

CrossMark
click for updatesCite this: *RSC Adv.*, 2014, 4, 64668Received 1st September 2014
Accepted 18th November 2014

DOI: 10.1039/c4ra09557j

www.rsc.org/advances

A novel process to prepare a thin silica shell on the PDDA-stabilized spherical Au nanoparticles assisted by UV light irradiation†

Lifeng Hang,^{ab} Cuncheng Li,^c Tao Zhang,^c Xinyang Li,^a Yanchun Wu,^{ab} Dandan Men,^{ab} Guangqiang Liu^a and Yue Li^{*ab}

A modified polyol process is a convenient route to prepare mono-dispersed, uniform spherical Au nanospheres stabilized by Poly Diallyl Dimethyl Ammonium Chloride (PDDA). However, Au nanospheres with PDDA coatings possess a high zeta potential and such PDDA coatings can not be removed easily, leading to a difficulty in coating a silica layer on surfaces of Au nanospheres, further resulting in the limitation of the applications of these monodispersed Au nanoparticles (NPs). Herein, we develop a novel route to coat a silica layer on PDDA stabilized Au nanospheres assisted by UV light irradiation without the use of a silane coupling agent as the surface primer. PDDA-stabilized Au nanospheres showed high a positive zeta potential (36.7 mV), which is disadvantageous to coat a layer of thin silica shell. In our strategy, UV light irradiation with high power was applied to PDDA stabilized Au nanoparticles and part of PDDA on Au nanoparticles was degraded, producing lower positive zeta potential (14.7 mV), which guaranteed that silica shell could be easily formed on the surface of Au sphere under such a low zeta potential. The thickness of silica shell could be successfully tuned from 2 nm to 8 nm by adjusting the concentration of TEOS. As far as we know, this is first report to coat the silica layer on PDDA stabilized Au nanospheres. Such monodispersed Au spherical nanoparticles with controlled silica coatings could be extended to important applications in SERS applications, electrochemistry after self-assembled into monolayer particle arrays.

1. Introduction

In recent years, investigations of metal nanomaterials have made great achievements in different fields, *i.e.* chemistry, physics and biology. Au nanoparticles (NPs) with controlled

morphology and size are well studied because of their unique properties,^{1–3} *i.e.* surface plasmon resonance (SPR),^{4–8} fluorescence^{9–11} and electrochemistry.^{12–14} Au NPs can be applied in many fields, such as nonlinear optical switching,¹⁵ immuno-assay labeling,^{16,17} and Surface Raman spectroscopy enhancement (SERS).^{18–23}

In recent studies, colloidal Au particles can be further tailored by coating their surfaces with uniform, thin shells made of dielectric materials, such as silica. Monodispersed Au NPs with thin silica shells could be used as the SERS-active nanostructures, the presence of silica shell keeps the Au NPs from agglomerating, it also protects the SERS-active nanostructures to avoid directly contacting with detected organic molecules, hence preventing catalytic reaction between Au NPs and organic molecules under laser irradiation in SERS measurement process.²⁴ Additionally, these Au nanoparticles coated with thick silica shells could be easily self-assembled into long-range ordered lattices (or photonic crystals) over large areas, the periodic arrays with Au nanospheres exhibited different optical properties compared with those crystallized from pure silica colloids with an optical band gap in the visible region.²⁵ Moreover, various functional groups are easily incorporated onto the surface of silica-coated nanoparticles for different applications *via* the co-condensation of TEOS and functionalized silanes.²⁶

At present, chemical reduction methods have been developed to prepare the Au NPs, such as sodium citrate reduction.^{27–29} For instance, seeding growth of colloidal Au is the main process to prepare gold nanoparticles which can be coated silica shell.^{30,31} Sodium citrate was used as a reducing agent to reduce HAuCl₄ into nanoparticles and it was also used as stabilize agent to disperse the Au NPs in solution. Brust *et al.* used a strong reducing agent of NaBH₄ to prepare Au NPs in the solvent composed of HAuCl₄ and alkylmercaptans. To prepare Au@SiO₂ core-shell nanostructures, three methods have been developed, *i.e.* sodium silicate hydrolysis,²⁴ sol-gel,²⁵ reverse microemulsion.³² Sodium silicate hydrolysis is used to coat citrate-stabilized Au NPs with silica shells, and the silane coupling agent of APTES should be firstly modified to the Au

^aKey Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China. E-mail: yueli@issp.ac.cn

^bUniversity of Science and Technology of China, Hefei 230026, P. R. China

^cKey Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, Shandong, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra09557j

NPs surface evenly. The sol-gel process was reported previously that the silica shell was directly formed with TEOS hydrolysis during the alkaline. This method is suitable for coating more than 10 nm shell thickness on Au NPs. Jackie *et al.*³² developed a reverse microemulsion method to coat small Au NPs (<20 nm) with silica. By above methods, the all gold cores which they synthesized were uneven or non-spherical.

