Gold Nano-cluster Occurred With a Supermolecule Linker and Its Application

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The preparation and characterization of gold nanoparticles (~6 nm in diameter) modified with mono-6-thio-β-cyclodextrin (II) is described. The resulting monolayer-protected gold nanoparticles are water-soluble and more stable. The concentration of II plays a crucial role for the distribution of the modified nanoparticles. When the ratio of concentration of II to $HAuCl_4$,$[II]/[HAuCl_4] \geq 0.93$, a stable gold nanoparticle with uniform distribution and diameter of 6.0 ± 0.9 nm will be obtained. The recognition of modified gold nanoparticles to organic guest molecule is researched. The modified gold nanoparticles can make the electrochemical reduction current of nitrobenzene decrease and can be self-assembled in three-dimensional to form spherical clusters with ligand of methylene green.

INTRODUCTON

Following description of the Brust protocol for the synthesis and capping of gold colloids with alkanethiols in nonpolar organic solvents [1], there have been a number of reports on the surface capping or modification of gold colloids. Then metal nanoparticles stabilized by thiol molecules have become a popular area of interdisciplinary research, including topics such as self-assembly of nanocomposites [2–4], catalysis [5,6], and chemical and biological sensing [7,8]. Because the properties of metal colloidal particles can be affected or even controlled by the surface-attached ligands [1], recently, several groups [9–21] are applying themselves to the modification of metal nanoparticle surfaces with synthetic receptors in order to use well-known molecular recognition interactions to control particle assembly.

As a representative of the supermolecular host compounds, cyclodextrins (CDs) bear well-defined molecular recognition abilities. At present, the research work on taking CD derivatives as capping ligands is focused on the attachment of perthiolated CDs (SH-CDs) on metal nanoparticle surfaces. Liu *et al*. have reported the modification of gold [15–18], platinum [19], palladium [19–21] nanoparticles with SH-CDs, which makes this nanocomposite system processing the best features of two worlds: the electronic, magnetic, and/or catalytic properties of the metal cores with the molecular recognition ability of the protecting organic monolayers [18]. The resulting CD-modified nanospheres can be used as multisite hosts for binding of guests in the solution. Ultimately, nanoparticles are introduced into research in supermolecular chemistry.

As capping ligand, monothiolated CDs were found to be less efficient than SH-CDs [22]. There are only several reports about the preparation of monothiolated CDs modified metal nanoparticles. However, monothiolated CDs are more stable and its preparation is more facile than perthiolated CDs. In this article, the method for preparing water-soluble gold nanoparticles (~6 nm in diameter) modified with covalently-attached monothiolated β-CD is reported. The experimental results show those gold nanoparticles modified with monothiolated β-CD are stable and have the ability of binding guests.

EXPERIMENTAL

Synthesis of Mono-6-thio-β-cyclodextrin

All reagents used in this paper were of analytical grade and used as commercially available. Double
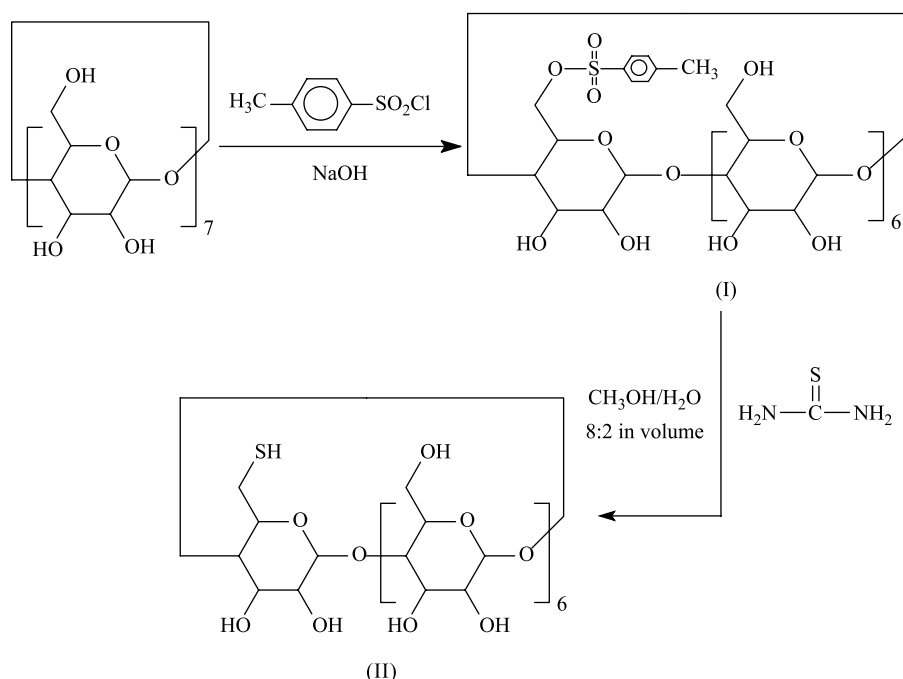
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FIGURE 1   The route for the synthesis of mono-6-thio-β-cyclodextrin.

