Front. Chem. China 2009, 4(1): 44–47
DOI 10.1007/s11458-009-0005-z

RESEARCH ARTICLE

Caihong NIU, Ying WU, Zhenping WANG, Zheng LI, Rong LI

Synthesis and shapes of gold nanoparticles by using transition metal monosubstituted heteropolyanions as photocatalysts and stabilizers

© Higher Education Press and Springer-Verlag 2009

Abstract Gold nanoparticles were prepared via a simple photoreduction technique in the presence of transition metal monosubstituted Keggin heteropolyanions (PW11M, M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}), in which PW11M acted as reducing agent, photocatalyst and stabilizer. The results indicated that the formation rate and morphology of the nanoparticles strongly depended on the kind of transition metal substituted in heteropolyacid and the preparation conditions, such as irradiation time and propan-2-ol amount. The photoreduction rates of PW11Zn and PW11Fe were faster than those of PW11Ni and PW11Cu. The shapes of the nanoparticles synthesized in the presence of PW11Fe and PW11Zn were nearly uniform spheres, whereas the morphologies of the nanoparticles synthesized in the presence of PW11Ni and PW11Cu were found to contain a mixture of flat triangular/hexagonal structures as well as spheres. Increases in the irradiation time and the propan-2-ol amount could make the morphology of nanoparticles uniform and shorten the formation time of the nanoparticles.

Keywords heteropolyanion, photoreduction, gold nanoparticle

Polyoxometalates are remarkable in chemical, structural and electronic versatility. The redox chemistry of polyoxometalates is characterized by their ability to undergo stepwise, multielectron reversible redox reactions without structure alteration [1,2]. The best known of the structural types of polyoxometalate is the Keggin heteropoly acid, which can be reduced in a plethora of ways, for example, photochemically, electrolytically, and with reducing reagents [1,3,4]. A novel and facile method has been proposed to synthesize metal nanoparticles directly in aqueous solutions by use of Keggin polyoxoanions to serve as reducing reagents, photocatalysts, and stabilizers. Troupis, Hiskia, and Papaconstantinou [5,6] demonstrated that several metal ions (Ag^-, Pd^{2+}, Au^{III}, and Pt^{IV}) could form metal nanoparticles in the presence of photochemically reduced Keggin heteropolyanions $[SiW_{12}O_{40}]^{5-}$ and $[PW_{12}O_{40}]^{4-}$. Mandal and coworkers [7] reported that photochemically generated $[PW_{12}O_{40}]^{4-}$- capped gold nanoparticles enable the reduction of Ag^+ on the surface of the gold nanoparticles to form Au-Ag core-shell bimetallic nanoparticles under further irradiation from UV light. The best characteristic of the method is that the reaction proceeds at room temperature within seconds and utilizes a mild reductant, Keggin heteropolyanion.

It is well known that the relative rates of photoreduction of the Keggin heteropolyanions mainly depend on their redox potentials. When the concentrations of heteropolyanions in the solution, for example $PW_{12}O_{40}{}^{4-}$, $SiW_{12}O_{40}{}^{5-}$, are adjusted to be the same, the relative rates of photoreduction of the heteropolyanions follow the order $SiW_{12}O_{40}{}^{5-} > PW_{12}O_{40}{}^{4-}$, in accordance with the redox potentials of the heteropolyanions: $E^o(SiW_{12}O_{40}{}^{4-/5-}) = 0.057$ V and $E^o(PW_{12}O_{40}{}^{3-/4-}) = 0.221$ V versus NHE [8,9]. It can be anticipated that the redox properties of the substituted heteropolyanions will be different from the nonsubstituted heteropolyanions, and will affect the reaction of the formation of metal nanoparticles. To explore the effect of substituted heteropolyanions, we have used the family of transition metal monosubstituted heteropolyanions formulated as $[PW_{11}MO_{39}]^{n-}$ (M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) (short for $PW_{11}M$) that can be considered as derived from the nonsubstituted Keggin heteropolyanion $[PW_{12}O_{40}]^{3-}$ (abbreviated as $[PW_{12}]$) by simply replacing one of the external constituent atoms, W, and its terminal oxygen atom by a transition metal atom, M. The gold nanoparticles were prepared via a simple photoreduction technique in the presence of monosubstituted Keggin

---

Translated from *Chinese Journal of Applied Chemistry*, 2007, 24(7) (in Chinese)

Caihong NIU, Ying WU (✉), Zhenping WANG, Zheng LI, Rong LI
College of Chemistry and Chemical Engineering, Soochow University, Suzhou 215123, China
E-mail: yingwu@suda.edu.cn

heteropolyanion [$PW_{11}M$]. The results indicated that formation rate and morphology of the gold particles strongly depended on the kind of transition metal substituted in heteropolyacid and the preparation conditions, such as irradiation time and concentration of propan-2-ol.