A modified polyol process is a convenient route to prepare monodispersed, uniform Au NPs with different shapes, *i.e.* Au nanooctahedra.³³ Monodispersed spherical nanoparticles can be also easily obtained by further chemical etching.³⁴ In this method, PDDA (Poly Diallyl Dimethyl Ammonium Chloride) is used as surfactants to synthesize gold nanooctahedron in ethylene glycol, then HAuCl₄ solution is added into the Au octahedra colloid as chemical etching agent, the shaper corner of Au nanooctahedra is removed and the shape of Au nanocrystal is changed from octahedra to sphere. Those PDDA-stabilized Au NPs with spherical shapes are perfect monodispersed and could be kept for a long time. Compared with the traditional micro-emulsion method, PDDA replaces the generally used surfactants such as cetyltrimethylammonium bromide (CTAB)³⁵ or cetyltrimethylammonium chloride (CTAC)^{36,37} as stabilizing agent.

However, the PDDA coated Au nanospheres dispersed in water possess a high zeta potential and such PDDA on nanospheres is difficult to be removed, resulting in a difficulty to further coat silica layer on their surface. This fact further causes the limitation of the applications of these monodispersed Au NPs. Therefore, until now, there has no report that PDDA-stabilized Au NPs can be coated with thin silica shell less than 10 nm. However, if the PDDA on the surface of Au NPs is removed completely, the Au NPs will agglomerate quickly. If those colloids can be further tailored by coating their surfaces with uniform, thin shells made of dielectric materials such as silica, those core-shell nanostructures could be extended to use them into many fields.

In this paper, we develop a novel method to remove partial PDDA on Au NPs by ultraviolet (UV) light irradiation to lower their zeta potential in solution, and then a thin silica shell was successfully coated on surface of Au NPs to form the core-shell structure by sol-gel route. We used UV light to irradiate the Au NPs in order to break down a part of the PDDA, then silica coatings on Au nanospheres by using base-catalyzed hydrolysis of tetraethyl orthosilicate (TEOS) to generate silica sols, followed by nucleation and condensation of these sols onto the surfaces of Au NPs without any silane coupling agent. By this strategy, the silica coating on Au nanospheres could be tuned from 2 nm to 8 nm by controlling concentration of TEOS. Such controlled silica thickness on monodispersed Au spherical nanoparticles has important applications in SERS enhancement after self-assembled into monolayer particle arrays and removed the silica layers by reactive ion etching.

2. Experimental section

2.1 Materials

Poly Diallyl Dimethyl Ammonium Chloride (PDDA, Mw-400 000–500 000), hydrogen tetrachloroaurate (HAuCl₄),

ethylene glycol, 2-propanol, tetraethyl orthosilicate (TEOS) and ammonia (28%) were all purchased from Sinopharm. All solutions were prepared using deionized water from a MilliQ system.

2.2 Method

2.2.1 The synthesis of PDDA-stabilized monodispersed Au spherical nanoparticles. PDDA-stabilized Au NPs (120 nm in diameter) were synthesized following a reported method.^{33,34,38} In a typical synthesis, a 0.4 mL portion of PDDA was introduced into 49 mL of ethylene glycol solution in a glass vial. The mixture was vigorously stirred with a magnetic blender for 1–2 min at room temperature and ambient conditions. A 0.025 mL of 0.5 M HAuCl₄ (0.0125 mmol) aqueous solution was introduced into above solution under stirring. The bottle containing the as-prepared gold precursor solution was sealed and subsequently heated at 195 °C in an oil-bath for 30 min, which is close to the boiling point of ethylene glycol, 198 °C. Then HAuCl₄ (0.0125 mmol) solution was added into the above mixture solution for 2 min for further chemical etching, and a red color of solution appeared.

2.2.2 Preparing silica coating on Au spherical nanoparticles. The as prepared Au spherical NPs were washed by centrifugation at 15 000 rpm with deionized water twice to remove the excess PDDA. The purified PDDA-stabilized Au NPs were redispersed in 5 mL deionized water to make a solution. Then ultraviolet (UV) lamp with main wavelength 184 and 256 nm (power, 10 W) directly irradiated the above solution for 30 min. And then a mixture of 8.7 mL of 2-propanol (AR) mixed and 50 μL of ammonia (28%) was added into the prepared gold colloidal solution to keep the pH about 10. After 1 min, 2.4 μL of tetraethyl orthosilicate (TEOS) dissolved in 1.2 mL of 2-propanol was slowly added into solution drop by drop, and the mixture solution was vigorously stirred for 2 h at room temperature to ensure complete polymerization of silica. The product was separated by centrifugation at 3000 rpm for 5 min and then dispersed in deionized water. Further growth of the silica shells would require adding more silica sources into the reaction system.

