

# One-step preparation and characterization of PDDA-protected gold nanoparticles

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## Abstract

Poly(diallyl dimethylammonium) chloride (PDDA), an ordinary and watersoluble cationic polyelectrolyte, was investigated for its ability to generate and stabilize gold colloids from a chloroauric acid precursor. In this reaction, PDDA acted as both reducing and stabilizing agents for gold nanoparticles (AuNPs). More importantly, PDDA is a quaternary ammonium polyelectrolyte, which shows that the scope of the reducing and stabilizing agents for metal nanoparticles can be extended from the amine-containing molecules to quaternary ammonium polyelectrolytes or salts. UV–vis spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS) and Fourier transform infrared (FTIR) were used to characterize the synthetic AuNPs. The PDDA-protected AuNPs obtained are very stable and have relative narrow size distribution. © 2005 Elsevier Ltd. All rights reserved.

**Keywords:** One-step preparation; Poly(diallyl dimethylammonium) chloride; Quaternary ammonium polyelectrolytes

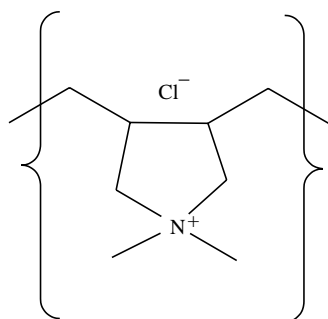
## 1. Introduction

In recent years, metal nanoparticles have attracted considerable attention because of their unique optical, electrical and other properties [1–3]. Gold nanoparticles (AuNPs) are the most stable metal nanoparticles and have been widely studied. Up to now, various methods for the preparation of AuNPs have been reported and reviewed, which include chemical reduction, photolysis, radiolysis, sonochemistry and thermolysis reduction, two-phase synthesis methods and etc. [4]. Among them, the most convenient and popular method is chemical reduction in which metal ions are reduced by a reducing agent such as sodium borohydride, sodium citrate, hydrogen, and alcohol [5–7]. To avoid aggregation of metal colloids, a common strategy is to use a protecting agent such as thiols, surfactants, polymers, and dendrimers that can also control the particle size and introduce functionality to the particle surface [8–11].

Polyelectrolytes are often used to modify substrate surface and colloids, exploiting the electrostatic attraction for their deposition [12,13]. As a branch of charged polymer, polyelectrolytes can be deposited on substrate surfaces layer-by-layer, enabling to control the total polymer thickness by the number of layers deposited [14]. Because of electrosteric stabilization, polyelectrolytes can also be used as stabilizing agents for colloids [15]. Mayer and co-workers investigated various polyelectrolytes as colloid stabilizers in solution where  $\text{Ag}^+$  was reduced with the addition of  $\text{KBH}_4$  [16]. Youk et al. described the preparation of AuNPs from a polyelectrolyte complex solution of terthiophene amphiphiles [17]. However, the result was not satisfactory due to the time-consuming of preparation and the poor stability of as-prepared colloids. Irshad et al. reported the preparation of AuNPs using poly(sodium acrylate), which acted as both reducing and stabilizing agents [18]. However, any insoluble materials need to be filtered and removed in the synthetic procedure and AuNPs formed by polyelectrolytes were found to be less uniform in size and shape. One-step synthesis of polyelectrolyte-protected AuNPs with the use of linear polyethylenimine to serve as reducing and protecting agent has been recently reported from our laboratory [19]. In this article, we reported a heat-treatment-based strategy for preparation of polyelectrolyte-protected AuNPs with the use of poly(diallyl dimethylammonium) chloride (PDDA, as shown in Scheme 1) to act

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Scheme 1. The molecular structure of PDDA.

both as the reducing and stabilizing agents simultaneously. According to our knowledge, this is the first report about synthesis of AuNPs by using the quaternary ammonium polyelectrolyte, which extends the scope of both the reducing and stabilizing agents for preparation of metal nanoparticles from the amine-containing molecules to quaternary ammonium polyelectrolytes or salts.

## 2. Experimental section

PDDA (50% wt in water, molecular weight 20000) was purchased from Aldrich and  $\text{HAuCl}_4$  and NaOH from Beijing Chem. Co. All reagents were used as received without further purification. The water used was purified through a Millipore system. In a typical experiment, 250  $\mu\text{L}$  PDDA (4 wt% in water), 40 mL water, 200  $\mu\text{L}$  0.5 M NaOH and 100  $\mu\text{L}$   $\text{HAuCl}_4$  (10 mg/mL) were added into a beaker. After thoroughly mixed for 2 min, the mixed solution maintained at 100  $^\circ\text{C}$  for several minutes until the color of the solution changed to red and no further color change occurred. Through accurately control the reaction time and use an inverted culture dish covered on the beaker to avoid the reaction liquid vaporized rapidly, we can get reproducible result.

