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Preparation of Gold Nanoparticles Protected with Polyelectrolyte

Xu Ping SUN[1,2], Zhe Ling ZHANG[1], Bai Lin ZHANG[1], Xian Dui DONG[1],
Shao Jun DONG[1]*, Er Kang WANG[1,]*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022
[2]Department of Chemistry, Sichuan Normal College, Nanchong 637002

Abstract: Gold nanoparticles were synthesized through the reduction of tetrachlorauric acid ($HAuCl_4$) by $NaBH_4$, with polyethyleneimine(PEI) as stabilizer. The nanoparticles were characterized by UV-vis spectroscopy and atomic force microscopy(AFM).

Keywords: Gold nanoparticle, polyelectrolyte, UV-vis spectroscopy, AFM.

Metal nanoparticles protected by polymers can be highly useful for a variety of applications[1,2]. Heller *et al.* have demonstrated the “steric” stabilization of colloidal solutions by adsorption of flexible macromolecules[3]. Pugh *et al.* have confirmed the stabilization of colloidal solution with polyelectrolytes which are capable of combining both steric and electrostatic stabilization[4]. Mayer *et al.* have synthesized silver nanoparticles in the presence of cationic polyelectrolytes[5]. Liu *et al.* have prepared gold nanoparticles encapsulated with PDDA[6]. Henglein has synthesized silver nanoparticles where various polymer stablizers were tried, the result was that nanoparticles with the most narrow size distribution and best optical properties were obtained when Polyethyleneimine(PEI) was used as stablizer[7].

In this work, we synthesize gold nanoparticles through the reduction of $HAuCl_4$ by $NaBH_4$ in the presence of branched PEI, UV-vis spectroscopy and AFM confirmed that the gold nanoparticles were well-dispersed, highly stable and positively charged.

Experimental

All aqueous solutions were prepared with ultrapure water($18M\Omega.cm^{-1}$, Millipore system), $HAuCl_4$, branched PEI(Average Mw:25,000) obtained from Aldrich and $NaBH_4$ bought from Sanpu chemical engineering Ltd. Corp (Shanghai, China) were used without further purification.

Colloids were synthesized as follows: 80 µL $HAuCl_4$(1.24%) was added into 10 mL

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[*] E-mail: dongsj@ns.ciac.jl.cn. ekwang@ns.ciac.jl.cn

distilled water, after stirring for one minute, 20 μL PEI(18.3%) was added into the mixture, with stirring for one minute, then the $NaBH_4$ solution was added drop-by-drop until the mix turned red with vigorous stirring, and kept stirring for five minutes , then stored at 4°C.

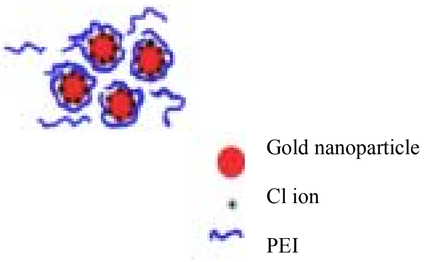
The optical spectra of colloidal gold were acquired on CARY 500 Scan UV-vis-NIR Spectrophotometer. AFM image was acquired using a Digital Instrument Nanoscope IIIa in Contact Mode, a freshly cleaved mica(1.5 cm×1.5 cm) was immersed in 10 mL colloid solution for 1h, then dried under air atmosphere for AFM characterization.

Results and Discussion

PEI is a highly branched aliphatic polyamine whose amine groups exist in primary, secondary and tertiary forms. A most prominent feature of PEI is its extremely high cationic charge density which was used to protect gold nanoparticles in this work.

