Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 45 (2004) 2181–2184

polymer

www.elsevier.com/locate/polymer

One-step synthesis and characterization of polyelectrolyte-protected gold nanoparticles through a thermal process

Xuping Sun, Shaojun Dong, Erkang Wang*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5626, Changchun, Jilin 130022, People's Republic of China

Received 1 November 2003; received in revised form 28 December 2003; accepted 5 January 2004

Abstract

Polyelectrolyte-protected gold nanoparticles have been facilely obtained by heating an amine-containing polyelectrolyte/$HAuCl_4$ aqueous solution without the additional step of introducing other reducing agents. All experimental data indicate that different initial molar ratio of polyelectrolyte to gold can lead to the formation of dispersed nanoparticles, quasi one-dimensional aggregates of nanoparticles or bulk metal deposits. More importantly, the growth kinetics of gold particles thus formed can be tuned by changing the initial molar ratio of polyelectrolyte to gold.

Keywords: One-step synthesis; Polyelectrolyte; Gold nanoparticles

1. Introduction

Nanoscale particles of noble metals hold promise for use as advanced materials with novel electronic, optical and thermal properties as well as catalytic properties due to their potential applications in the fields of physics, chemistry, biology, medicine, material science and their different interdisciplinary fields [1–3]. The synthesis and characterization of metal nanoparticles have thus attracted considerable attention from a fundamental and practical point of view [4–7]. To date, many methods including chemical reduction of metal salts, photolysis or radiolysis of metal salts, ultrasonic reduction of metal salts, displacement of ligands from organometallic compounds etc. have been used to prepare gold nanoparticles [8]. However, in situ chemical reduction of tetrachloroauric acid ($HAuCl_4$) precursor is still a general route. Since nanoparticles tend to be fairly unstable in solution, special precautions have to be taken to avoid their aggregation or precipitation. The most common strategy is the use of stabilizer, which not only prevents their aggregation, but also results in functionalized particles [9,10].

In recent years, the use of polyelectrolytes as building blocks for the creation of multilayer thin films has undergone rapid expansion because of the simplicity and wide variability of this method and the film thickness-controllable capability [11]. Polyelectrolytes are also used in industrial applications such as water filtration, paper making and mineral processing because of the fact that the adsorption of charged polyelectrolytes to oppositely charged colloids may turn intercolloidal repulsion into attraction and lead to flocculation [12]. However, Pugh et al. have confirmed the stabilization of colloids with polyelectrolytes which are capable of combining both steric and electrostatic stabilization resulting in electrosteric stabilization [13], and polyelctrolyte stabilized gold nanoparticles have been synthesized where the $AuCl_4^-$ precursor was reduced with the addition of a reductant such as BH_4^-, and polyelectrolytes acted only as a stabilizer [14,15]. More recently, Youk et al. have synthesized gold nanoparticles from a polyelectrolyte complex solution of terthiophene amphiphiles where the synthesized terthiophene derivative was used as reductant and poly(sodium 4-styrenesulfonate) was used to improve the solubility of the derivative [16]. However, the result was not satisfactory due to the time-consuming of preparation and the poor stability of as-prepared colloids.

---

* Corresponding author. Tel.: +86-4315262003; fax: +86-431-5689711. *E-mail address:* ekwang@ciac.jl.cn (E. Wang).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.01.010

To our knowledge, polyelectrolyte has never been used as reducing agent for the preparation of gold nanoparticles. We present herein that linear polyethylenimine (LPEI) shown in Fig. 1, a kind of cationic polyelectrolyte, can induce $HAuCl_4$ to spontaneously form gold nanoparticles via heating a LPEI/$HAuCl_4$ aqueous solution, with the use of LPEI to serve as reducing agent and protective agent. In additionally, different initial molar ratios of LPEI (repeating unit) to gold can lead to the formation of dispersed gold particles or quasi one-dimensional aggregates of gold particles, however, extreme molar ratios only result in the formation of bulk metal deposits.

