

Size-Controlled Synthesis of Colloidal Gold Nanoparticles at Room Temperature Under the Influence of Glow Discharge

Xi Liang · Zhou-jun Wang · Chang-jun Liu

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Abstract Highly dispersed colloidal gold (Au) nanoparticles were synthesized at room temperature using glow discharge plasma within only 5 min. The prepared Au colloids were characterized with UV–visible absorption spectra (UV–vis), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) equipped with an energy dispersion X-ray spectrometer (EDX). UV–vis, XPS and EDX results confirmed that Au³⁺ ions in HAuCl₄ solution could be effectively reduced into the metallic state at room temperature with the glow discharge plasma. TEM images showed that Au nanoparticles were highly dispersed. The size of colloidal Au nanoparticles could be easily tuned in the nanometer range by adjusting the initial concentration of HAuCl₄ solution. Moreover, the as-synthesized Au colloids ($d_{av} = 3.64$ nm) exhibited good catalytic activity for glucose oxidation. The nucleation and growth of colloidal Au particles under the influence of the plasma was closely related with the high-energy electrons generated by glow discharge plasma.

Keywords Size · Au colloids · Plasma · Reduction · Glucose oxidation

Introduction

In the last decades, metal nanoparticles have attracted increasing interest because of their unique properties compared to bulk metals and their promising applications in catalysis, gas sensors, electronic/optical devices, medical diagnosis, etc. [1–3]. In particular, the development of water-dispersible metal nanoparticles (also called metal colloids) has drawn more attention, considering their direct catalytic or biological applications in aqueous media with less or no hazardous effects [4–6]. Among the various metal colloids studied to date, Au colloids have received special attention by virtue of their fascinating physical and chemical properties, especially the intriguing biological uses and catalytic activity in a number of reactions [7–9].

Up to now, various strategies have been developed for the synthesis of Au colloids, which can be generally classified into two groups: (1) The chemical reduction of Au ions using a reducing agent (such as NaBH₄, citrate, and ascorbate) with the protection of a stabilizer (typically an alkyl thiol or (4-dimethylamino) pyridine) [10, 11]; (2) Irradiation methods, including sonochemical, laser pulse, and photochemical techniques [12, 13].

Herein, we report a fast, facile, green, and economic method for the synthesis of the Au colloids in the absence of stabilizers, with the use of glow discharge plasma reduction at room temperature. Glow discharge, known as one of conventional cold plasmas, is characterized by high electron temperatures (as high as 10,000–100,000°C) and low gas temperatures (as low as room temperature) [14–16]. Spherical and mono-dispersed colloidal Au

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nanoparticles were successfully synthesized within only 5 min with this glow discharge plasma reduction route. The size of Au nanoparticles in the colloids could be effectively tuned in the nanometer range by adjusting the initial concentration of HAuCl_4 solution. Moreover, the as-synthesized Au colloids exhibited good catalytic activity for glucose oxidation.

Experimental

Preparation

The preparation of Au colloids is very simple and straightforward. As depicted in Fig. 1, only one step was needed to synthesize Au colloids from the HAuCl_4 aqueous solution using glow discharge plasma reduction.

The glow discharge plasma setup and plasma reduction protocol have been described in detail elsewhere [14–16]. Briefly, the HAuCl_4 solution (about 3.0 mL), loaded in a quartz boat, was placed inside a quartz tube (i.d. 35 mm) with two stainless steel electrodes (o.d. 30 mm). The system was evacuated by a mechanical vacuum pump. When the pressure was adjusted to 100–150 Pa, the glow discharge plasma was generated by applying 900 V to the electrode, using a high-voltage amplifier (Trek, 20/20C), with argon (>99.999%) as the plasma-forming gas. The signal input for the high-voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett-Packard, 33120A) with a 100-Hz square wave. The current was 4.5 mA. The plasma reduction time was only 5 min. The gas temperature of plasma was measured by infrared imaging (Ircon, 100PHT), indicating that the reduction was conducted at ambient temperature. The initial concentration of HAuCl_4 solution was 0.6 mM unless otherwise mentioned.