distilled water was used to prepare all solutions. mono-6-thio-β-cyclodextrin (II) was synthesized by the route as shown in Fig. 1.

β-CD reacted with *p*-toluenesulfonyl chloride in alkaline solution. According to Petter *et al.* [23], the product is mono-6-deoxy-6-(*p*-tolylsulfonyl)-β-cyclodextrin, (I). II was synthesized by the reaction of I with thiourea [24] in a mixed solvent of methanol and water (8:2 in volume). The product was recrystallized twice. To confirm the thio group in the product, $NaNO_2$ and HCl were added into the solution contained II. It was found that the solution turned red which indicated the existence of thio group in the product. IR spectrum of the product was taken by a FTIR spectrometer (Nicolet 740) with a KBr film. A weak peak at $2560\,cm^{-1}$ corresponding to the S-H stretch vibration was observed.

NMR spectra of β-CD and II in D_2O taken by AVANCE 2-Bay 600 MHz superconducting NMR spectrometer (Bruker) are shown in Fig. 2. Fig. 2a is the spectrum of β-CD, which is coincided with that reported by González-Gaitano *et al.* [25]. However, in the spectrum of II listed in Fig. 2b, there are two signals at δ = 3.00 and 2.70, which are assigned to the proton signals of 6'-CH_2 because of the replacement of OH with SH.

Preparation of II-modified Gold Nanoparticles

II-capped gold nanoparticles were prepared by the reduction of $AuCl_4^-$ with a similar method described in reference [18]. $NaBH_4$ (37.8 mg) and various amount of ligand, II, were dissolved in 10 mL of DMF, and $HAuCl_4$ (25 mg) in 10 mL of DMF was

quickly added. At moment the mixture became deep green to deep brown with increasing of the amount of the ligand. The mechanism for the formation of Au nanoparticles can be described as shown as in Fig. 3. At first, the gold nucleus quickly occurred with the reduction of $HAuCl_4$ by $NaBH_4$. Then the nucleus grew gradually. Meanwhile, II modified on the surface of the nanoparticles by formation of the S-Au