2. Experimental

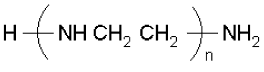
LPEI (molecular weight: 423) and $HAuCl_4$ were all purchased from Aldrich and used as received without further purification. All aqueous solutions were prepared with ultrapure water (18 M Ω cm^{-1}, Millipore system). Seven samples 1–7 were prepared as follow: In brief, 200 μl of $HAuCl_4$ (0.0243 mol/l), 20 ml of H_2O and the appropriate amount of LPEI with initial molar ratio 2:1, 3:1, 3.5:1, 5:1, 6.5:1, 8:1 and 9.5:1 of LPEI (repeating unit) to gold were added into seven respective weighing bottle, then heated at 60 °C for several minutes.

TEM measurements were made on a JEOL 2010 transmission electron microscopy operated at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared by place a drop of gold colloidal sample on carbon coated copper grid and dried at room temperature.

UV–vis spectra of the seven samples 1–7 and another two samples for in situ experiments were performed on a CARY 500 Scan UV–vis-near infrared (UV–vis-NIR) spectrophotometer.

3. Results and discussion

Seven samples 1–7 with corresponding initial molar ratio 2:1, 3:1, 3.5:1, 5:1, 6.5:1, 8:1 and 9.5:1 of LPEI (repeating unit) to gold were prepared to examine the influence of initial molar ratio on as-prepared nanoscale gold. Photograph of samples 1–7 is shown in Fig. 2. At molar ratio 3.5:1, 5:1, or 6.5, a purple or red color sample was obtained, giving evidence for the formation of dispersed gold nanoparticles [17]. However, lower molar ratio (2:1, 3:1) and higher molar ratio (8:1 and 9.5:1) resulted in blue or cyan colloid solution, suggesting the formation of particle aggregates [18], but serious aggregation was not noticed at these molar ratios. However, bulk gray metal deposits that precipitated from solution due to the coagulation of as-prepared particles were observed when initial molar ratio was lower than 1.5:1 or higher than 10:1.



$H{-}(NH\,CH_2\,CH_2)_n{-}NH_2$

Fig. 1. Chemical structure of LPEI.

Fig. 2. Photograph of seven samples 1–7 with initial molar ratio 2:1, 3:1, 3.5:1, 5:1, 6.5:1. 8:1 and 9.5:1 of LPEI (repeating unit) to gold (from left to right).

Fig. 3 shows typical TEM images of sample 1 (A), 4 (B) and 7 (C). Nanorods and large particles (~100 nm) with hexagonal shape are observed in sample 1, and these particles have a tendency to form quasi one-dimensional aggregates, as shown in Fig. 3(A). But at the initial molar ratio of 5:1, only dispersed nanoparticles (~25 nm in diameter) were obtained (Fig. 3(B)). Once the molar ratio was raised to 9.5:1, the formation of quasi one-dimensional aggregates are again noticed, as shown in Fig. 3(C).

The UV–vis absorption spectra of the freshly prepared seven samples are shown in Fig. 4. At the molar ratio of 2:1, two plasmon resonances can be clear seen at ~534 nm and ~702 nm which can be assigned to the transverse and longitudinal plasmon resonance, respectively [18], but the longitudinal plasmon resonance was more intense than the transverse plasmon resonance. At the molar ratio of 3:1, the intensity of transverse plasmon resonance grew and that of the longitudinal plasmon resonance decreased resulting in more intense transverse plasmon resonance. When the initial molar ratio was raised to 3.5:1, 5:1, 6.5:1 or 8:1, only the transverse plasmon resonance could be noticed. Once the molar ratio was changed to 9.5:1, two plasmon resonances, with the weak transverse plasmon resonance at ~538 nm and the strong longitudinal plasmon resonance at ~720 nm, occurred again. Yu et al. have attributed the longitudinal plasmon resonance to gold nanorod [19]. Willer and coworkers have found that gold nanoparticles aggregation can also result in the occurrence of longitudinal plasmon resonance due to interparticle plasmon coupling [20], which is also confirmed by another report [21]. We suggest that the most likely origin of the longitudinal plasmon resonance in our experiment is quasi one-dimensional aggregates, nanorods and large nanoparticles.

