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PAPER

Synthesis of highly stable dispersions of nanosized copper particles using L-ascorbic acid

Jing Xiong, Ye Wang, Qunji Xue and Xuedong Wu*

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Highly stable dispersions of nanosized copper particles with an average particle size less than 2 nm were synthesized using a straightforward, cost-effective, and green method. Nontoxic L-ascorbic acid was utilized as both a reducing agent and capping agent precursor in aqueous medium. The copper particles were characterized by ultraviolet-visible spectroscopy, transmission electron microscopy, and Fourier-transform infrared spectroscopy The mechanism of L-ascorbic acid on the reduction and stabilization of copper nanoparticles is also discussed.

1. Introduction

Metal nanoparticles have attracted much attention in nanoscale science and engineering technology over the past decade due to their unusual chemical and physical properties, such as catalytic activity, and novel electronic, optical and magnetic properties.[1–3] Their main application areas include catalysts, absorbents, chemical and biological sensors, optoelectronics, information storage, and photonic and electronic devices.[4–9] Various methods, such as wet chemical reduction, reverse micelles, and electrochemical and sonoelectrochemical techniques,[10–15] have been developed to synthesize metal nanoparticles because of the diversity and importance of these applications. Among the above methods, the wet chemical reduction method has the advantage over the others in easy control of the reaction process and production rate. The wet chemical reduction method is mostly achieved by reduction of a metal ion salt solution. There are three key factors in the reducing process: (i) the solvent medium, (ii) the reducing agent, and (iii) the capping agent. Most of wet chemical reduction methods reported to date rely heavily on organic solvents and use environmentally and biologically hazardous reducing agents (*i.e.*, hydrazine, sodium borohydride, dimethyl formamide, potassium bitartrate, formaldehyde, sodium hypophosphite or hydroxylamine hydrochloride, *etc*).[16–22]

Recently, there is an increased emphasis on the topic of green chemistry, which is defined as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.[23–26] There are 12 fundamental principles that any attempt must be comprehensively addressed in the design of synthetic routes, chemical analyses, or chemical processes.[27] Utilization of nontoxic chemicals, environmentally benign solvents, and renewable materials are key issues in the nanomaterials science field when considering a green synthetic strategy. Following this strategy, several synthetic methods relying on green chemistry have so far been reported, especially for noble metal nanoparticles. Raveendran *et al.*[28] prepared silver nanoparticles using water as a solvent, β-D-glucose as a reducing agent, and starch as a protecting agent. Liu *et al.*[29] synthesized gold nanocrystals using β-D-glucose as both the reducing and stabilizing agent. Raveendran *et al.*[30] also prepared Au, Ag, and Au–Ag nanoparticles in water, using glucose as the reducing agent and starch as the protecting agent. Nadagouda *et al.*[31] synthesized Ag and Pd nanoparticles using tea/coffee extract. Moulton *et al.*[32] fabricated Ag nanoparticles by reducing silver nitrate in solutions of tea extract or epicatechin. However, there are few reports on preparation of copper nanoparticles through a green method.[33,34] Copper nanoparticles play a crucial role in many applications such as lubricants, catalysts, thermal transfer nanofluids, electronic materials and optical devices.[35–37] Compared to other noble metals, copper is significantly cheaper and exhibits less of a electromigration effect when it is used in microelectronics. In addition, stable dispersion of nanosized copper particles can be used as a conductive ink to manufacture low-cost electronic components by ink-jet printing, which is a kind of additive printing process that offers many economical and environmental advantages compared to traditional mask-based photolithography methods.[38–40]

In this work, a simple, environmentally friendly, and cost-effective method for preparing highly stable dispersions of nanosized copper particles is reported. The reaction is carried out in an aqueous medium solution and L-ascorbic acid is used as both reducing and capping agent to prevent the aggregation of copper nanoparticles. No other polymer dispersant is added

Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 519 Zhuangshi Road, Zhenhai District, Ningbo, 315201, China. E-mail: xdwu@nimte.ac.cn; Fax: +86-574-86685159; Tel: +86-574-87914083

to avoid any adverse effect on the performance of products as organic residues.