2.3 Characterization

The morphologies of Au NPs and Au@SiO₂ NPs were characterized by scanning electron microscopy (SEM) (Sirion 200 FEG) and transmission electron microscopy (TEM) (JEM-2010 transmission electron microscope). The crystallinity of PDDA-stabilized Au NPs was characterized by powder X-ray diffraction (XRD, Philips X'pert Pro). The absorbance spectra were examined by the ultraviolet (UV)-vis spectrophotometry (Cary 500, Varn). The zeta potentials of pure Au NPs and UV light irradiated Au NPs in solution were characterized by zeta potential instrument (Zetasizer 3000hs, Malven). Infrared and Raman Spectrum of the PDDA-stabilized Au NPs without ultraviolet light treatment and after treated by UV light irradiation was examined by Fourier transform infrared – Raman spectroscopy (Nexus, Nicolet), XPS (X-ray photoelectron

spectroscopy) spectra were characterized by a instrument of ESCAIBMK2 used Al K α to stimulate the sample.

3. Results and discussion

3.1 PDDA-stabilized Au spherical nanoparticles

We used a modified polyol process to prepare the monodispersed, uniform Au nanooctahedra. Monodispersed spherical nanoparticles were obtained by further chemical etching, as shown in Fig. 1a and b. The results indicate that all of the products are spherical nanoparticles with narrow size distribution (average size: 116.5 ± 11.3 nm Fig. 1c). XRD pattern indicates that they are Au nanocrystals (Fig. 1d). Moreover, this synthetic procedure is convenient and it has advantages of no seeds, no foreign metal ions, and no pretreatment of the precursor.

3.2 Structural characterization of Au@SiO₂ core-shell nanoparticles

The PDDA stabilized Au spherical nanoparticles was irradiated by UV light for 30 min. Using the tetraethyl orthosilicate (TEOS) as precursor, the polymerization reaction of silica was applied on such UV light irradiated sample. The corresponding TEM image was shown in Fig. 2a. It indicates that core-shell nanoparticles with the uniform shell thickness of about 4 nm were obtained. The TEM image of core-shell nanoparticles with a large scale was shown in Fig. S1 (ESI[†]). Energy dispersive

spectrum (EDS) analysis for such core-shell nanoparticle confirms that the core-shell particles consisted of Au, Si, O (see Fig. 2b, the copper element come from TEM copper grid). The EDS reflects that a silica coating was formed on Au nanospheres. Our results indicate that the PDDA-stabilized Au NPs were treated by UV light, thin silica shells could be created on Au spherical nanoparticles.

In such Au@SiO₂ core-shell structures, the shell thickness would affect physical and chemical properties of nanoparticles. For example, silica layer could improve the physical, mechanical and chemical stability of Au NPs, with the continuous increase of silica shell thickness, its stable performance was getting better and better. The shell thickness of the Au@SiO₂ core-shell particles can be tuned by using different TEOS concentrations (see Fig. 3 and Fig. S2[†]). The TEOS concentrations of the stock solutions used in the reaction were 0.1, 0.2, 0.3, and 0.4 vol% in 1.2 mL 2-propanol with pH value of 10 for 2, 4, 5, and 8 nm silica shell thicknesses, respectively.

The optical properties of Au@SiO₂ core-shell nanoparticles were characterized using UV-visible spectroscopy, as shown in Fig. 4. Both original PDDA stabilized Au spherical nanoparticles and UV light irradiated Au nanospheres with silica shell showed surface plasmon resonance (SPR) absorption peaks centered at about 570 nm. Due to the light-admitting character of silica, the optical properties of Au cores did not change so much after coating silica shell and Au@SiO₂ nanoparticles still had a strong absorption. Although silica-coated samples with a thin shell did not show noticeable peak shift, a slight red-shift of the

