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Preparation of polychrome silver nanoparticles in different solvents

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Polychrome silver nanoparticles have been prepared by a soft solution approach under microwave irradiation from a solution of silver nitrate ($AgNO_3$) in the presence of poly(*N*-vinyl-2-pyrrolidone) without any other reducing agent. Different morphologies of silver colloids with charming colors could be obtained using different solvents as the reaction medium. The structures of the silver colloids were determined by X-ray powder diffraction. UV-Vis spectroscopy was used to follow the reaction process and to characterize the optical properties of the resultant silver colloids. The influence of the solvent on the morphology of silver was investigated.

Introduction

In recent years the preparation and characterization of nanostructured materials have become a topic of extreme interest because of their distinctive properties and potential uses in technological applications. It is found that the optic, electronic, magnetic, and catalytic properties of these particles depend on their size and shape. So, one of the challenges in nanoparticle synthesis is to control not only the particle size but also the particle shape and morphology as well.[1–5] Novel metal nanocrystallites such as silver and gold provide a more interesting research field due to their close-lying conduction and valence bands in which electrons move freely. The free electrons give rise to a surface plasmon absorption band, which depends on both the particle size and chemical surroundings.[6] Thus, the color of the colloids varies depending on the method of preparation and the state of aggregation.[7] In general, metal nanoparticles can be prepared and stabilized by various methods such as photochemical reduction,[8,9] electrochemical techniques[10,11] and chemical reduction.[12–14] In general terms, to obtain small particle sizes with narrow size distributions and good stability is the goal. However, along with the development of nanotechnology, multi-dimensional novel metal colloids with interesting optical properties may have wider applications.

As a quick, simple and energy efficient method, microwave synthesis has been developed and is widely used for the synthesis of solid materials.[15] Compared to conventional heating, microwave dielectric heating results from dipolar polarization as a consequence of dipole–dipole interactions between polar molecules and the electromagnetic field, and has become a very popular and useful technology as a non-conventional energy source in materials science.[16] This energy dissipation in the core of materials allows a much more regular distribution of heat compared to conventional heating. Efforts have been made to prepare nanoscale metal colloids and clusters with narrow size distribution by microwave irradiation.[17–21] Further more, homogeneous nucleation and a shorter crystallization time are distinct advantages over conventional methods in the field of metal nanoparticle preparation.[20] In this study, several solvents were used to synthesize silver nanoparticles using the microwave irradiation method. Silver colloids were successfully prepared by chemical reduction in different solvents under microwave irradiation. Different shaped and sized silver nanoparticles of interesting colors were synthesized. The influences of the solvent on the optical properties and the morphologies of the silver particles have been investigated. The possible progress of the formation of silver nanoparticles is also discussed.

Experimental

Materials and apparatus

Poly(*N*-vinyl-2-pyrrolidone) (PVP, $\bar{M}_W$ = 40 000, supplied by Fluka), silver nitrate ($AgNO_3$) and the solvents used in the study, such as pyridine, ethanol, *N*,*N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP), were analytical grade reagents and used as received. The apparatus used for the preparation was a National NN-S570MFS domestic microwave oven (1000 W, 2450 MHz).

Preparation of silver colloids

The approach involves the preparation of different PVP solutions containing inorganic salts (silver nitrate). The solutions were then put into the microwave oven where $AgNO_3$ was reduced to silver nanoparticles. In a typical procedure, the reaction solutions were prepared by dissolving 2.5×10^{-6} mol PVP and 3.0×10^{-4} mol $AgNO_3$ in 4 ml ethanol in a 50 ml Pyrex flask to obtain a homogeneous reaction mixture. Thereafter, the vial was topped with a screw cap to prevent the evaporation of the toxic and corrosive solvent. Then the vial was placed on the turntable of the microwave oven. The mixture was irradiated discontinuously at a power of 300 W for the duration of the reaction to prevent an increase of pressure. After irradiation, the dilute colloidal solutions with striking colors were cooled to room temperature for characterization.