2. Experimental

Materials

$CuCl_2 \cdot 2H_2O$ (Sinopharm Chemical Reagent Co., Ltd) acted as the precursor for the formation of Cu nanoparticles. L-ascorbic acid (Sinopharm Chemical Reagent Co., Ltd) acted both as reducing agent and capping agent. Deionized water was used in all experiments.

Preparation of dispersions of nanosized copper particles

In a typical preparation process, $CuCl_2 \cdot 2H_2O$ aqueous solution was prepared by dissolving $CuCl_2 \cdot 2H_2O$ (10 mmol) in 50 ml deionized water. A flask containing $CuCl_2 \cdot 2H_2O$ aqueous solution was heated to 80 °C in an oil bath with magnetic stirring. A 50 ml L-ascorbic acid aqueous solution of various concentrations (0.4, 0.6, 0.8 and 1.0 M) was added dropwise into the flask while stirring. The mixture was kept at 80 °C until a dark solution was obtained. The resulting dispersion was centrifuged at 8000 rpm for 15 min. The supernatant was placed under ambient conditions for 2 months.

Characterization

The UV-Vis absorption spectra of the produced dispersions were recorded on a UNICOWFZ UV-2000 spectrophotometer. The morphology and size of the as-synthesized Cu nanoparticles were characterized by transmission electron microscopy (TEM, Tecnai F20, 200 kV). FT-IR spectra were performed and recorded with a Fourier-transform infrared spectrophotometer (Nicolet 6700) between 4000 and 400 cm^{-1}, with a resolution of 0.09 cm^{-1}.

3. Results and discussion

UV-Vis studies on Cu nanoparticles

Nanosized particles exhibit unique optical properties having an exponential-decay Mie scattering profile with decreasing photon energy. Some transition-metal nanoparticles also show a distinct surface-plasmon band.[41] UV-Vis absorbance spectroscopy has proved to be a very useful technique for studying metal nanoparticles because the peak positions and shapes are sensitive to particle size. The effect of L-ascorbic concentration on the UV-Vis absorbance spectroscopy of the synthesized Cu nanoparticles is shown in Fig. 1. The first absorption peaks of different curves are all at around 330 nm corresponding to the oxidation product of L-ascorbic acid. This can be proved by another experiment, in which H_2O_2 was used as oxidant to react with L-ascorbic acid, and the product showed single peak at around 330 nm. The second absorption peaks are increasingly broadening with an increasing concentration of L-ascorbic acid. The surface plasmon peak of copper nanoparticles has been reported to be appear at around 570 nm. However, when the particle size is less than 4 nm, the distinctive plasmon peak is known to be broadened and replaced by a featureless absorbance, which increases monotonically towards higher

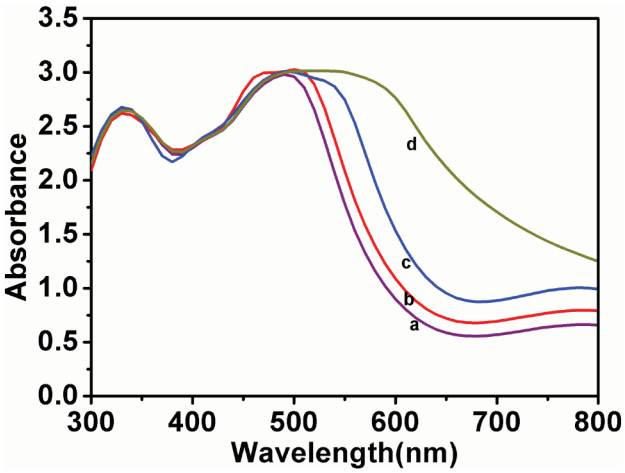


Fig. 1 The UV-Vis absorption spectra of Cu nanoparticles stabilized in L-ascorbic acid aqueous solution with various concentrations: (a) 0.4 M, (b) 0.6 M, (c) 0.8 M and (d) 1.0 M.