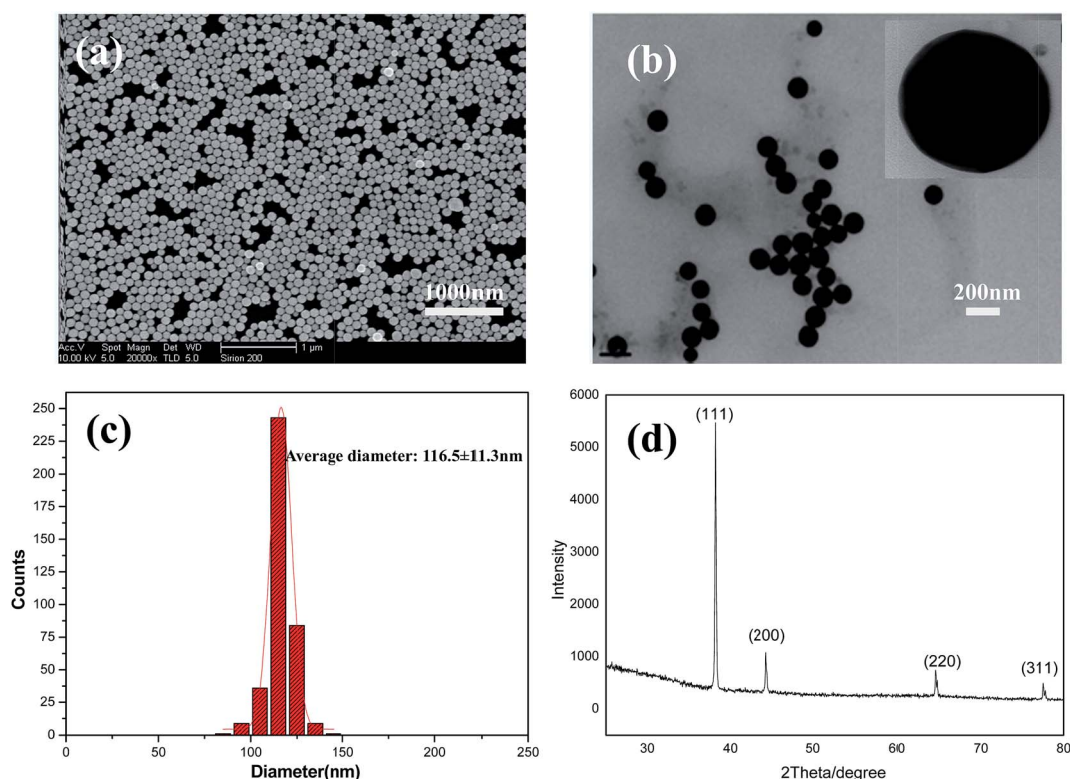


Fig. 1 (a) Field emission scanning electron microscope (FESEM) image of the original PDDA-stabilized Au NPs by a modified polyol process. (b) Corresponding transmission electron microscope (TEM) image. (c) Particle size distribution of Au nanospheres. (d) XRD of Au nanocrystals.

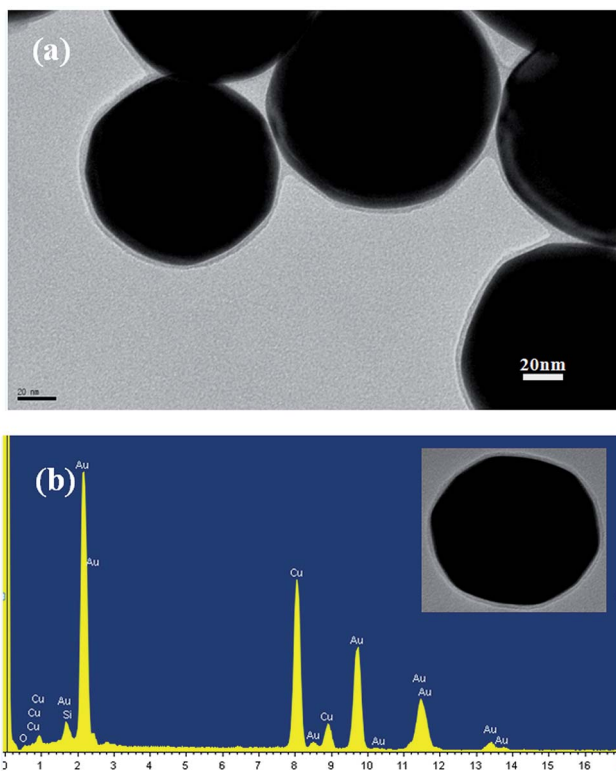


Fig. 2 (a) TEM image of core-shell nanoparticles obtained by UV light irradiated PDDA stabilized Au NPs and subsequent the polymerization reaction of silica under the pH = 10, 0.2 vol% in 1.2 mL 2-propanol. (b) The corresponding energy dispersive spectrum of as-prepared sample (a).

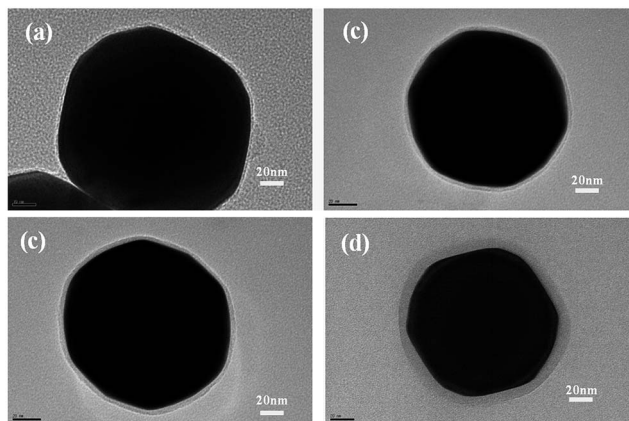


Fig. 3 TEM images of Au@SiO₂ core-shell particles with different shell thicknesses under the pH = 10, (a) 2 nm with 0.1 vol% in 1.2 mL 2-propanol, (b) 4 nm with 0.2 vol% in 1.2 mL 2-propanol, (c) 5 nm with 0.3 vol% in 1.2 mL 2-propanol, (d) 8 nm with 0.4 vol% in 1.2 mL 2-propanol.

SPR peak was observed with increasing silica thickness, because the refractive index of silica is slightly higher than that of water.