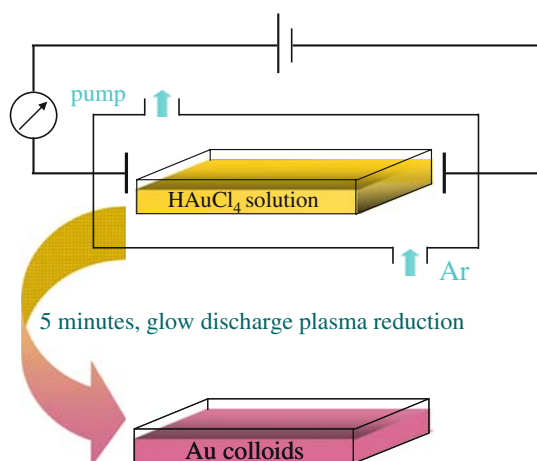


Fig. 1 Schematic diagram illustrating the one-step experimental procedure for the synthesis of Au colloids

Characterizations

The disappearance of $[\text{AuCl}_4]^-$ ions and the formation of Au nanoparticles were confirmed by UV–vis absorbance spectra (UV–vis) on a Beckman DU-8B UV–vis spectrophotometer. The as-synthesized Au colloids were used directly for the UV–vis analysis.

X-ray photoelectron spectroscopy (XPS) was performed on a Perkin–Elmer PHI-1600 spectrometer with $\text{Mg K}\alpha$ (1253.6 eV) radiation. Aluminum foils were used as the substrates for the XPS test. Before the XPS test, the as-synthesized sample was concentrated by centrifugation. Then, the concentrated samples were dropped onto the substrates and dried in a vacuum chamber. The binding energy for the tested element was calibrated from the C 1 s peak (284.6 eV) of the surface adventitious carbon.

Transmission electron microscopy (TEM) images were recorded on a Philips TECNAI $\text{G}^2\text{F}20$ system equipped with energy dispersion X-ray spectroscopy (EDX). The samples for TEM and EDX analysis were prepared by placing a drop of the as-synthesized colloids onto a carbon-coated Cu grid followed by slow evaporation of solvent at ambient condition. The average particle size (A_v) and standard deviation (SD) were calculated by counting 200 particles from more than five TEM images of different areas of the Cu grid.

Catalytic Reaction

The glucose oxidation was used as the model reaction for the as-synthesized Au colloids. The reaction was performed in a semi-batch glass reactor (250 mL) equipped with a stirrer, a gas supply system, a pH electrode (HANNA Instruments) and a burette containing NaOH (1 M). After introducing the as-synthesized Au colloids into the oxygen saturated glucose solution (50 mL, 0.4 M), the reaction was initiated and conducted at 50°C under atmospheric pressure with the pH maintaining at 9. The mixture was stirred at 2,000 rpm, while oxygen was bubbled through at 400 mL min^{-1} . The acids formed during the oxidation of glucose were neutralized by the addition of NaOH solution, and the consumptions of alkali were recorded accordingly. The selectivity was determined by analyzing the reaction product with HPLC (Agilent 1100 series).

Results and Discussion

The novel glow discharge plasma reduction technique has been successfully applied to the preparation of supported nanoparticles in heterogeneous catalysts and unsupported nanoparticles in ionic solution, which is proved to be green, economical, and non-time-consuming [14–18]. However,

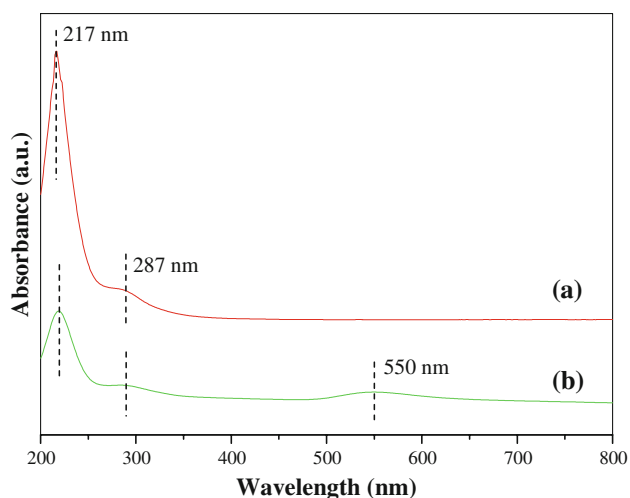


Fig. 2 The UV–vis absorbance spectra of aqueous HAuCl_4 solution *a* before and *b* after plasma reduction

it is the first attempt to extend this novel reduction technique for the preparation of colloidal metal nanoparticles in aqueous solution. Therefore, as a first step, we employed the UV–vis, XPS TEM, and EDX characterizations to confirm whether the metal ions in the aqueous solution could be reduced effectively into the metallic state.