energies.[42–44] In our work, the resulting copper dispersion did not show a plasmon peak at around 570 nm, but displayed a broadened peak at a short wavelength, indicating the presence of very small separated Cu nanoparticles (the average particle size is less than 4 nm). Based on the above results, we can infer that a higher L-ascorbic acid concentration leads to a more effective capping capacity of L-ascorbic acid and then smaller Cu nanoparticles.

The dispersion became colorless when L-ascorbic acid was added, and gradually turned to yellow, orange, brown and finally dark (see Fig. 2). In order to clarify the reaction process, 0.2 M $CuCl_2 \cdot 2H_2O$ reacted with 1.0 M L-ascorbic acid, and the UV-Vis absorption spectra were recorded every 2 h. The time evolution of the UV-Vis absorption spectra is shown in Fig. 2. Initially, there is no characteristic absorption peak. After 2 h of the reaction, the absorption peak can be observed. There is an intensity increase and red shift of the second absorption peaks with the reaction progressing. This phenomenon is due to the growth of copper nanoparticles. The reaction (including the reduction reaction process and Cu NPs growth process) was completed after 14 h as the UV-Vis absorption curves of 14 h and 16 h almost overlapped.

Size and morphology analyses

Transmission electron microscopy (TEM) was used to study the morphology and the size distribution of the collected particles. The typical TEM images of the as-synthesized copper nanoparticles are shown in Fig. 3. In general, the particles are isotropic (*i.e.*, low aspect ratio) and spherical in shape. The mean particle diameter observed is less than 2 nm. The histograms of the Cu nanoparticle size distributions are also presented in Fig. 3.

The observed patterns indicate a high degree of monodispersity of the Cu nanoparticles. In addition, the histograms reveal a decrease in particle size with an increase of L-ascorbic acid concentration. The sizes of the copper nanoparticles with various concentrations of L-ascorbic acid (0.4 M, 0.6 M, 0.8 M, and 1.0 M) are 1.87 ± 0.35 nm, 1.68 ± 0.35 nm, 1.57 ± 0.21 nm, and 1.34 ± 0.14 nm respectively. The reason

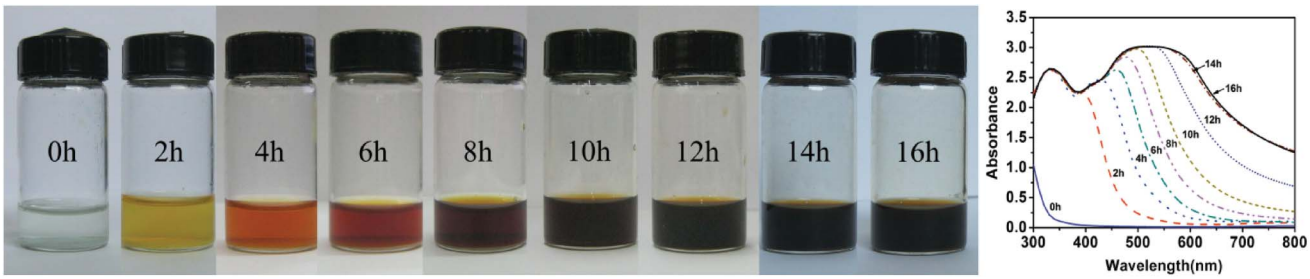


Fig. 2 The time evolution of the dispersion photographs and the UV-Vis absorption spectra.