The pH of the mature solution also had an important influence on the growth and integrity of silica shells. During the reaction, ammonia was used as catalyst and it affected the reaction rate. If the pH of solution was greater than 11, the hydrolysis rate of TEOS was so fast that separated silica particles

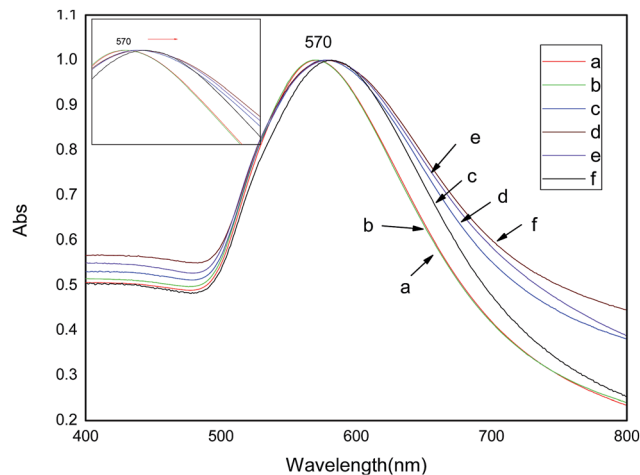


Fig. 4 UV-vis absorption spectra of (a) the original PDDA stabilized Au NPs, (b) UV light irradiated Au NPs with silica shell, (c–f) Au@SiO₂ core-shell particles with different shell thickness. shell thickness: (c) 2 nm, (d) 4 nm, (e) 5 nm, (f) 8 nm.

and uneven silica shell would be formed in Fig. 5. The reaction under pH value of 10 in solution proceeded relatively mild to guarantee a uniform thin silica shell on the surface of Au NP to be formed. Therefore, 50 μ L (ammonia 28%) was injected into solution to make the pH value approximately 10. By controlling the above factor, the growth of the uniform silica shell can be controlled.

3.3 Formation mechanism of silica shell on UV light irradiated PDDA stabilized Au spherical NPs

In most reported processes, citrate-stabilized gold nanoparticles^{35–37} or CTAB-stabilized gold nanoparticles²⁷ were used as the starting material for silica coating. However, such gold particles dispersed in solution were unstable and tended to aggregate quickly. The PDDA-stabilized Au NPs can overcome this problem and easily to preserve, because the molecular chain of PDDA with high positive charge density is not sensitive

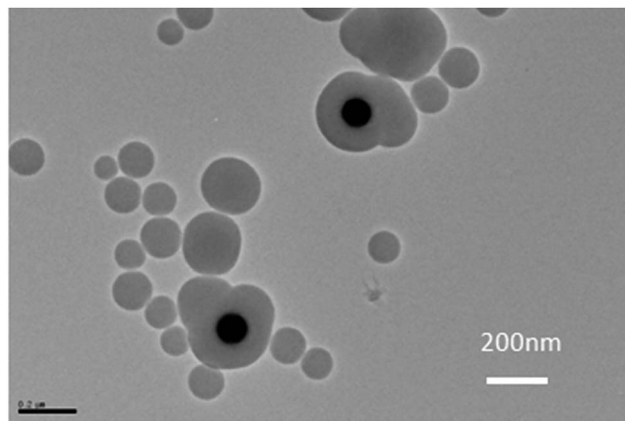


Fig. 5 TEM images of Au NPs with ultraviolet light treatment (controlling the rates of TEOS solution drop by drop) reacting at the pH of 11, 0.2 vol% of TEOS in 1.2 mL 2-propanol.

to the pH value. We detected the zeta potential of pure PDPA-stabilized Au NPs (see Fig. S3†) and observed the zeta potential more than 36.7 mV under the pH of 7.

Generally, negative colloidal particle will be formed in hydrolytic process of TEOS using ammonia as catalyst. The PDPA stabilized Au nanoparticles possess rich positive charges and their solution has a high positive zeta potential of 36.7 mV. Such positive zeta potential will lead to a rapid interaction between negative silica colloids and positive Au nanoparticles with PDPA on their surface due to strong attraction between each other, hence it makes it difficult to well control the deposit process of negative silica colloids with uniform thickness on PDPA stabilized Au nanoparticles, especially for thin thickness less than 10 nm. We found that, for the Au NPs without ultraviolet light treatment, the silica shell was not uniform, and the nanoparticles were agglomerated in Fig. 6.

However, after UV light irradiation for 30 min, we observed the zeta potential of Au NPs became significantly lower (See Fig. S3†) and it was changed from previous 36.7 mV to 14.7 mV. Because PDPA with dual olefinic bond can intensely absorb the light of the wavelength of 256 and 182 nm, and the covalent bond become very unstable. The infrared spectrum of the PDPA-stabilized Au NPs and without ultraviolet light treatment and after treated by UV light irradiation for 30 min was shown in Fig. S4.† The FTIR spectrum of PDPA shows some characteristic peaks at near 2940 cm^{-1} (C–H stretching vibration from the methyl), the weak peaks from 1410 to 1450 cm^{-1} (C–H bending vibration of methyl and methylene), the peaks of 1088 and 1041 cm^{-1} (the stretching vibration of C–N), and 883 cm^{-1} (the bending vibration of =C–H). The absorption peak at 1635 cm^{-1} in two lines is stretching vibration of C=C, which comes from the unsaturated impurity existing in PDPA chain. The absorption peak at 3440 cm^{-1} corresponds to the hydroxyl (–OH), because of the water absorbed on the sample. However, some peaks (1088 cm^{-1} , 883 cm^{-1}) of the sample which was treated by UV light irradiation for 30 min were disappeared, thus it suggests that parts of PDPA on Au nanoparticle surface might have been degraded.