Experimental techniques

The X-ray diffraction patterns (XRD) were recorded on a Shimadzu XD-3A X-ray diffractometer using Cu-Kα radiation (λ = 0.1542nm) operated at 50 kV and 100 mA. The experiments were performed in the diffraction angle range of 2θ = 30–80°. The ultraviolet–visible (UV-Vis) spectra were used to follow the reaction process and to characterize the optical properties, and were measured in quartz cuvettes with a Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. Deionized water was used as the reference. Transmission electron microscopic (TEM) and selected area electron diffraction (SAED) analyses were performed with a Hitachi 600 microscope operating at 120 kV. Samples were prepared by drying a drop of the colloid on a TEM grid with the sample allowed to dry completely at room temperature. Approximately 150 nanoparticles from each sample were measured manually for size distribution.

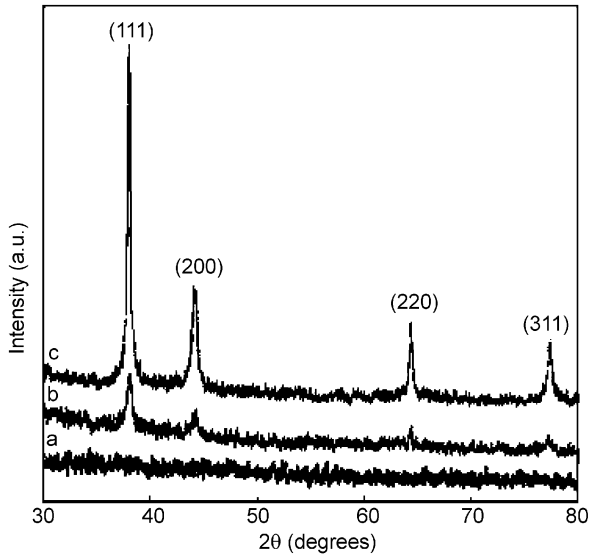

Fig. 1 XRD patterns of as-prepared silver colloid in different solvents. a. ethanol and pyridine; b. DMF; c. NMP.

Results and discussion

XRD analysis

The structure of as-prepared silver colloids was investigated by X-ray powder diffraction (XRD) analysis. Typical XRD patterns of the silver colloids prepared by the present microwave irradiation method in different solvents are shown in Fig. 1. No diffraction peaks were observed for the samples prepared in either ethanol or pyridine (Fig. 1a). The corresponding electron diffraction results also indicated that only amorphous silver particles were obtained. However, with DMF and NMP as the solvents, four distinct diffraction peaks were observed at 2θ values of 38.1°, 44.3°, 64.4°and 77.3°, respectively, corresponding to the (111), (200), (220) and (311) crystalline planes of cubic Ag (JCPDS cards 4-0783). The broad nature of the XRD peaks could be attributed to the nano-size of the particles. Of the four solvents, DMF (ε = 36.7 and bp 153 °C) and NMP (ε = 32 and bp 202 °C), which have higher relative permittivities and boiling points compared to pyridine (ε = 12.3 and bp 115 °C) and ethanol (ε = 24.6 and bp 79 °C), are the favored solvents for the formation of silver crystals under microwave irradiation. This result indicates that the dielectric properties and the boiling points of the solvents may have an important influence on the crystallinity and the growth of silver particles.

TEM anaylsis

The TEM images of the as-prepared silver nanoparticles in different solvents are shown in Fig. 2. It is apparent that silver nanoparticles formed in different solvents have different shapes and sizes. As Fig. 2a shows, the silver colloids, which were obtained in pyridine under microwave irradiation, are nearly uniformly spherical in shape and well-dispersed. The average diameter of particles is about 8 nm with a narrow size distribution, which may be due to the coordinating ability of the N atom in pyridine. Most of the isolated particles in the sample prepared in ethanol are spherical and a few faceted nanocrystals can also be seen from the TEM (Fig. 2b). The particle size is about 32 nm. The low boiling point of ethanol and pyridine did not favor the growth and ripening of crystals. This was also proved by the XRD analysis. It is interesting to note that silver nanoparticles obtained in DMF have regular geometrical shape. Most of them are triangular (edge length = 50–100 nm) or truncated triangular nanoprisms, which will be discussed further in the Optical properties section (Fig. 2c). Each nanoprism (Fig. 2c, inset) is a single crystal, which was