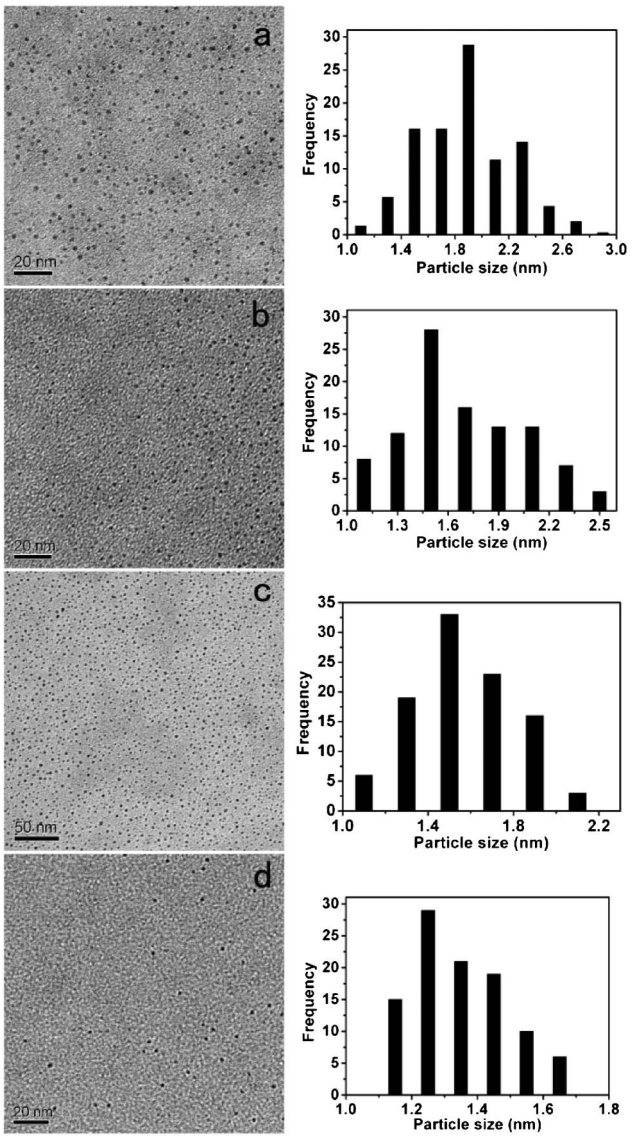


Fig. 3 TEM images and particle size distribution of the synthesized copper nanoparticles with various concentrations of L-ascorbic acid. The average particle sizes are: (a) 0.4 M, d = 1.87 ± 0.35 nm; (b) 0.6 M, d = 1.68 ± 0.35 nm; (c) 0.8 M, d = 1.57 ± 0.21 nm; (d) 1.0 M, d = 1.34 ± 0.14 nm.

is that L-ascorbic acid molecules encapsulate Cu^{2+} and reduce Cu^{2+} into Cu(0), then the oxidation products adsorb on the resulting Cu nanoparticle surfaces, preventing the particles from growing further. As a result, ultrafine Cu nanoparticles can be obtained. The number of Cu^{2+} encapsulated in L-ascorbic acid molecules decreases with the increasing concentration of L-ascorbic acid, leading to the formation of smaller Cu nanoparticles (which will be further discussed in the mechanism section).

The resulting dispersion was further examined with EDS, and the result is shown in Fig. 4. The EDS spectrum only exhibits the characteristic peaks of Cu, suggesting that the obtained product is composed of pure Cu.

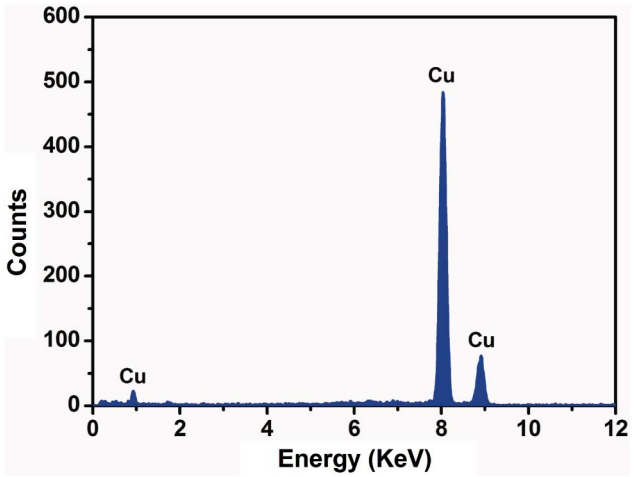


Fig. 4 EDS spectrum of the Cu nanoparticles stabilized in L-ascorbic acid aqueous solution.