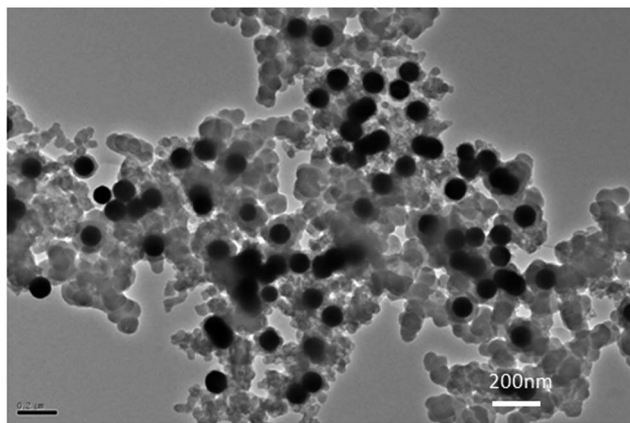


Fig. 6 TEM image of Au NPs without ultraviolet light treatment under experimental conditions: pH = 10, 0.2 vol% of TEOS in 1.2 mL 2-propanol.

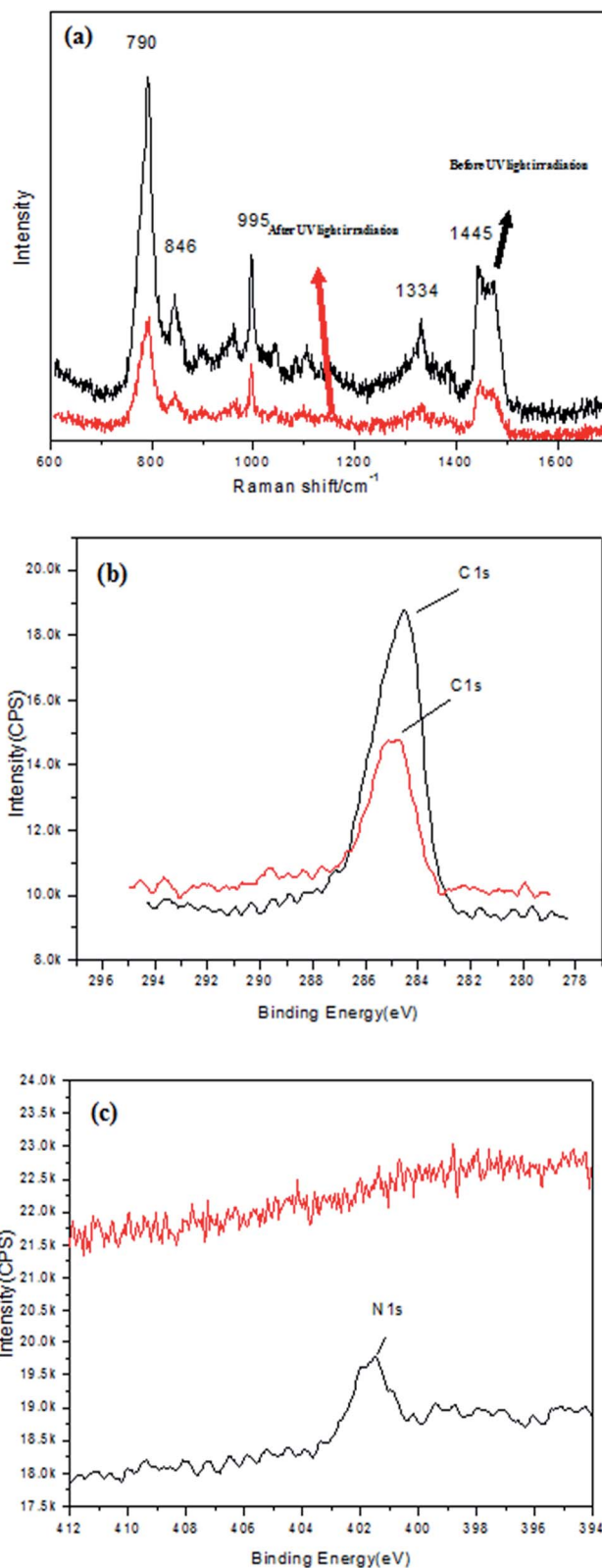


Fig. 7 (a) Raman Spectra of the PDPA-stabilized Au NPs in PDPA-stabilized Au NPs before (black line) and after (red line) UV light irradiation treatment for 30 min at the same sample. (b) and (c) the XPS spectra of C1s and N1s of PDPA-stabilized Au NPs, respectively.