1 Experimental section

1.1 Reagents

$H_3PW_{12}O_{40}\cdot xH_2O$, $HAuCl_4$ and propan-2-ol were purchased from Sinopharm Group Chemical Reagent Co., Ltd. $[PW_{11}MO_{39}]^{n-}$ (M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) were prepared following the method reported by He [10]. All other chemicals are reagent grade.

1.2 Apparatus

The morphology of the nanoparticles was measured on a Tecnai G2 20 Model transmission electron microscope (TEM) (FEI Co.). Absorption spectra were measured on a Shimadzu UV 2240 UV-Vis spectrophotometer.

1.3 Experimental procedures

A typical experiment was as follows: 5 mL 1×10^{-2} mol/L $PW_{11}M$, 10 mL 1×10^{-3} mol/L $HAuCl_4$ solution and 2 mL propan-2-ol were added to a beaker equipped with cool water circulating. The mixture solution was deaerated firstly, and then irradiated by UV light (500 W high voltage mercury vapor lamp) for a moment under continuous stirring. The color of the solution changed from colorless to blue, then to pink, indicating the formation of gold nanoparticles. The nanoparticles were separated by high speed centrifugation, and washed twice with water. The separated nanoparticles were finally redispersed in water.

2 Results and discussion

2.1 Effect of the kind of transition metal substituted in heteropolyacid

Figure 1(a) and (b) show the UV-Vis spectra of the gold nanoparticle solutions synthesized in the presence of $PW_{11}M$ (M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+}) irradiated for 40 min and 90 min, respectively. The 530 nm bands are attributed to the surface plasmon resonance (SPR) in spherical gold particles. It can be seen that (Fig. 1): in the first 40 min of irradiation time the SPR bands of the spherical gold particles could be observed with the photocatalysts $PW_{11}Fe$ and $PW_{11}Zn$, while there were no changes in the absorption spectra in the presence of photocatalysts $PW_{11}Cu$ and $PW_{11}Ni$. It is suggested that the photoreduction rates of photocatalysts $PW_{11}Zn$ and $PW_{11}Fe$ were faster than those of photocatalysts $PW_{11}Ni$ and $PW_{11}Cu$. However, at the prolonged irradiation time of 90 min, the SPR bands of the spherical gold particles were all observed. It should be noticed that the SPR bands were broad and there was a red shift to 550 nm in the presence of photocatalysts $PW_{11}Cu$ and $PW_{11}Ni$.