Fourier transform-infrared (FT-IR) characterization

FT-IR spectroscopy was used to investigate the interactions between different species and changes in chemical compositions of the mixtures. Fig. 5a shows the FT-IR spectrum for pure L-ascorbic acid. The stretching vibration of the carbon-carbon double bond and the peak of enol hydroxyl were observed at 1674 cm^{-1} and 1322 cm^{-1}, respectively. These peaks disappeared after the reaction and new peaks were observed at 3481 cm^{-1}, 1718 cm^{-1}, and 1681 cm^{-1} (Fig. 5b). These peaks correspond to the hydroxyl, oxidated ester carbonyl groups, and conjugated carbonyl groups, respectively. These results indicate the presence of the polyhydroxyl structure on the surface of copper nanoparticles. The polyhydroxyl structure has an excellent dispersion effect on copper nanoparticles (which will be discussed in detail in the mechanism section).

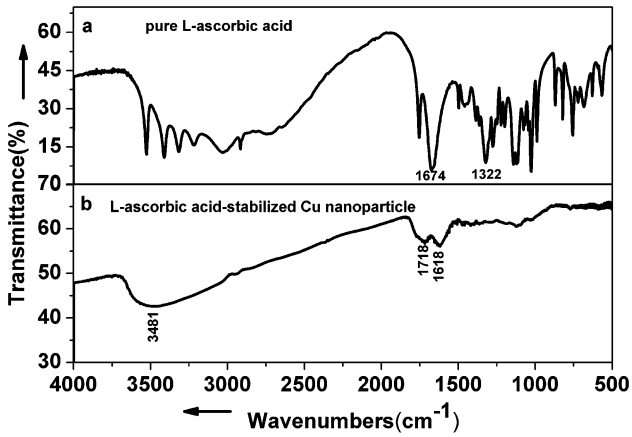


Fig. 5 FT-IR spectra of (a) pure L-ascorbic acid and (b) L-ascorbic acid-stabilized Cu nanoparticles.

The stability of Cu nanoparticles

The stability of nanoparticle dispersions is a key factor in their applications. In order to prevent the agglomeration of nanoparticles, several capping agents have been added into reaction media. In this work, L-ascorbic acid was used as both reducing and capping agent without any other special capping agent. The aqueous L-ascorbic acid-stabilized Cu nanoparticle dispersion was centrifuged at 8000 rpm for 15 min. A small amount of precipitate was obtained from the bottom of the centrifuge tube. The precipitate was found to be completely soluble in aqueous solution again after the shaking of the centrifuge tube. In addition, the supernatant obtained by centrifuging was placed under ambient conditions and no sign of sedimentation was observed even after 2 months of storage. The photos of the dispersions before and after the storage are shown in Fig. 6. This indicates that the L-ascorbic acid-stabilized Cu nanoparticles are highly stable due to the extreme capping effect of the L-ascorbic acid and the dispersion effect of the polyhydroxyl structure.