Shown in Fig. 2 were the UV–vis absorbance spectra of aqueous HAuCl_4 solution before and after plasma reduction. Before the plasma reduction (Fig. 2a), the solution displayed a strong absorption band at 217 nm and a shoulder at 287 nm, both of which were due to the ligand-to-metal charge transfer (LMCT) bands of $[\text{AuCl}_4]^-$ ions between gold and chloro ligands [19–21]. After 5-min plasma reduction (Fig. 2b), the LMCT bands of the $[\text{AuCl}_4]^-$ decreased dramatically, suggesting that the Au^{3+} ions in HAuCl_4 solution were effectively reduced into the metallic state [22]. Moreover, a broad band centered at about 550 nm, which was assigned to the plasmon band of Au nanoparticles (2–10 nm), could be evidently observed [23, 24]. The UV–vis results proved that, with the glow discharge plasma reduction, colloidal Au nanoparticles could easily be synthesized from the aqueous HAuCl_4 solution.

The chemical state of Au species in the obtained colloids was also examined by the XPS test. As shown in Fig. 3, two peaks were observed, and no other peaks could be deconvoluted. For the binding energy, the $\text{Au } 4f_{7/2}$ peak was centered at 83.1 eV and the $\text{Au } 4f_{5/2}$ peak at 86.7 eV, both of which were slightly lower than the standard values of the bulk Au metal [25]. These slight negative shifts could be rationalized in terms of the unique microenvironments during the plasma reduction [26]. It can be readily inferred from the XPS results that the plasma

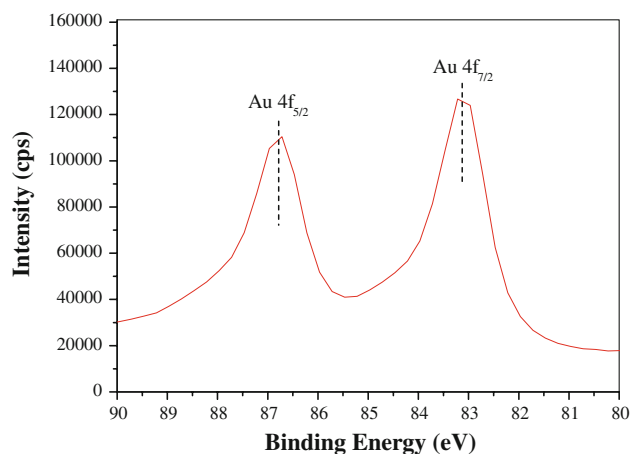


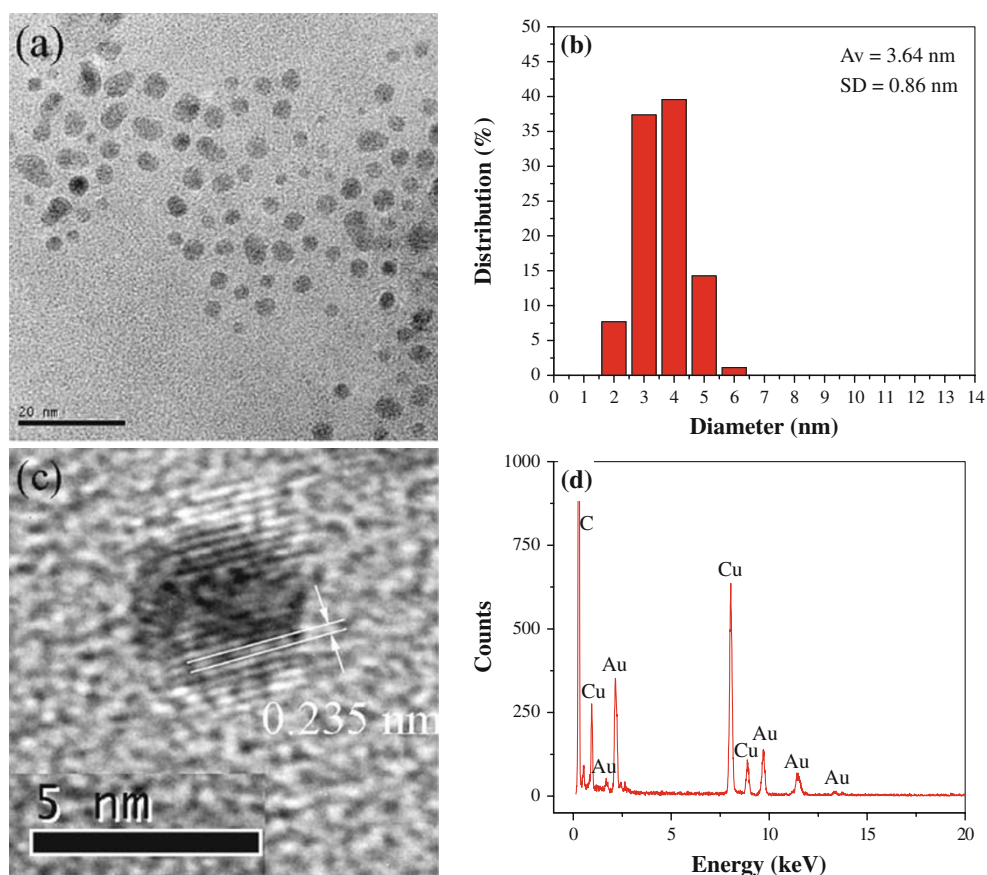
Fig. 3 XPS spectra of Au 4f for plasma reduced colloidal Au nanoparticles