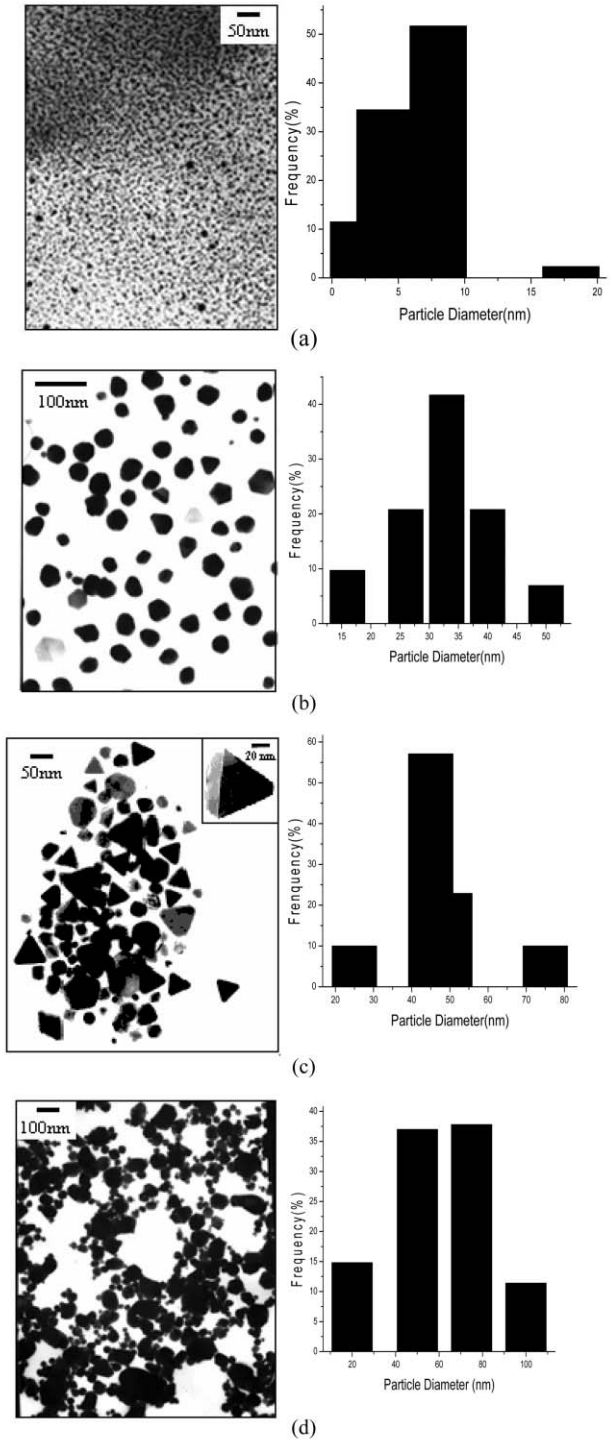

Fig. 2 TEM images and size distribution histograms of as-prepared silver nanoparticles in different solvents (microwave conditions: 300 W, irradiated for 16 min). a. Pyridine; b. ethanol; c. DMF, inset showed a single silver nanoprism; d. NMP.

confirmed by electron diffraction analysis. In NMP (Fig. 2d), the regularity of the ''nanoprisms'' formed is very low and electron diffraction analysis showed that the particles are polycrystal. Some aggregation can also be observed. These results further confirmed that the solvents have significant influence on the morphology of the silver particles formed under microwave irradiation.

Optical properties

The position and shape of the plasmon absorption of noble metal nanoclusters are strongly dependent on the particle size,

dielectric medium, and surface-adsorbed species.[22,23] The formation process and the optical properties of the silver nanoparticles can also be identified from both the color change and the UV-Vis spectra of the solutions.

The UV-Vis absorption spectra of the aqueous solutions containing as-prepared silver nanoparticles are shown in Fig. 3. The change of peak position and the shape of the absorption spectra were obvious during the whole reaction process. With ethanol as solvent, the color of the solution changed from yellow to light brown as the reaction progressed. There is only one symmetric absorption peak at *ca.* 420 nm (Fig. 3A), which is the characteristic surface plasmon resonance of spherical silver nanoparticles.[24] With longer irradiation time, the plasmon absorption maximum shifted slightly towards longer wavelengths as the particles became larger. With pyridine as the solvent, the color of the product was transparent yellow. There is one sharp absorption peak at *ca.* 403 nm (Fig. 3B), which showed relatively little change during the reaction due to the stronger coordination ability of pyridine through the N atom. We also found as the irradiation time increased and the reaction progressed, the absorption band became sharper. This result indicates that the particle size is similar throughout the reaction which is consistent with the theoretical prediction.[25] Compared with the absorption of silver nanoparticles obtained in ethanol, the narrowness and blue shift of the absorption band of those prepared in pyridine may be attributed to the size effect of the silver nanoparticles, which is consistent with the TEM results.