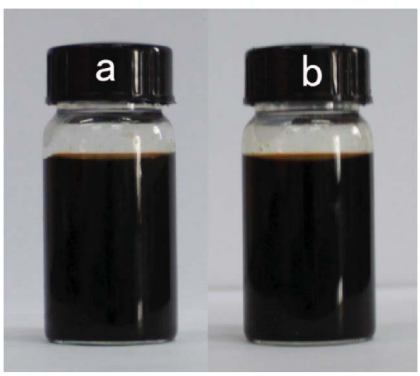
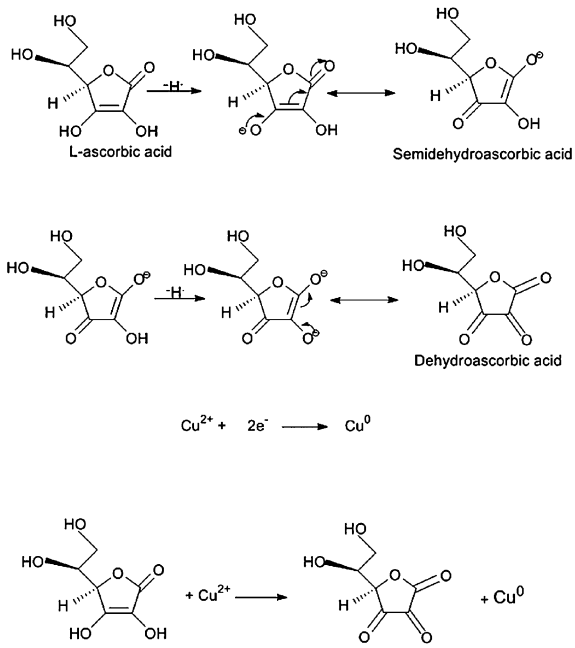


Fig. 6 The photos of the dispersions (a) before and (b) after 2 months of storage.

Possible mechanism

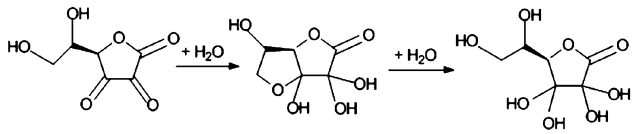
The above results show that well-dispersed copper nanoparticles can be obtained through the reduction of Cu^{2+} using L-ascorbic acid as both the reducing and capping agent. The structure of L-ascorbic acid is presented in Scheme 1. L-ascorbic acid is a highly water-soluble compound with strong polarity. It behaves as a vinylogous carboxylic acid in which the electrons in the double bond, hydroxyl group lone pair, and the lactone ring carbonyl double bond form a conjugated system. As such, the structure of L-ascorbic acid gives enough reducibility to convert Cu^{2+} ions into Cu(0) nanoparticles. The redox equation of L-ascorbic acid and copper ions can be expressed in Scheme 1.



Scheme 1 The reduction reaction equation for the formation of Cu nanoparticles.

As illustrated in Scheme 1, L-ascorbic acid serves as a stable (electron + proton) donor in interactions, and is converted into the radical ion called "semidehydroascorbic acid" and then dehydroascorbic acid. Dehydroascorbic acid and L-ascorbic acid together constitute the redox system (reduction potential ~0.060 V *vs.* SCE) which is sufficient to reduce Cu^{2+} to Cu (reduction potential is 0.340 V *vs.* SCE). Besides, it should be noted that L-ascorbic acid has also played the role of stabling agent during the reaction process. The possible mechanism of L-ascorbic acid on the effective stability of copper nanoparticles can be explained from two aspects. One is, the capping effect of L-ascorbic acid in the reduction process. The lone pair electrons in the polar groups of L-ascorbic acid can occupy two sp orbits of the copper ion to form a complex compound. The L-ascorbic acid is thus capped with copper ions, then synthesizes Cu(0) nanoparticles through reduction of Cu^{2+} inside the nanoscopic templates. In the presence of nanoscopic templates, small copper nanoparticles are easily formed. The other explanation is the dispersion effect of the oxidation product of L-ascorbic acid on the copper nanoparticles after the completion of the reduction reaction. L-ascorbic acid is converted into dehydroascorbic acid through oxidation. The dehydroascorbic acid has three carbonyls in its structure. The 1,2,3-tricarbonyl is too electrophilic to survive more than a few milliseconds in aqueous solution, and the 6-OH and the 3-carbonyl groups form the hemiacetal rapidly. Hydration of the

2-carbonyl is also observed.[45] Finally, the polyhydroxyl structure is obtained through irreversible hydrolysis of the ester bond (Scheme 2).[46]



Scheme 2 Irreversible hydrolysis of dehydroascorbic acid.