To gain further insight into the influence of the initial molar ratio on the growth kinetics of as-prepared gold particles, another two in situ UV–vis absorption experiments were performed at constant temperature 60 °C with the time interval of 60 s. Fig. 5 shows the time-dependent UV–vis absorption of these two samples with initial molar ratio 5:1 (A) and 10:1 (B). At molar ratio 5:1, the induced time was short (ca. 2 min), which was evidenced by the appearance of transverse plasmon resonance centred at ~528 nm. With the elapsed time, the transverse plasmon resonance grew in intensity and narrowed gradually, and these changes ceased within 30 min. At the molar ratio of

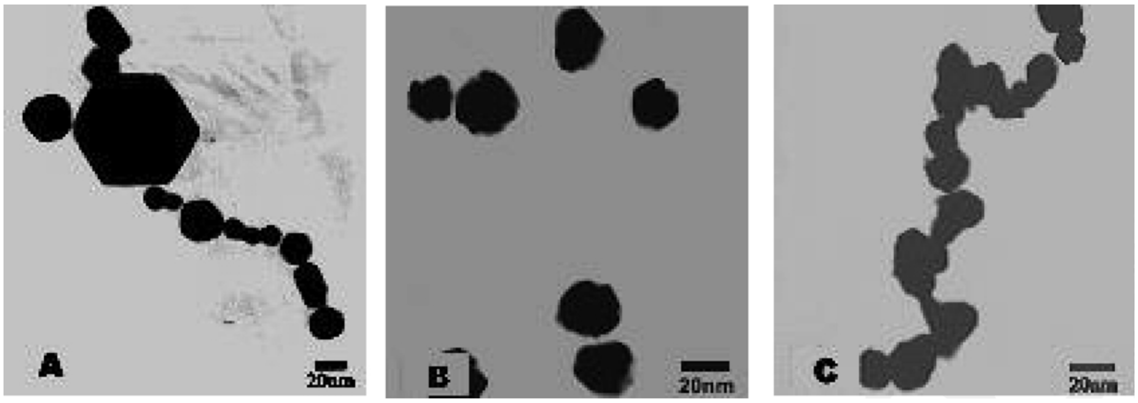


Fig. 3. Typical TEM images of sample 1 (A), 4 (B) and 7 (C).

10:1, the induced time was also short (ca. 2 min), supported by the occurrence of corresponding transverse plasmon resonance. With the elapsed time, however, the transverse plasmon resonance grew in intensity first (from curve 1 to curve 4), then decreased distinctly in intensity and red-shifted gradually with the occurrence of a longitudinal plasmon resonance and the longitudinal plasmon resonance grew in intensity and red-shifted gradually (from line 5 to line 11). After thirty-five minutes, these changes ceased and a weak transverse plasmon resonance and a distinct longitudinal plasmon resonance were observed.

4. Conclusions

We have presented a thermal process for the one-step synthesis of polyelectrolyte-protected gold nanoparticles or quasi one-dimensional aggregates of nanoparticles by changing initial molar ratio of polyelectrolyte (repeating unit) to gold, with the use of polyelectrolyte to serve as reducing agent and protective agent. More importantly, gold nanoparticles thus formed are highly useful, for example, in variety of catalytic applications [14] and in the biomedical and bioanalytical field and as building blocks for the creation of thin films [22].

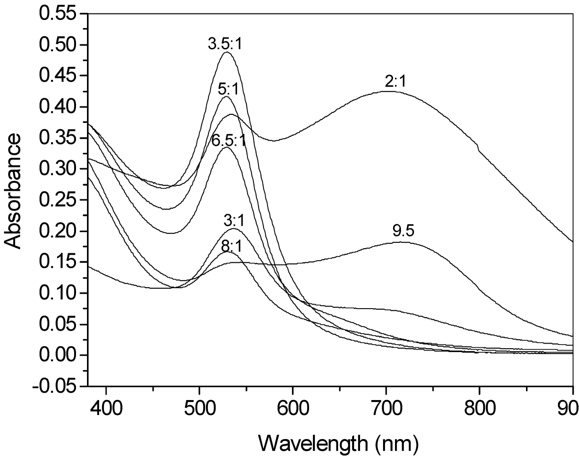


Fig. 4. UV–vis absorption spectra of seven samples 1–7 with initial molar ratio 2:1, 3:1, 3.5:1, 5:1, 6.5:1, 8:1 and 9.5:1 of LPEI (repeating unit) to gold.