Using DMF as the solvent, as the reaction progressed, the solution was observed to change from colorless to transparent yellow to light brown, and then to mauve with some opalescence. As shown in Fig. 3C, when the sample was irradiated for 3 mins, an intense absorption peak at 414 nm was observed attributed to the characteristic surface plasma excitation of spherical silver nanoparticles (Fig. 3Ca).[24] After irradiation for 8 min, a new red-shifted peak was observed at 481 nm together with a small peak at 347 nm and a discernable shoulder at 414 nm. As the irradiation time was further increased, apart from the three absorption bands at 347 nm, 414 nm and 481 nm, another new band was observed at a longer wavelength. The color change and the presence of various absorption bands indicates the existence of silver particles of various shapes and sizes at various irradiation time, and that the final product has an anisotropic morphology. With NMP as the solvent, which has a high relative permittivity and high boiling point, only one peak at 406 nm was observed and the color of the solution remained yellow after irradiation for 3 min. After irradiation for 8 min, the color of the solution turned taupe, accordingly three peaks at 351 nm, 422 nm and 710 nm were observed in the UV-Vis spectra (Fig. 3D). The peaks at 351 nm and 422 nm remained unchanged and the peak at 710 nm shifted to longer wavelengths as the reaction time was increased.

It is known that the color of metal particles is caused by the sum of the effects of absorption and scattering of visible light.[25] According to Mie's theory,[26] small spherical nanocrystals should exhibit a single surface plasmon band, whereas anisotropic particles should exhibit two or three bands, depending on their shape. Absorption spectra of larger metal colloidal dispersions can exhibit broad or additional bands in the UV-Vis range due to the excitation of plasma resonances or quadrupole and higher multipole plasmon excitation.[27] The UV-Vis spectra from this work show distinct quadrupole plasmon resonances for the silver nanoparticles prepared in both DMF and NMP. The 347 nm (351 nm) peak is the out-of-plane quadrupole resonance, the 481 nm peak is the in-plane quadrupole resonance, the 600 nm (770 nm) peak is the in-plane dipole plasmon resonance, and the peak at 414 nm (422 nm) is the out-of-plane dipole plasmon resonance.[28] It has been demonstrated both theoretically and experimentally that the long wavelength resonance of the in-plane dipole plasmon resonance is very sensitive to the aspect (length to diameter) ratio of the particles.[1,11,28] From the absorption band, the different processes involved of the formation of the silver nanoparticles in different solvents under microwave irradiation is also demonstrated. All of these silver colloidal aggregates were stable for several months.

