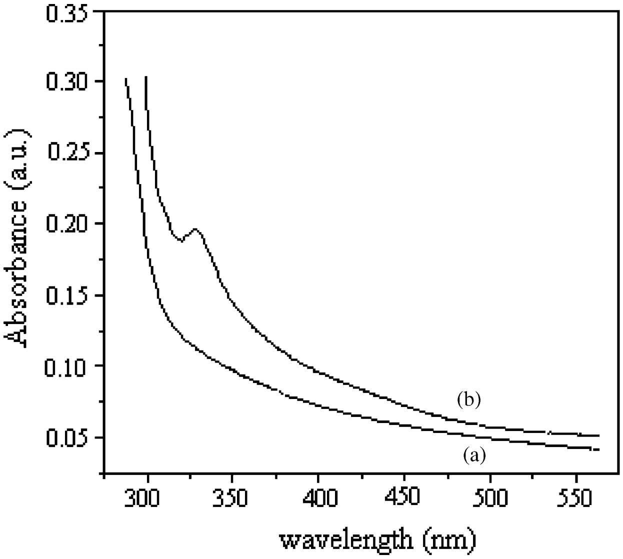

FIG. 4. UV–vis absorption spectra of pure HP (a) and Ag_2S nanoparticles obtained in the presence of HP (b).

UV–Vis Spectra

The generation of Ag_2S nanoparticles could also be identified from both the color change and the UV–vis spectrum of the as-prepared products. Pure HP solution exhibited nearly no absorption in the selected region (Fig. 4(a)). Upon the addition of thioacetamide, a black solution was obtained and an absorption peak was observed at 330 nm (Fig. 4(b)), which may be due to the formation of Ag_2S nanocrystallites (17).

In the preparation process, we found that Ag_2S nanoparticles obtained in HP were more stable than noncapped Ag_2S nanoparticles. In contrast to uncapped Ag_2S nanoparticles which precipitated from the solution immediately after the reaction, HP-capped Ag_2S nanoparticles did not suffer any observable change after 3 months. This could be confirmed by the fact that no red-shift was observed in the absorption band of the HP-capped Ag_2S nanoparticles.

Reaction Process

The formation process of Ag_2S nanocrystallites in HP could be described as follows. When thioacetamide was added to the HP/Ag^+ solution, it gradually released sulfide ions upon decomposition, then the released sulfide ions combined with silver ions to form Ag_2S as described in Eqs. [1] and [2].

$$CH_3CSNH_2 \rightarrow CH_3CN + H_2S, \qquad [1]$$

$$2Ag^+ + H_2S \rightarrow Ag_2S + 2H^+. \qquad [2]$$

IR spectroscopy was used to analyze the interactions between HP and metal ions in the reaction process. The absorption C=O stretching peak of HP was at $1719\,cm^{-1}$. After the addition of $AgNO_3$, the absorption peak shifted to $1715\,cm^{-1}$, implying the existence of weak coordinative chemical bonding between O and Ag. When thioacetamide was introduced, this band re-shifted to $1719\,cm^{-1}$, which may be due to the de-coordination of HP–silver complex.

HP played a key role in the formation of Ag_2S nanoparticles with small size and narrow size distribution. First, the coordination between HP and Ag^+ could determine the spatial site of nucleation and prevent the aggregation of initially formed Ag_2S particles. Secondly, although HP had a less perfect structure than dendrimers, it still took the unique three-dimensional structure and could provide reaction sites including its interior or periphery. After the de-coordination of HP–silver complex, Ag_2S nanoparticles were still well stabilized may be due to the steric effect of HP.

CONCLUSION

This work showed that it was possible to prepare Ag_2S nanoparticles in HP through *in situ* reaction with thioacetamide as the sulfur source in DMF solution at room temperature. X-ray diffraction results showed that a pure β-Ag_2S phase was obtained in the as-prepared nanoparticles. Transmission electron microscopic (TEM) analysis revealed a uniform spherical shape for Ag_2S nanoparticles, with an average size of about 4–10 nm, and confirmed the role of HP in the formation of Ag_2S nanoparticles with small size and narrow size distribution. This method can be extended to other metal chalcogenides/polymer systems.

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