reduction could effectively reduce the Au^{3+} ions into the metallic state.

The representative TEM images of Au colloids were presented in Fig. 4. Figure 4a, b showed that spherical Au nanoparticles were highly dispersed in the colloids with an average particle size of 3.64 nm (standard deviation, $\text{SD} = 0.86$ nm). To visually observe the atomic structure of Au nanoparticles, a high-resolution TEM analysis was performed (Fig. 4c). The lattice fringes with $d = 0.235$ nm were clearly visible, which could be attributed to the (111) planes of Au. This result was consistent with the aforementioned UV–vis and XPS characterizations, suggesting the successful synthesis of colloidal Au nanoparticles. The EDX spectrum (Fig. 4d) provided further evidence for the Au nanoparticles.

Au nanoparticles were renowned for their size-dependent unique physical and chemical properties. Therefore, size-controlled synthesis of colloidal Au nanoparticles would be crucial for their use as advanced materials in potential applications or as model materials in fundamental studies [27, 28]. In this new synthesis method, the initial concentration of the aqueous HAuCl_4 solution was found to be a key parameter for the realization of size-controlled synthesis of colloidal Au nanoparticles. As illustrated in Fig. 5, by increasing the initial concentration of HAuCl_4 solution to 1.0, 1.5, and 2.0 mM, spherical and mono-dispersed Au nanoparticles with the average particle size of 5.88, 7.95, and 9.84 nm were obtained, respectively. The histograms of size distributions of these particles were also included in Fig. 5, with a standard deviation (SD) of 1.27, 1.60, and 1.67 nm, respectively. Figure 6 clearly demonstrated that the size of colloidal Au nanoparticles could be easily tuned in the nanometer range by adjusting the initial concentration of the HAuCl_4 solution.

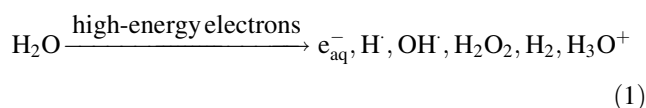
Fig. 4 TEM results: **a** typical TEM image of colloidal Au nanoparticles (*scale bar*: 20 nm); **b** size distribution of colloidal Au nanoparticles (A_v is the average particle size, and SD denotes the standard deviation of the size distribution); **c** high-resolution TEM image of the Au nanoparticle (*scale bar*: 5 nm); **d** EDX spectrum of Au nanoparticle



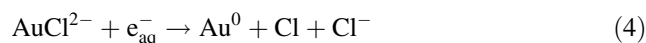
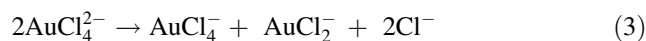
It was reported that colloidal Au nanoparticles exhibited a surprising activity in the glucose oxidation reaction under mild conditions [29]. Therefore, we employed the glucose oxidation as the model reaction to test the catalytic activity of the synthesized Au colloids. Since Au colloids exhibited selectivity nearly 100% in the model reaction (as determined by HPLC), the conversion could be measured conveniently from the consumptions of NaOH, which was added during reaction to maintain a constant pH value for the reaction medium. As shown in Fig. 7, colloidal Au nanoparticles ($d_{av} = 3.64$ nm) behaved as an active catalyst allowing 52% glucose conversion in the first 30 min and reaching a plateau of 58% glucose conversion after 120 min. This catalytic result was comparable with that reported in the literature, which provided 30% conversion in the first 15-min reaction [29].