UV–vis spectra were collected on a CARY 500 Scan UV–vis–near infrared (UV–vis–NIR) spectrophotometer. TEM measurements were made on a JEOL 2000 transmission electron microscope operated at an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried at room temperature. Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII using Mg as the exciting source. The sample for XPS characterization was prepared by placing 100  $\mu\text{L}$  of the AuNP on a clean glass slide. Fourier transform infrared (FTIR) was carried out using a Nicolet 520 SXFTIR spectrometer. The spectra were obtained by spreading the samples on  $\text{CaF}_2$  with an average of 120 scans and 4  $\text{cm}^{-1}$  resolutions.

## 3. Results and discussion

Information about the AuNPs concentration (absorbance), particle size (position of  $\lambda_{\text{max}}$ ), and dispersity of particle size in solution (width of absorbance band) can be obtained from

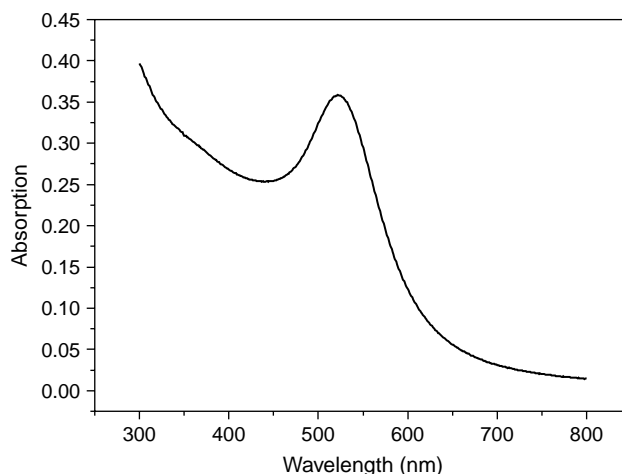


Fig. 1. UV–vis absorption spectrum of an aqueous solution of PDDA-protected AuNPs.

the optical spectra of gold colloids solution. Fig. 1 gives the UV–vis spectrum of the gold colloids, showing a characteristic surface plasmon absorption center at 522 nm, which is typical for AuNPs of about 12 nm in diameter [20].

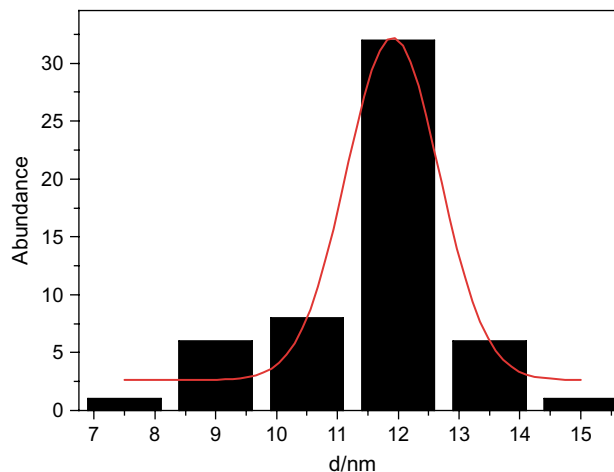
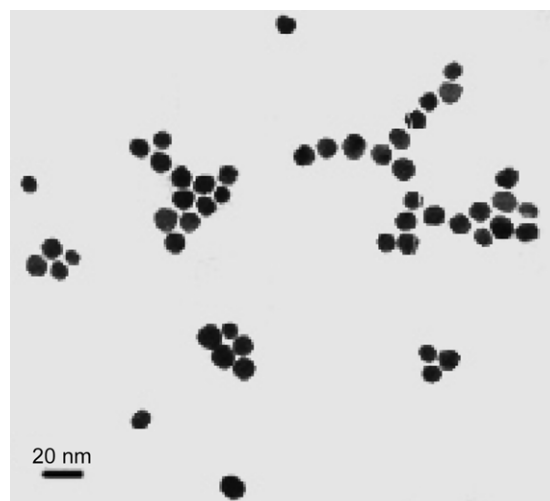


Fig. 2. Typical TEM image (up) and the corresponding particle size distribution histogram (bottom) of PDDA-protected AuNPs.

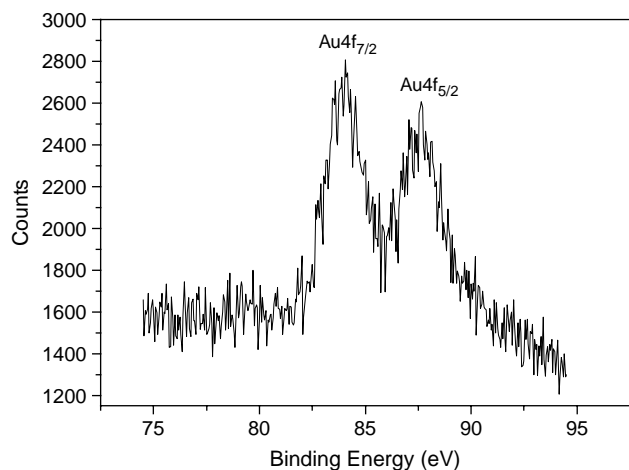


Fig. 3. XPS spectrum of PDDA-protected AuNPs.