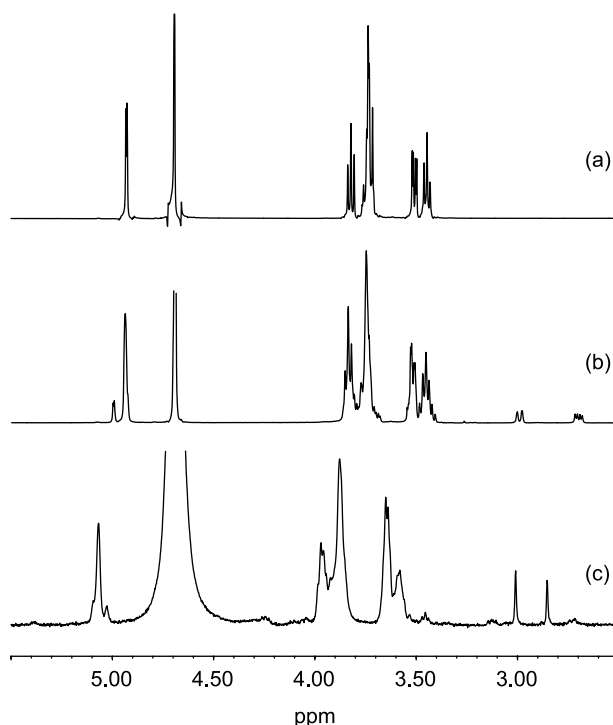FIGURE 2 ^{1}H NMR spectra of β-CD (a), compound II (b) and II-modified gold nanoparticles (c) in D_2O.
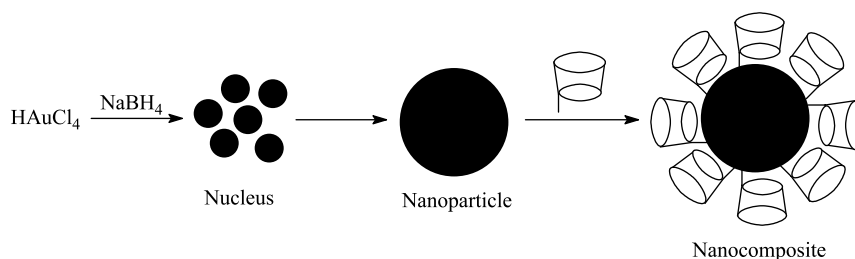
FIGURE 3   Mechanism of II-modified gold nanoparticles formation.

bond, which will prevent the collection among the gold nanoparticles. After 24 h stirring, the precipitate was collected by centrifugation and washed with 25 mL of DMF for three times and then with 25 mL ethanol/water (9:1 in volume) for four times. At last, the precipitate, II-modified gold nanoparticles, was dried at 60°C in a vacuum oven for 24 h and characterized by FTIR, UV, ^{1}HNMR, TEM, and XRD.

RESULTS AND DISCUSSION

Characterization of II-modified Gold Nanoparticles

The FTIR spectra, taken by Nicolet 740 FTIR spectrometer with KBr film, of II and II-modified gold nanoparticles are shown in Fig. 4a. Comparing the spectrum of II (Fig. 4a) with that of II-modified gold nanoparticles (Fig. 4b), the peak at 2560 cm^{-1} occurred by S-H stretch observed in Fig. 4a disappeared in Fig. 4b. The other of the spectra is identical. The result confirmed the binding of II on the surface of gold nanoparticles.

Fig. 2c shows the ^{1}H NMR spectra, taken by AVANCE 2-Bay 600 MHz superconducting NMR spectrometer (Bruker), of II-modified gold nanoparticles with the solvent of D$_2$O. The peaks of ^{1}H NMR of II-modified gold nanoparticles are broad and shift downfield a little comparing to free II. Similarly, the broad peak has been observed in bipyridyl or alkanethiolate-modified metal nanoparticles [26]. In these systems, the NMR peaks for the protons

closer to the metal surface are more seriously broadened, while the effect is less obvious for the protons that are further away. Fast relaxation and environmental heterogeneities are thought to be responsible for these lines broadening effects [18]. These results indicate clear evidence for the attachment of II on the surface of the gold nanoparticles.

The X-ray powder diffraction (XRD) spectrum was taken by M03XFH (MAC Science) X-ray diffractometer operated at a voltage of 40 kV and a current of 40 mA with CuKα radiation (λ = 0.154056 nm). Fig. 5 shows the XRD spectrum of II-modified gold nanoparticles prepared when [II]/[HAuCl$_4$], a ratio of the concentration of II to the concentration of HAuCl$_4$ is 1.16:1. The diffraction features at 2θ of 38.22°, 44.44°, 64.96°, 78.00°, and 82.14° correspond to the (111), (200), (220), (311), and (222) planes of the standard cubic phase of Au, respectively [27]. As expected, the XRD peaks of the nanocrystallites were considerably broadened compared to the bulk Au because of the finite size of the crystallites. According to the Debye-Scherrer equation, from the width of the diffraction peak the average diameter of the gold nanoparticles is calculated as 7.9 nm.