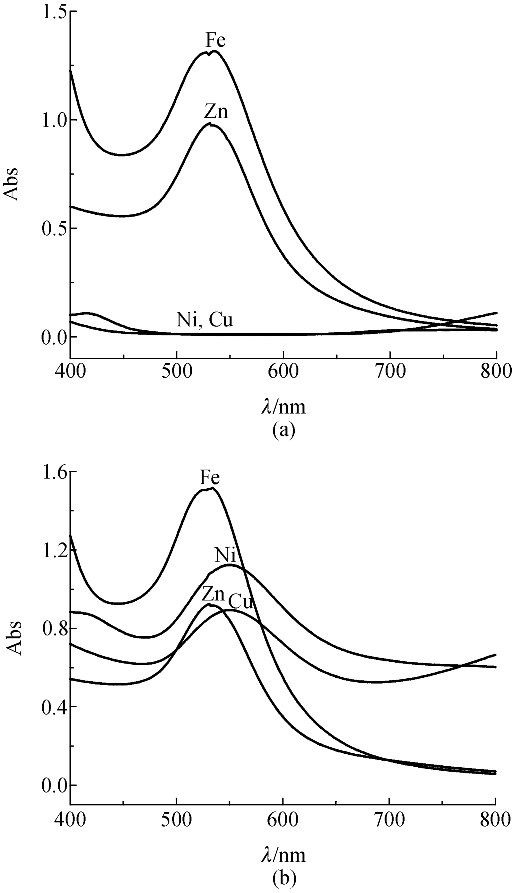
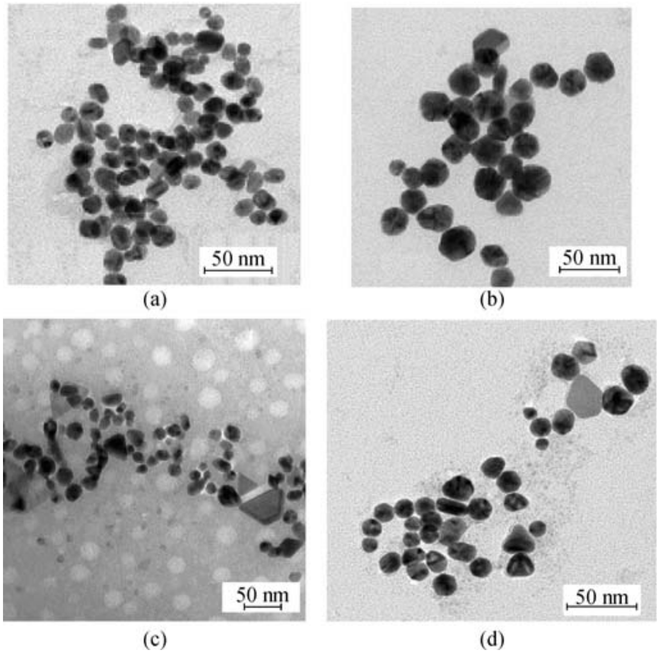


Fig. 1 UV-Vis spectra of the gold nanoparticle solutions synthesized in the presence of $PW_{11}M$. (M = Zn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}) with irradiation time 40 min (**a**) and irradiation time 90 min (**b**)

The gold nanoparticles obtained were characterized by TEM. The representative TEM images are shown in Fig. 2. The shapes of the gold nanoparticles obtained in the presence of photocatalysts $PW_{11}Fe$ and $PW_{11}Zn$ were nearly uniform spheres [Fig. 2(a) and (b)], similar to the shape of the nanoparticles obtained in the presence of photocatalysts SiW_{12} and PW_{12} [5,7], whereas the morphologies of the nanoparticles synthesized in the presence of photocatalysts $PW_{11}Ni$ and $PW_{11}Cu$ were found to contain a mixture of flat triangular/ hexagonal structures as well as spheres [Fig. 2(c) and (d)]. The results are consistent with UV-Vis spectra analysis of the gold nanoparticles obtained in the presence of photocatalysts $PW_{11}Ni$ and $PW_{11}Cu$. The broad and red-shifted SPR bands of gold nanoparticles are due to the coexistence with polygonal shaped nanoparticles.



(a) (b) (c) (d)

Fig. 2 TEM images of gold nanoparticles obtained in the presence of $PW_{11}M$. (**a**) Synthesized by $PW_{11}Fe$, irradiation time 40 min; (**b**) synthesized by $PW_{11}Zn$, irradiation time 40 min;(**c**) Synthesized by $PW_{11}Ni$, irradiation time 90 min; (**d**) synthesized by $PW_{11}Cu$, irradiation time 90 min.

In the previous studies of Sastry [11,12] they suggested that the formation of the gold nanotriangles is a kinetically driven process and is a result of aggregation and rearrangement of smaller-sized particles, which act as the nuclei for further growing into anisotropic, triangular structures. The low rate of reduction of gold ions using the photocatalysts $PW_{11}Ni$ and $PW_{11}Cu$ might possibly facilitate the oriented growth of the nuclei and thus should promote the formation of anisotropic nanoparticles. We have also observed that the gold nanoparticles synthesized in the presence of photocatalysts $PW_{11}Fe$ and $PW_{11}Zn$ are extremely stable. The lifetime of the nanoparticles obtained using photocatalyst $PW_{11}Fe$ is even longer than for months without any observable change at room temperature. In contrast, the aggregation and precipitation of the anisotropic gold nanoparticles obtained in the presence of photocatalysts $PW_{11}Ni$ and $PW_{11}Cu$ take place easily.