This result is consistent with that of FT-IR analysis. The extensive number of hydroxyl groups can facilitate the complexation of Cu nanoparticles to the molecular matrix by inter and intramolecular hydrogen bonding, and thus prevent the aggregation of Cu nanoparticles.

4. Conclusions

In summary, we have demonstrated a facile green method to synthesize low-cost monodispersed Cu nanoparticles (ranging from 1.34 ± 0.14 nm to 1.87 ± 0.35 nm in size on average with a narrow size distribution and a uniform shape) by employing L-ascorbic acid as both the reducing and capping agent. The prepared dispersions of copper nanoparticles are highly stable and do not show any sign of sedimentation even after storage for 2 months. Since the reagents used in the reaction medium are completely non-toxic and environmentally friendly, this green method can be readily used for biomedical applications. Moreover, the highly stable solution of dispersed copper nanoparticles can be used as conductive ink for applications such as printed electronics.

Acknowledgements

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References

1 W. P. Halperin, *Rev. Mod. Phys.*, 1986, **58**, 533–606.
2 M. A. El-Sayed, *Acc. Chem. Res.*, 2001, **34**, 257–264.
3 S. R. Emory and S. Nie, *J. Phys. Chem. B*, 1998, **102**, 493–497.
4 L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693–2730.
5 A. C. Templeton, D. E. Cliffel and R. W. Murray, *J. Am. Chem. Soc.*, 1999, **121**, 7081–7089.
6 R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger and C. A. Mirkin, *Science*, 1997, **277**, 1078–1081.
7 M. Salerno, J. R. Krenn, B. Lamprecht, G. Schider, H. Ditlbacher, N. Felidj, A. Leitner and F. R. Aussenegg, *Opto-Electron. Rev.*, 2002, **10**, 217–224.
8 L. M. Liz-Marzan, *MRS Bull.*, 2001, **26**, 981–985.
9 Y. Li, F. Qian, J. Xiang and C. M. Lieber, *Mater. Today*, 2006, **9**, 18–27.
10 D. V. Goia and E. Matijevic, *New J. Chem.*, 1998, **22**, 1203–1215.
11 C. L. Lee, C. C. Wan and Y. Y. Wang, *Adv. Funct. Mater.*, 2001, **11**, 344–347.
12 I. Capek, *Adv. Colloid Interface Sci.*, 2004, **110**, 49–74.
13 A. Taleb, C. Petit and M. P. Pileni, *Chem. Mater.*, 1997, **9**, 950–959.
14 B. S. Yin, H. Y. Ma, S. Y. Wang and S. H. Chen, *J. Phys. Chem. B*, 2003, **107**, 8898–8904.
15 J. J. Zhu, S. W. Liu, O. Palchik, Y. Koltypin and A. Gedanken, *Langmuir*, 2000, **16**, 6396–6399.
16 F. Bonet, V. Delmas, S. Grugeon, R. H. Urbina, P. Y. Silvert and K. Tekaia-Elhsissen, *Nanostruct. Mater.*, 1999, **11**, 1277–1284.
17 C. J. Murphy, T. K. San, A. M. Gole, C. J. Orendorff, J. X. Gao, L. Gou, S. E. Hunyadi and T. Li, *J. Phys. Chem. B*, 2005, **109**, 13857–13870.