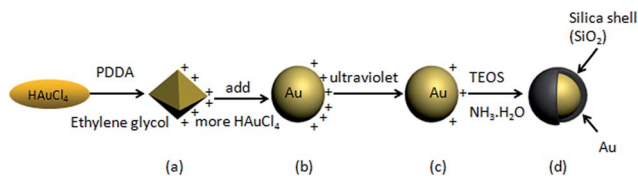


Fig. 8 Schematic illustration of formation of silica coating on PDDA stabilized Au nanoparticles by UV light irradiation. (a) PDDA-stabilized gold octahedral nanoparticles, (b) PDDA-stabilized gold spherical nanoparticles, (c) Au NPs treated by ultraviolet light, (d) Au@SiO₂ nanoparticles.

Raman spectra were further used to confirm such the degradation of PDDA under UV light irradiation. In Fig. 7a, the Raman spectrum of PDDA before UV light irradiation reflected some main characteristic peaks at 790, 846, 995, 1334, 1445 cm⁻¹, which originates from PDDA. After UV light irradiation, the Raman intensity of was much lower than before. XPS spectra of the elements (C and N) in PDDA-stabilized Au NPs before (black line) and after (red line) UV light irradiation were shown in Fig. 7b and c, one can find the intensity of C1s peak became weaker after ultraviolet light treatment (Fig. 7b) and N1s peak completely disappeared. The results of Raman spectra and XPS also suggested part of PDDA on the surfaces of Au nanoparticle was degraded under UV light irradiation. Such degradation of PDDA resulted in a lower the zeta potential. This low zeta potential still has ability to well disperse the Au nanospheres in solution and it is propitious to control deposition process of colloidal silica on the surface of Au nanoparticles. Therefore, the uniform silica coating could be formed from 2 nm to 8 nm on Au nanoparticle surfaces by controlling the TEOS concentration in our experiments.

Formation mechanism of silica shell on UV light irradiated PDDA stabilized Au spherical NPs was schematically illustrated in Fig. 8. The gold octahedral nanoparticles were first prepared by a modified polyol process in a facile sequential process commencing with the treatment of HAuCl₄ in ethylene glycol with the PDDA surfactant (Fig. 8a). When HAuCl₄ solution was added into the Au octahedra colloids, the shape of Au nanocrystal evolved from octahedron to sphere due to chemical etching effect (Fig. 8a–b). In order to reduce the zeta potential of PDDA-stabilized Au NPs, UV light was applied to degrade the partial PDDA (Fig. 8b–c). Finally, a resulted silica shell with various thickness of 2–8 nm was formed by different concentration of tetraethyl orthosilicate (TEOS) in alkaline conditions (Fig. 8c–d).

4. Conclusion

We develop a novel route to prepare silica coating on PDDA stabilized Au nanospheres assisted by UV light irradiation without use of a silane coupling agent as the surface primer. By this strategy, we overcome the challenge to make silica coating on PDDA stabilized Au nanoparticle and successfully achieve the monodispersed Au@SiO₂ nanospheres with controlled silica thickness from 2 to 8 nm. PDDA-stabilized Au

nanospheres with high positive zeta potential (36.7 mV) made it difficult to coat a layer of thin silica shell on them. In our route, UV light irradiation was used to treat PDDA stabilized Au nanoparticles and part of PDDA on Au nanoparticles could be degraded, hence their positive zeta potential is lowered to 14.7 mV, silica shell could be easily prepared on the surface of Au spheres under such low zeta potential. This is the first report to coat the silica layer on PDDA stabilized Au nanospheres. These monodispersed Au spherical nanoparticle controlled silica thickness have important applications in SERS applications, electrochemistry, biosensors *etc.*

Acknowledgements

The authors acknowledge the financial support from the National Basic Research Program of China (Grant no. 2012CB932303), Recruitment Program of Global Experts (C), Natural Science Foundation of China (Grant no. 51371165), Cross-disciplinary Collaborative Teams Program in CAS, CAS/SAFEA International Partnership Program for Creative Research Teams. C. Li as a Taishan Scholar Endowed Professor acknowledges the supports from Shandong province and UJN.