One of the unique properties of gold nanoparticles is a strong surface plasmon (SP) resonance band observable in the UV-vis region. The wavelength and the intensity of SP band depend on particle size, interparticle distance, and dielectric medium properties [28,29]. To assess the influence of the concentration of II on the evolution of the nanocrystals,
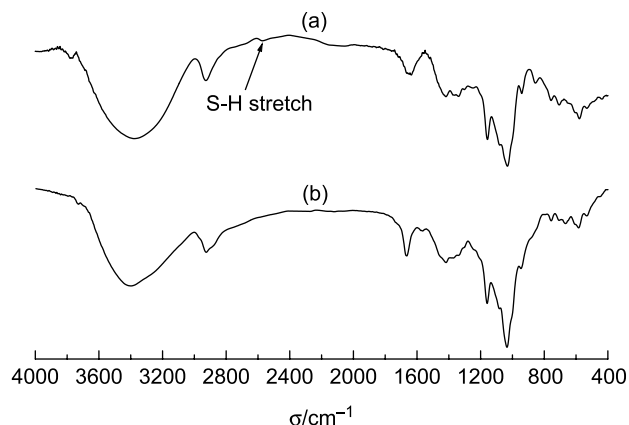

FIGURE 4   IR spectra of II (a) and II-modified gold nanoparticles at [II]/[HAuCl$_4$] = 1.16:1(b).
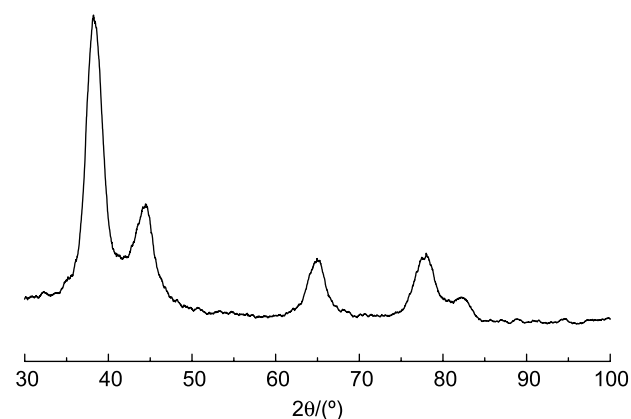

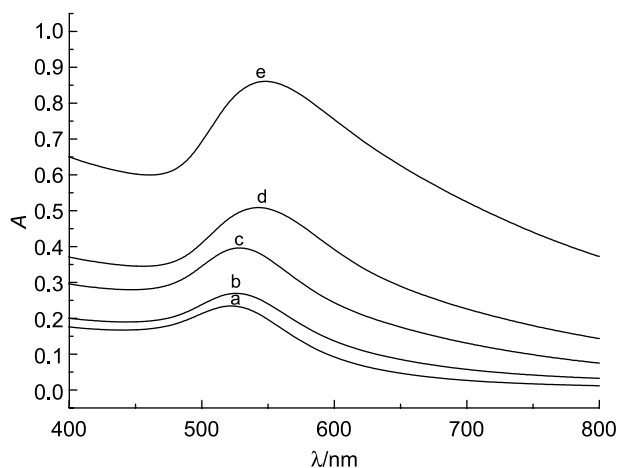FIGURE 5   XRD pattern of II-modified gold nanoparticles at [II]/[HAuCl$_4$] = 1.16:1.

FIGURE 6 UV-vis spectra of II-capped gold nanoparticles at different [II]/[HAuCl$_4$]. [II]/[HAuCl$_4$]: a. 1.16:1, $\lambda_{max} = 522.5$ nm; b. 0.93:1, $\lambda_{max} = 525.5$ nm; c. 0.70:1, $\lambda_{max} = 529.0$ nm; d. 0.47:1, $\lambda_{max} = 542.5$ nm; e. 0.23:1, $\lambda_{max} = 549.5$ nm.

II-modified gold nanoparticles were prepared under different [II]/[HAuCl$_4$]: 1.16:1; 0.93:1; 0.70:1; 0.47:1; 0.23:1. Their UV-vis spectra in water are shown in Fig. 6. With the ratio of [II] to [HAuCl$_4$] decreases, the UV-vis peak becomes broad gradually, and the red shift for the SP band is observed which indicates that the aggregation of the gold nanoparticles increases,

which may be due to less efficiency of ligand, II. At low concentration of II, there are not enough II to bind on the surface of the nanoparticles, which results in gold nanoparticles aggregating.