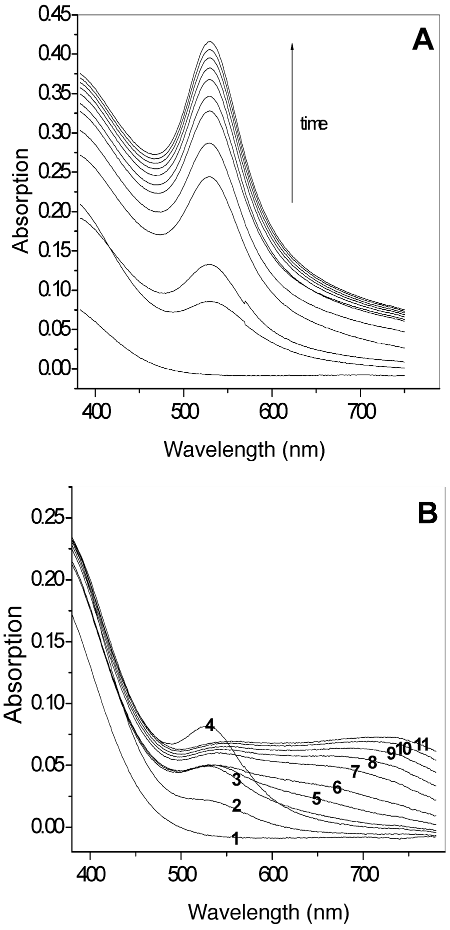


Fig. 5. Time-dependent UV–vis absorption spectra of two samples with initial molar ratio 5:1 (A) and 10:1 (B) of LPEI (repeating unit) to gold performed at 60 °C with time interval of 60 s.

Acknowledgements

We thank the National Natural Science Foundation of China for financial support of this research (NO. 299750258 and 20075028). X. Sun appreciates support for this work from the Department of Chemistry, Xihua Normal College in changchun.

References

[1] Fendler JH. Nanoparticles and nanostructured films. Weinheim: VCH; 1998.
[2] Klabunde KJ. Nanoscale materials in chemistry. Weinheim: VCH; 2001.
[3] Wei Y, Cao C, Jin R, Mirkin CA. Science 2002;297:1536.
[4] Kiwi J, Gratzel M. J Am Chem Soc 1979;101:7214.
[5] Schmid G. Chem Rev 1992;92:1709.
[6] Brust M, Walker M, Bethell D, Schiffrin DJ, Whyman R. J Chem Soc, Chem Commun 1994;801.
[7] Spatz JP, Roesher A, Mollor M. Adv Mater 1996;8:337.
[8] Roucoux A, Schulz J, Patin H. Chem Rev 2002;102:3757.
[9] Shipway AN, Katz E, Willner I. ChemPhysChem 2000;1:18.
[10] Rao NR, Kulkarni GU, Thomas PJ, Edwards PP. Chem Soc Rev 2000; 29:27.
[11] Decher G, Schlenoff JB. Multilayer thin films. Weinheim: VCH; 2003.
[12] Borukhov I, Andelman D, Orland H. J Phys Chem B 1999;103:5042.
[13] Pugh TL, Heller W. J Polym Sci 1960;47:219.
[14] Mayer ABR, Mark JE. J Macromol Sci Pure Appl Chem 1997;A34: 2151.
[15] Liu Y, Wang Y, Claus RO. Chem Phys Lett 1998;298:315.
[16] Youk JH, Locklin J, Xia C, Park M-K, Advincula R. Langmuir 2001; 17:4681.
[17] Hussain I, Brust M, Papworth AJ, Cooper AI. Langmuir 2003;19: 4831.
[18] Gittins DI, Caruso F. J Phys Chem B 2001;105:6846.
[19] Yu Y-Y, Chang S-S, Lee C-L, Wang CRC. J Phys Chem B 1997;101: 6661.
[20] Shipway AN, Lahav M, Gabai R, Willner I. Langmuir 2000;16:8789.
[21] Norman T, Grant C, Magana D, Zhang J, Liu J, Cao D, Bridges F, van Buuren A. J Phys Chem B 2002;106:7005.
[22] Mayya KS, Schoeler B, Caruso F. Adv Funct Mater 2003;13:183.