References

- 1 K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668–677.
- 2 I. Gavazzi, M. V. Nermut and P. C. Marchisio, *J. Cell Sci.*, 1989, **94**, 85.
- 3 J. Ge, Q. Zhang and T. Zhang, *Angew. Chem., Int. Ed.*, 2008, **47**, 8924–8928.
- 4 K. L. Kelly, E. Coronado, L. L. Zhao and G. C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668–677.
- 5 G. Mie, *Ann. Phys.*, 1908, **25**, 377–445.
- 6 V. Amendola and M. Meneghetti, *J. Phys. Chem. C*, 2009, **113**, 4277–4285.
- 7 P. N. Njoki, I. I. S. Lim, D. Mott, H. Y. Park, B. Khan, S. Mishra, R. Sujakumar, J. Luo and C. J. Zhong, *J. Phys. Chem. C*, 2007, **111**, 14664–14669.
- 8 T. G. Schaaff, M. N. Shafiqullin, J. T. Khoury, I. Vezmar, R. L. Whetten, W. G. Cullen, P. N. First, C. GutierrezWing, J. Ascensio and M. J. JoseYacaman, *J. Phys. Chem. B*, 1997, **101**, 7885–7891.
- 9 G. Hodes, *Adv. Mater.*, 2007, **19**, 639–655.
- 10 T. Huang and R. W. Murray, *J. Phys. Chem. B*, 2001, **105**, 12498–12502.
- 11 G. L. Wang, R. Guo, G. Kalyuzhny, J. P. Choi and R. W. Murray, *J. Phys. Chem. B*, 2006, **110**, 20282–20289.
- 12 D. Lee, R. L. Donkers, G. L. Wang, A. S. Harper and R. W. Murray, *J. Am. Chem. Soc.*, 2004, **126**, 6193–6199.
- 13 D. T. Miles and R. W. Murray, *Anal. Chem.*, 2003, **75**, 1251–1257.
- 14 B. M. Quinn, P. Liljeroth, V. Ruiz, T. Laaksonen and K. Kontturi, *J. Am. Chem. Soc.*, 2003, **125**, 6644–6645.
- 15 G. Carotenuto, G. P. Pepe and L. E. Nicolais, *J. Phys. B: At., Mol. Opt. Phys.*, 2000, **16**, 11.

- 16 T. A. Taton, C. A. Mirkin and R. L. Letsinger, *Science*, 2000, **289**, 1757–1760.
- 17 C. S. Holgate, P. Jackson, P. N. Cowen and C. C. Bird, *J. Histochem. Cytochem.*, 1983, **31**, 938–944.
- 18 M. Fleischmann, P. J. Hendra and A. J. McQuillan, *Chem. Phys. Lett.*, 1974, **26**, 163–166.
- 19 C. M. Ruan, W. Wang and B. H. Gu, *J. Raman Spectrosc.*, 2007, **38**, 568–573.
- 20 K. Kneipp, H. Kneipp, I. Itzkan, R. R. Dasari and M. S. Feld, *Chem. Rev.*, 1999, **99**, 2957–2976.
- 21 C. M. Ruan, W. Wang and B. H. Gu, *Anal. Chem.*, 2006, **78**, 3379–3384.
- 22 W. Wang, C. M. Ruan and B. H. Gu, *Anal. Chim. Acta*, 2006, **567**, 121–126.
- 23 X. M. Qian, X. H. Peng, D. O. Ansari, Q. Yin-Goen, G. Z. Chen, D. M. Shin, L. Yang, A. N. Young, M. D. Wang and S. M. Nie, *Nat. Biotechnol.*, 2008, **26**, 83–90.
- 24 D. Y. Wu, J. F. Li, B. Ren and Z. Q. Tian, *Chem. Soc. Rev.*, 2008, **37**, 1025–1041.
- 25 Y. Lu, Y. Yin, Z. Y. Li and Y. Xia, *Nano Lett.*, 2002, **7**, 785–788.
- 26 S. Liu and M. Han, *Adv. Funct. Mater.*, 2005, **15**, 961.
- 27 G. Frens, *Nature, Phys. Sci.*, 1973, **241**, 20–22.
- 28 J. Turkevitch, P. C. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55–75.
- 29 C. H. Munro, W. E. Smith, M. Garner, J. Clarkson and P. C. White, *Langmuir*, 1995, **11**, 3712–3720.
- 30 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, **7**, 801–802.
- 31 K. R. Brown, D. G. Walter and M. J. Natan, *Chem. Mater.*, 2000, **12**, 306–313.
- 32 Y. Han, J. Jiang, S. S. Lee and Y. Y. Jackie, *Langmuir*, 2008, **24**, 5842–5848.
- 33 C. C. Li, K. L. Shuford, Q. H. Park, W. P. Cai, Y. Li, E. J. Lee and S. O. Cho, *Angew. Chem., Int. Ed.*, 2007, **46**, 3264–3268.
- 34 C. C. Li, L. Sun, Y. Q. Sun and T. Teranishi, *Chem. Mater.*, 2013, **25**, 2580–2590.
- 35 F. X. Chen, G. Q. Xu and T. S. A. Hor, *Mater. Lett.*, 2003, **57**, 3282–3286.
- 36 P. G. Yin, T. T. You, E. Z. Tan, J. Li, X. F. Lang, L. Jiang and L. Guo, *J. Phys. Chem. C*, 2011, **115**, 18061.
- 37 M. Shen, Y. K. Du, P. Yang and L. Jiang, *J. Phys. Chem. Solids*, 2005, **66**, 1628–1634.
- 38 C. C. Li, K. L. Shuford, M. H. Chen, E. J. Lee and S. O. Cho, *ACS Nano*, 2008, **9**, 1760–1769.