The symmetric and narrow peak suggests a smaller average particles size and more monodisperse size range.

To confirm and characterize the size and size distribution of AuNPs, TEM was used to analyze the AuNPs synthesized. Fig. 2 shows typical TEM image and the corresponding particle size distribution histogram of the AuNPs. As shown in Fig. 2, all of the AuNPs are almost spherical and well separated from each other. The size distribution histogram shown in Fig. 2 bottom reveals that the average diameter of AuNPs is to be  $\sim 12$  nm with narrow size distribution.

XPS measurements were performed to identify and characterize the PDDA-protected AuNPs prepared as shown in Fig. 3. XPS spectrum of the PDDA-protected AuNPs shows the Au4f<sub>5/2</sub> and Au4f<sub>7/2</sub> doublet with binding energies of 87.6 and 84.0 eV, respectively, which are typical value for Au in zero oxidation state, indicating the chloroauric acid was successfully reduced by PDDA [21]. If the experiment was conducted in the same way just without adding PDDA, we failed to synthesis AuNPs, indicating directly that PDDA acts as a reductant for the formation of AuNPs.

To clearly characterize the structure changes of PDDA after reaction, FTIR measurement was adopted as shown in Fig. 4. The FTIR spectrum of PDDA-protected AuNPs (Fig. 4(b)) is

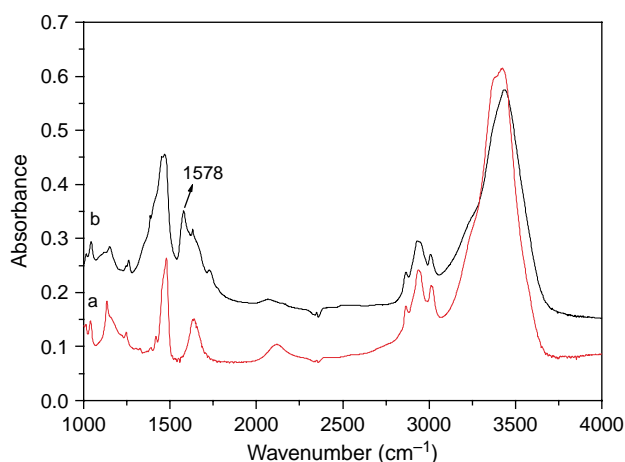


Fig. 4. FTIR spectra of PDDA (a) and PDDA-protected AuNPs (b).

similar to that of original PDDA (Fig. 4(a)), although the difference shown in slight shift of wavenumber is also observed. The FTIR spectrum of PDDA obtained is well agreed with that reported by Yang, providing the peaks assignment of PDDA [22]. The slight shift of wavenumber in FTIR spectrum after its reaction maybe comes from the interaction between the PDDA and AuNPs, which also occurred by mixing the PDDA with multiwall carbon nanotubes [22]. The apparent difference between the two FTIR spectra in Fig. 4 is the appearance of a new peak at  $1578\text{ cm}^{-1}$ , which is in assignment to C=C and C=N in-plane vibration [23]. This may prove that C=C and C=N are produced after PDDA reacted with H<sub>2</sub>AuCl<sub>4</sub>.

More importantly, the PDDA-protected AuNPs show a remarkable colloidal stability and without any observable flocculation or aggregation for at least 3 months, suggesting PDDA is a very effectively protecting agent for AuNPs. The excellent stability of the AuNPs arises from electrosteric effect of PDDA [15,16]. This kind of exceptional stability is also agreed with the result reported by Mayer et al., who used PDDA only as a protecting agent for AgNPs [16]. It is note that adjusting to a suitable pH value is very important for preparation of PDDA-protected AuNPs. Without adding NaOH, we cannot synthesize PDDA-protected AuNPs in the same condition as stated in experimental section. It also needs to point out that PDDA-protected AuNPs can be slowly formed at room temperature after storing at least 1 day. However, PDDA-protected AuNPs can be rapidly synthesized within several minutes through heating to boil, obviously raising temperature can accelerate this reaction.

#### 4. Conclusion

In conclusion, the present method describes a simple, one-step approach to the formation of gold–polyelectrolyte nanocomposites in which PDDA acts as both reducing and stabilizing agents. Moreover, the PDDA-protected AuNPs are very stable and have narrow size distribution. More importantly, through the present method, the scope of reducing and stabilizing agents for preparation of metal nanoparticles extends from the amine-containing molecules to the quaternary ammonium polyelectrolytes or salts.

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