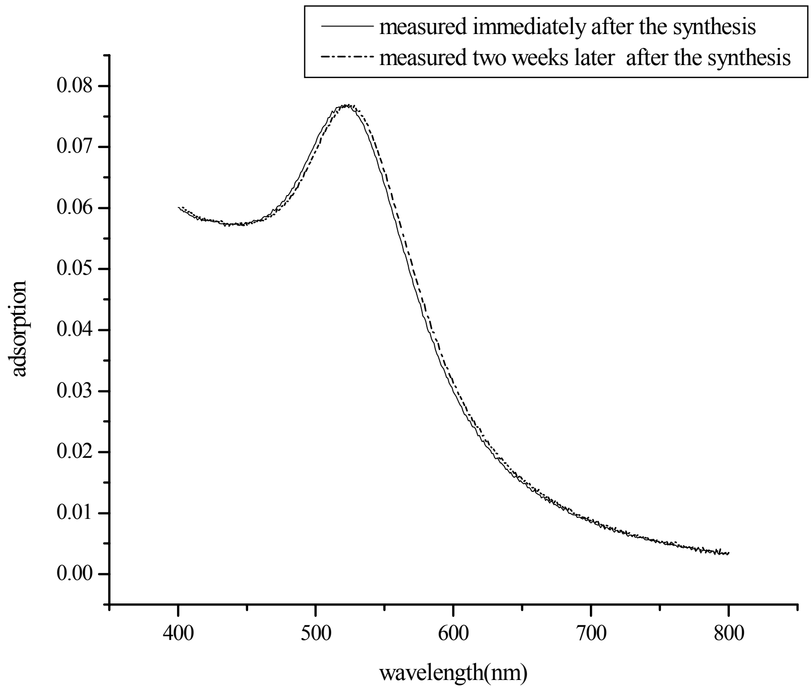
When $NaBH_4$ was added, colloidal nucleation was achieved and began to grow. At first, Cl^- was adsorbed on the surface of colloids, resulting in the negatively charged colloids. Under vigorous stirring, PEI diffused quickly to the colloids and was adsorbed on the surface of colloids because of the electrostatic interactions between positively charged PEI and negatively charged colloids which resulted in positively charged colloids. The high cationic charge density and the "steric" effect of PEI kept each nanoparticles apart which resulted in the formation of stable colloids(**Figure 1**).

Figure 1 Gold nanoparticls encapsulated with Cl^- and PEI



UV-vis spectra of as-prepared colloids characterized were shown in **Figure 2**. The solid line was the result measured immediately after the synthesis, and the dash line was the result measured two weeks after the synthesis. The sharp peak indicated the colloids well-dispersed. From the maximum adsorption at 520 nm we canconclude the size of colloid is about 12 nm in diameter[8]. A negligible red shift after two weeks confirmed that the colloids were still stable.

Figure 2 UV-vis spectroscopy of colloids measured immediately(solid line) and two weeks later(dash line)

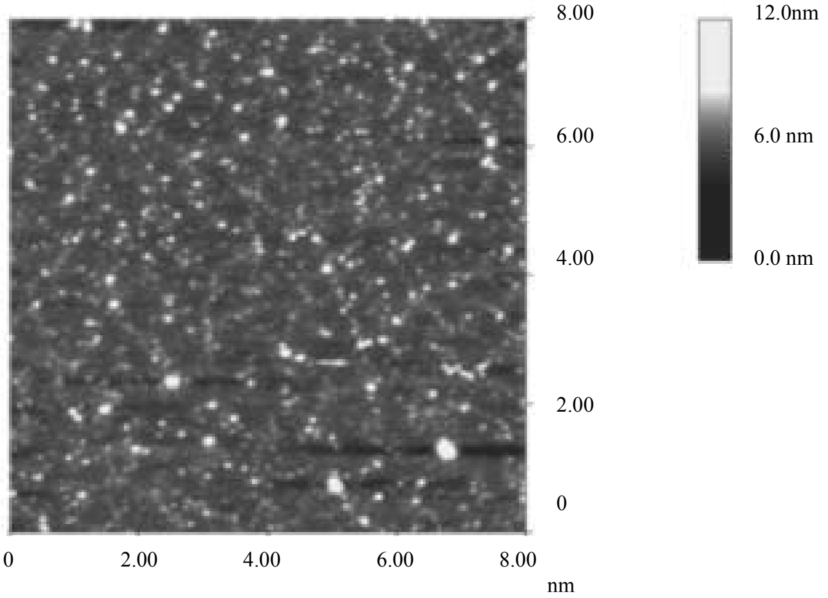


AFM image is shown in **Figure 3**. In general, mica is negative and cannot easily adsorb negatively charged particles because of electrostatic repulsion. However there were a large number of colloids adsorbed on mica within 1h, which showed that as-prepared colloids were positively charged, *i.e.*, colloids were indeed encapsulated with PEI.

Conclusions

In this work, we have synthesized gold nanoparticles protected with PEI. The results showed that as-prepared colloids are positively charged, well-dispersed and highly stable.

Figure 3 AFM image of gold nanoparticles absorded on mica(scan range:8 μm×8 μm)



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