18 I. Pastoriza-Santos and L. M. Liz-Marzan, *Langmuir*, 1999, **15**, 948–951.
19 Y. W. Tan, X. H. Dai, Y. F. Li and D. B. Zhu, *J. Mater. Chem.*, 2003, **13**, 1069–1075.
20 K. S. Chou and C. Y. Ren, *Mater. Chem. Phys.*, 2000, **64**, 241–246.
21 Y. Lee, J. R. Choi, K. J. Lee, N. E. Stott and D. Kim, *Nanotechnology*, 2008, **19**, 415604.
22 N. Leopold and B. Lendl, *J. Phys. Chem. B*, 2003, **107**, 5723–5727.
23 M. Poliakoff and P. Anastas, *Nature*, 2001, **413**, 257–257.
24 J. M. DeSimone, *Science*, 2002, **297**, 799–803.
25 M. Poliakoff, J. M. Fitzpatrick, T. R. Farren and P. T. Anastas, *Science*, 2002, **297**, 807–810.
26 P. T. Anastas and T. C. Williamson, *Green Chemistry: Designing Chemistry for the Environment*, American Chemical Society, 1996, 1-17.
27 S. L. Y. Tang, R. L. Smith and M. Poliakoff, *Green Chem.*, 2005, **7**, 761.
28 P. Raveendran, J. Fu and S. L. Wallen, *J. Am. Chem. Soc.*, 2003, **125**, 13940–13941.
29 J. C. Liu, G. W. Qin, P. Raveendran and Y. Kushima, *Chem.-Eur. J.*, 2006, **12**, 2132–2138.
30 P. Raveendran, J. Fu and S. L. Wallen, *Green Chem.*, 2006, **8**, 34–38.
31 M. N. Nadagouda and R. S. Varma, *Green Chem.*, 2006, **8**, 516–518.
32 M. C. Moulton, L. K. Braydich-Stolle, M. N. Nadagouda, S. Kunzelman, S. M. Hussain and R. S. Varma, *Nanoscale*, 2010, **2**, 763–770.
33 Y. C. Zhang, R. Xing and X. Y. Hu, *J. Cryst. Growth*, 2004, **273**, 280–284.
34 C. W. Wu, B. P. Mosher and T. F. Zeng, *J. Nanopart. Res.*, 2006, **8**, 965–969.
35 S. Tarasov, A. Kolubaev, S. Belyaev, M. Lerner and F. Tepper, *Wear*, 2002, **252**, 63–69.
36 A. G. Nasibulin, P. P. Ahonen, O. Richard, E. I. Kauppinen and I. S. Altman, *J. Nanopart. Res.*, 2001, **3**, 385–400.
37 F. E. Kruis, H. Fissan and A. Peled, *J. Aerosol Sci.*, 1998, **29**, 511–535.
38 C. M. Hong and S. Wagner, *IEEE Electron Device Lett.*, 2000, **21**, 384–386.
39 S. K. Volkman, Y. N. Pei, D. Redinger, S. Yin and V. Subramanian, *Mat. Res. Soc. Symp. Proc*, 2004, **814**, 151–156.
40 J. S. Kang, H. S. Kim, J. Ryu, H. Thomas Hahn, S. Jang and J. W. Joung, *J. Mater. Sci.: Mater. Electron.*, 2010, **21**, 1213–1220.
41 S. W. Chen and J. M. Sommers, *J. Phys. Chem. B*, 2001, **105**, 8816–8820.
42 I. Lisiecki and M. P. Pileni, *J. Am. Chem. Soc.*, 1993, **115**, 3887–3896.
43 I. Lisiecki and M. P. Pileni, *J. Phys. Chem.*, 1995, **99**, 5077–5082.
44 I. Lisiecki, F. Billoudet and M. P. Pileni, *J. Phys. Chem.*, 1996, **100**, 4160–4166.
45 R. C. Kerber, *J. Chem. Educ.*, 2008, **85**, 1237–1242.
46 E. Kimoto, H. Tanaka, T. Ohmoto and M. Choami, *Anal. Biochem.*, 1993, **214**, 38–44.