2.2 Effect of the preparing conditions

As discussed in previous studies [11,13], the formation rate and morphology of the nanoparticles strongly depend on the properties of the material and the types of reductant. Besides this, preparation conditions have a very important role in the synthesis of nanoparticles, such as irradiation time, the amount of reductant, the reaction temperature, stirring rate and coexisting ions.

Figure 3 shows the UV-Vis absorption spectra of the gold nanoparticle solution synthesized in the presence of photocatalyst $PW_{11}Fe$ with increasing irradiation time. Before irradiation, curve a in Fig. 3 shows that there was no distinct absorption band in the wavelength range of 400 nm to 800 nm in the spectrum. After UV light irradiation for 20 min, the UV-vis spectrum in this solution (curve b, Fig. 3) shows an SPR band of gold nanoparticles at around 530 nm. The color of the solution changed from colorless to blue pink, then to bluish-red, indicating formation of gold nanoparticles. The tail of the UV-vis spectrum (from 600 nm to 800 nm) raised is due to the absorption of reduced $PW_{11}Fe$ (curve b, Fig. 3), the

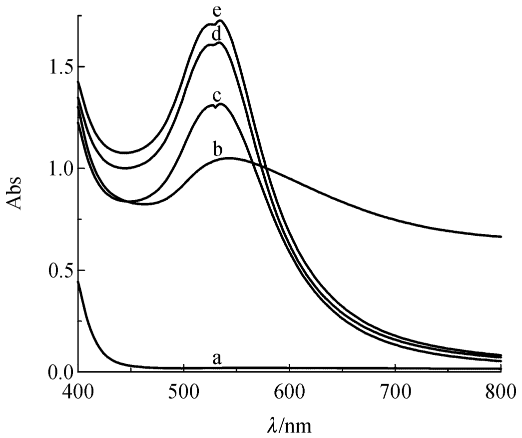


Fig. 3 UV-Vis spectra of the gold nanoparticles solutions synthesized in the presence of $PW_{11}Fe$ Irradiation time/min: (**a**) 0; (**b**) 20; (**c**) 40; (**d**) 60; (**e**) 90

characteristic of one-electron-reduced Keggin polyoxometalate [5]. With the irradiation time increasing, the SPR band of gold nanoparticles at 530 nm developed gradually, and the absorption of reduced $PW_{11}Fe$ was damped (curves c, d, e, Fig. 3). The results suggest that prolonging irradiation time will promote generation of reduced $PW_{11}Fe$, which results in a certain amount of gold nanoparticle formation. With overextended irradiation times, the gold nanoparticles become too large to be stable, and cause aggregation and precipitation easily.

Figure 4 demonstrates the effect of the amount of propan-2-ol on the formation rate and morphology of the nanoparticles in the presence of photocatalyst $PW_{11}Ni$. When the amount of propan-2-ol is smaller than 1 mL, there are no gold nanoparticles obtained (curves a, b, Fig. 4). When the amount of propan-2-ol reaches 2 mL, the SPR band of obtained gold nanoparticles is observed at 550 nm, and it develops with increasing amounts of propan-2-ol (curve c, Fig. 4). When the amount of propan-2-ol reaches 5 mL and after UV light irradiation for 20 min, the mixture solution changes color to light pink easily. The SPR band of obtained gold nanoparticles shows an increasing and blue shift to 530 nm (curve d, Fig. 4). The TEM picture reveals that the gold nanoparticles obtained in the presence of photocatalyst $PW_{11}Ni$ were nearly uniform spheres (Fig. 5), which is different from Fig. 2c (using 2 mL of propan-2-ol) obviously. The results indicated that high concentrations of propan-2-ol could speed up the formation process of the gold nanoparticles.