The mechanism for the radiation-induced reduction of $AuCl_4^-$ ions can be adopted to interpret the nucleation and growth of Au nanoclusters in the present work [30, 31]. Highly energetic electrons represent the most important character of glow discharge plasma. These high-energy species can induce the dissociation and ionization of the

water molecules in the aqueous solution to generate the reducing agents:



The generated hydrated electrons e_{aq}^- serve as the reducing agents for the formation of gold nanoparticles:



Furthermore, the high-energy electrons play a key role in protecting the produced colloidal Au nanoparticles from aggregation. The plasma reduced Au nanoparticles could retain some electric charge and repel each other, resulting in the uniform and stable distribution of Au nanoparticles in the colloids. Further investigations regarding the mechanism and kinetics of plasma reduction are being conducted for a better understanding.

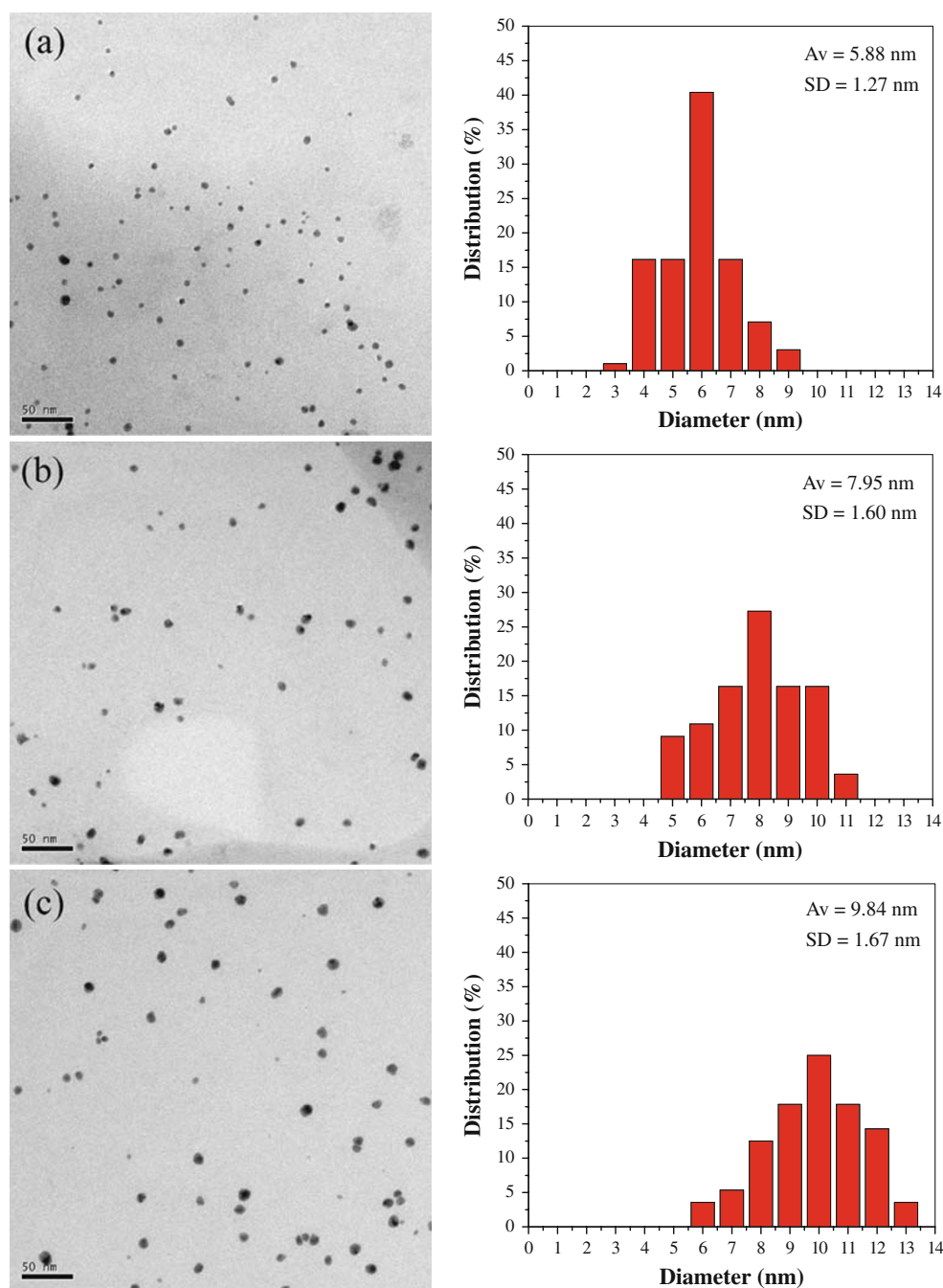


Fig. 5 Typical TEM images and the corresponding size distributions of colloidal Au nanoparticles synthesized by varying the initial concentration of the aqueous HAuCl_4 solutions: **a** 1.0 mM, $A_v = 5.88$ nm, $SD = 1.27$ nm; **b** 1.5 mM, $A_v = 7.95$ nm,