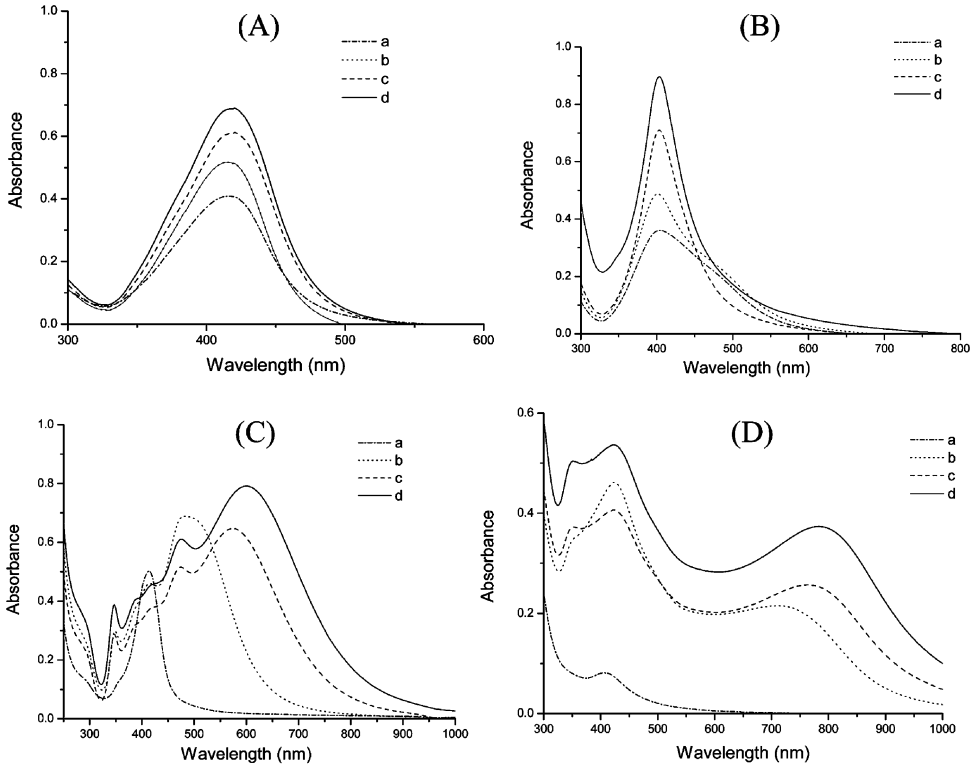

Fig. 3 UV-Vis spectra of silver nanoparticles prepared in different solventsat different time under microwave irradiation. A. Ethanol; B. Pyridine; C. DMF; D. NMP. Microwave conditions (300 W): a. 3 min; b. 8 min; c. 12 min; d. 16 min.

In our study, AOT, *n*-dodecanethiol, and poly(*N*-methylacrylamide) were also used as stabilizers to prepare silver in DMF, but no characteristic absorption peak of silver was observed in the UV-Vis spectrum. This implies that PVP not only served as the stabilizer but also as a weaker reducing agent to reduce silver ions to silver under microwave irradiation. We also proved that in the presence of PVP, $AgNO_3$ could be reduced to silver clusters in ethanol.[29] Further experimental results showed that the particle shape and the reduction rate distinctly depended on PVP : $AgNO_3$ mole ratio. A higher ratio of the PVP : $AgNO_3$ resulted in a faster reduction of silver ions to silver under microwave irradiation. Meanwhile, DMF and ethanol may also have reducing ability. Pastoriza-Santos and Liz-Marzan[12] showed the ability of DMF to reduce Ag^+ ions to the zerovalent metal, even at room temperature and in the absence of any external agent. Toshima[30] commented on the extensive use of ethanol as a reducing agent, either using PVP or other protecting polymers. But with NMP and pyridine as solvents in the presence of PVP, the reducing phenomenon may mainly be due to the reducing ability of PVP.

The exact mechanism for the formation of different shape and morphology of the silver particles in different solvents is still unclear. El-Sayed *et al.*[31] provided two reasonable explanations for the formation of faceted particles: (1) the growth rates vary at different planes of the particles; (2) particle growth competes with the coordinating action of stabilizers. In the PVP/$AgNO_3$ system, PVP can kinetically control the growth rates of various faces by interacting with these faces through adsorption and desorption. Furthermore, PVP in different solvents may have different constitutions, and different solvents have different complexing abilities with silver ions. All these factors may kinetically control the growth of the silver particles and lead to those of different shape, size and morphology. On the other hand, the slow dissolution of the small silver particles into the solution might also play a certain role in achieving anisotropic growth of the large silver particles.[32] It was found that the character of the solvents used in this microwave irradiation method played a crucial role in the formation and growth of the silver nanoparticles.

Conclusions

Polychrome silver nanoparticles obtained by microwave irradition and chemical reduction of silver ions in different solvents with PVP have been studied. The dielectric properties and the boiling points of the solvents had an important effect on the crystallinity of the silver nanoparticles. Higher boiling point solvents were advantageous to the higher crystallinity of the silver nanoparticles. Silver nanoparticles prepared in different solvents had different morphologies and sizes, which were demonstrated in TEM images and UV-Vis spectra. In pyridine, spherical silver nanoparticles with an average size of 8 nm were formed. The solution was yellow and only one sharp symmetric absorption peak at *ca.* 403 nm was observed in the UV-Vis spectrum. In ethanol, most of the particles formed were spherical of 32 nm and a few faceted nanocrystals could also be seen from the TEM, but few had a triangular morphology. The solution was light brown and had an absorption peak at *ca.* 420 nm. Nanoprisms with two distinct quadrupole plasmon resonances in the UV-Vis spectra were observed using DMF as the solvent and the solution was mauve with some opalescence. While in NMP, a taupe solution was obtained and "nanoprisms" with lower regularity were formed, and exhibited three peaks in the UV-Vis spectrum. The possible mechanism for the formation of silver nanoparticles in organic solvents in the presence of PVP under microwave irradiation has also been discussed.