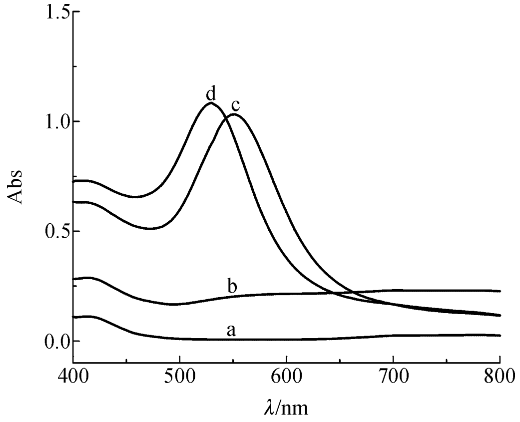


Fig. 4 UV-Vis spectra of the gold nanoparticles obtained in the presence of $PW_{11}Ni$ using different amounts of propan-2-ol V (propan-2-ol)/mL: (**a**) 0.2; (**b**) 1.0; (**c**) 2.0; (**d**) 5.0

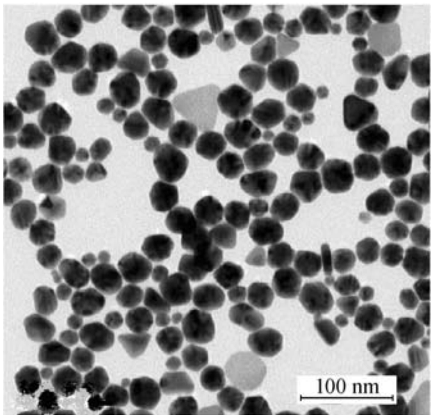


Fig. 5 TEM image of gold nanoparticles synthesized in the presence of $PW_{11}Ni$ using 5.0 mL propan-2-ol

References

1. Papaconstantinou E. Photochemistry of Polyoxometallates of Molybdenum and Tungsten and/or Vanadium. Chem Soc Rev, 1989, 18: 1–31
2. Wang E B, Hu C W, Xu L. Introduction to polyacid chemistry. Beijing: Chemical Inductry Press, 1998, 87
3. Toshihiro Yamase. Photo- and Electrochromism of Polyoxometalates and Related Materials. Chem Rev, 1998, 98(1): 307–325
4. Weinstock I A. Homogeneous-Phase Electron-Transfer Reactions of Polyoxometalates. Chem Rev, 1998, 98(1): 113–170
5. Troupis A, Hiskia A, Papaconstantinou E. Synthesis of Metal Nanoparticles by Using Polyoxometalates as Photocatalysts and Stabilizers. Angew Chem Int Ed, 2002, 41(11): 1911–1914
6. Mandal S, Das A, Srivastava R, and Sastry M. Keggin Ion Mediated Synthesis of Hydrophobized Pd Nanoparticles for Multifunctional Catalysis. Langmuir, 2005, 21(6): 2408–2413
7. Mandal S, Selvakannan P R, Pasricha R, Sastry M. Keggin Ions as UV-Switchable Reducing Agents in the Synthesis of Au Core-Ag Shell Nanoparticles. J Am Chem Soc, 2003, 125(28): 8440–8441
8. Troupis A, Hiskia A, Papaconstantinou E. Photocatalytic Reduction and Recovery of Copper by Polyoxometalates. Environ Sci Technol, 2002, 36(24): 5355–5362
9. Troupis A, Hiskia A, Papaconstantinou E. Selective photocatalytic reduction–recovery of palladium using polyoxometallates. Applied Catalysis B: Environmental, 2004, 52: 41–48
10. He H M, Sun T, Jiang D Z. Study on Preparation and Characterization of Hydrotalcites Pillared with Tri-atomic Heteropoly Anions of P-W System.Chinese Journal of Inorganic Chemistry, 1994, 10(3): 272–277 (in Chinese)
11. Shankar S S, Rai A, Ahmad A, Sastry M. Controlling the Optical Properties of Lemongrass Extract Synthesized Gold Nanotriangles and Potential Application in Infrared-Absorbing Optical Coatings. Chem Mater, 2005, 17(3): 566–572
12. Rai A, Singh A, Ahmad A, Sastry M. Role of Halide Ions and Temperature on the Morphology of Biologically Synthesized Gold Nanotriangles. Langmuir, 2006, 22(2): 736–741
13. Sarma T K and Chattopadhyay A. Starch-Mediated Shape-Selective Synthesis of Au Nanoparticles with Tunable Longitudinal Plasmon Resonance. Langmuir, 2004, 20(9): 3520–3524