$SD = 1.60$ nm; **c** 2.0 mM, $A_v = 9.84$ nm, $SD = 1.67$ nm. Scale bar: 50 nm. A_v is the average particle size, and SD denotes the standard deviation of the size distribution

Conclusions

Highly dispersive and catalytically active colloidal gold nanoparticles were synthesized within only 5 min by the novel glow discharge plasma reduction technique. The size

of colloidal Au nanoparticles could be easily tuned in the nanometer range by adjusting the initial concentration of HAuCl_4 solution. The as-synthesized Au colloids ($d_{av} = 3.64$ nm) exhibited good catalytic activity for the reaction of glucose oxidation. Moreover, initial results

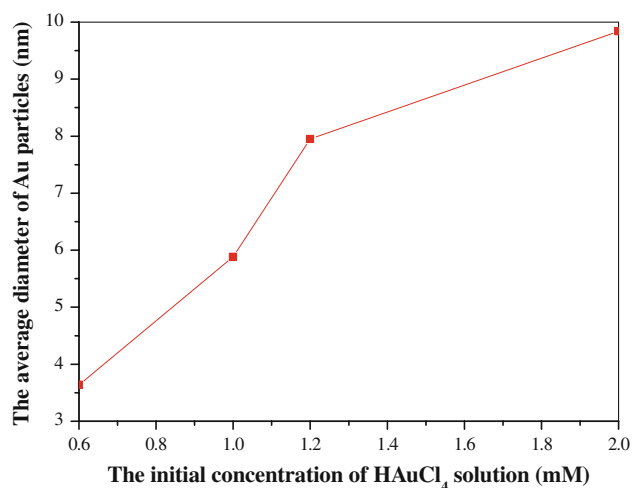


Fig. 6 The relationship between the initial concentration of HAuCl₄ solution and the average diameter of the obtained Au nanoparticles

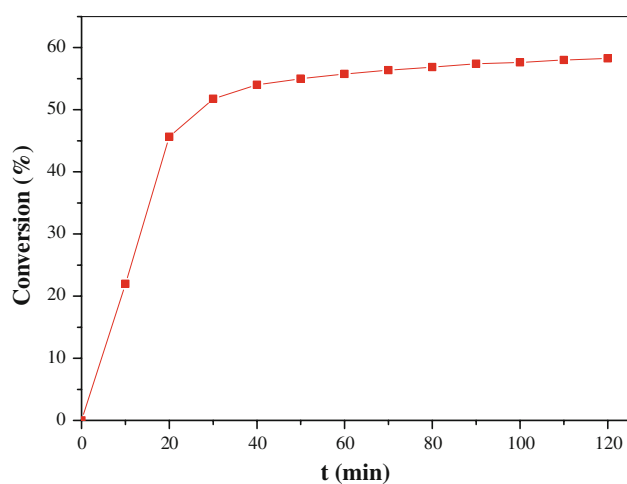


Fig. 7 Catalytic activity of colloidal Au nanoparticles in glucose oxidation reaction

indicated that this new synthesis method could be easily extended to the preparation of Pd colloids and other noble metal ions.

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