Acknowledgements

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References

1 S. Link, M. B. Mohamed and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 3073.
2 M. Moffitt, H. Vali and A. Eisenberg, *Chem. Mater.*, 1998, **10**, 1021.
3 A. Fukuoka, Y. Sakamoto, S. Guan, S. Inagaki, N. Sugimoto, Y. Fukushima, K. Hirahara, S. Iijima and M. Ichikawa, *J. Am. Chem. Soc.*, 2001, **123**, 3373.
4 B. Gates, Y. Yin and Y. Xia, *J. Am. Chem. Soc.*, 2000, **122**, 12582.
5 S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein and M. A. El-Sayed, *Science*, 1996, **272**, 1924.
6 S. Kapoor, *Langmuir*, 1998, **14**, 1021.
7 S. De, A. Pal, N. R. Jana and T. Pal, *J. Photochem. Photobiol. A*, 2000, **131**, 111.
8 F. Mafuné, J. Y. Kohno, Y. Takeda and T. Kondow, *J. Phys. Chem. B*, 2000, **104**, 8333.
9 H. H. Huang, X. P. Ni, G. L. Loy, C. H. Chew, K. L. Tan, F. C. Loh, J. F. Deng and G. Q. Xu, *Langmuir*, 1996, **12**, 909.
10 J. J. Zhu, S. W. Liu, O. Palchik, Y. Koltypin and A. Gedanken, *Langmuir*, 2000, **16**, 6396.
11 Y. Y. Yu, S. S. Chang, C. L. Lee and C. R. Chris Wang, *J. Phys. Chem. B*, 1997, **101**, 6661.
12 I. Pastoriza-Santos and L. M. Liz-Marzan, *Langmuir*, 1999, **15**, 948.
13 W. Yu, Y. Wang, H. Liu and W. Zheng, *J. Mol. Catal. A*, 1996, **112**, 105.
14 L. N. Lewis and N. Lewis, *J. Am. Chem. Soc.*, 1986, **108**, 7228.
15 K. J. Rao and P. D. Ramesh, *Bull. Mater. Sci.*, 1995, **18**, 447.
16 L. Perreux and L. André, *Tetrahedron*, 2001, **57**, 9199.
17 X. H. Liao, J. M. Zhu, J. J. Xu and H. Y. Chen, *Chem. Commun.*, 2001, 937.
18 W. X. Tu and H. F. Liu, *Chem. Mater.*, 2000, **12**, 564.
19 W. Y. Yu, W. X. Tu and H. F. Liu, *Langmuir*, 1999, **15**, 6.
20 C. S. Cundy, *Collect. Czech. Chem. Commun.*, 1998, **63**, 1699.
21 I. Pastoriza-Santos and L. M. Liz-Marzan, *Langmuir*, 2002, **18**, 2888.
22 P. V. Kamat, M. Flumiani and G. V. Hartland, *J. Phys. Chem. B*, 1998, **102**, 3123.
23 A. Heilmann, A. Kiesow, M. Gruner and U. Kreibig, *Thin Solid Films*, 1999, **175**, 343.
24 S. T. He, J. N. Yao, P. Jiang, D. X. Shi, H. X. Zhang, S. S. Xie, S. J. Pang and H. J. Gao, *Langmuir*, 2001, **17**, 1571.
25 K. Sudhir, *Langmuir*, 1998, **14**, 1021.
26 G. Mie, *Ann. Phys.*, 1908, **25**, 377.
27 P. V. Kamat, M. Flumiani and G. V. Hartland, *J. Phys. Chem. B*, 1998, **102**, 3123.
28 R. C. Jin, Y. W. Cao, A. Mirkin Chad, K. L. Kelly, C. Schatz George and J. G. Zheng, *Science*, 2001, **294**, 1901.
29 X. F. Qian, J. Yin, S. Feng, S. H. Liu and Z. K. Zhu, *J. Mater. Chem.*, 2001, **11**, 2504.
30 H. Y. N. Toshima, *J. Macromol. Sci.: Chem.*, 1979, **A13**, 727.
31 J. M. Petroski, Z. L. Wang, T. C. Green and M. A. El-Sayed, *J. Phys. Chem. B*, 1998, **102**, 3316.
32 Y. G. Sun, B. Gates, B. Mayers and Y. Xia, *Nano Lett.*, 2002, **2**, 165.