TEM images are taken on transmission electron microscopy (Philips TECNAI–12). Fig. 7 shows the TEM images of above nanoparticles. At high ratio of the concentration of II to HAuCl$_4$ (for example, [II]/[HAuCl$_4$] = 1.16:1 as shown in Fig. 7a), the spherical particles with uniform distribution and diameter of 6.0 ± 0.9 nm measured by manual with the assumption of circle particles where the number of particles analyzed are 300. The diameter value measured from TEM image is closed to that determined by X-ray. When the amount of II decreases, although the dimension of the particles is similar, the tendency of the aggregation for the particles increases. Therefore the aggregation of the nanoparticles is the reason to make the UV-vis peak broaden and red shift.

Formation of Spherical Nanoparticle Clusters

CDs can form inclusion complexes by incorporating guest molecules into their hydrophobic cavities [30]. Therefore II-modified gold nanoparticles should have the ability binding guest molecules.
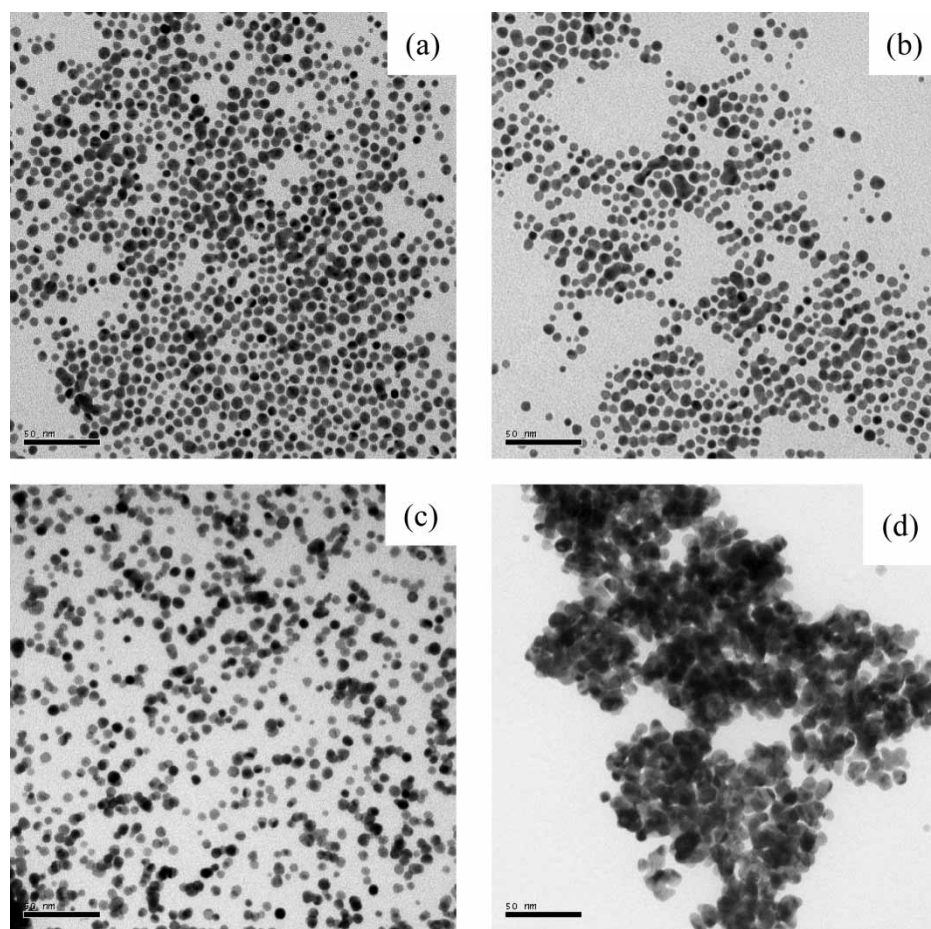

FIGURE 7   TEM images of II-capped gold nanoparticles at different [II]/[HAuCl$_4$]: a. 1.16:1; b. 0.93:1; c. 0.70:1; d. 0.23:1.
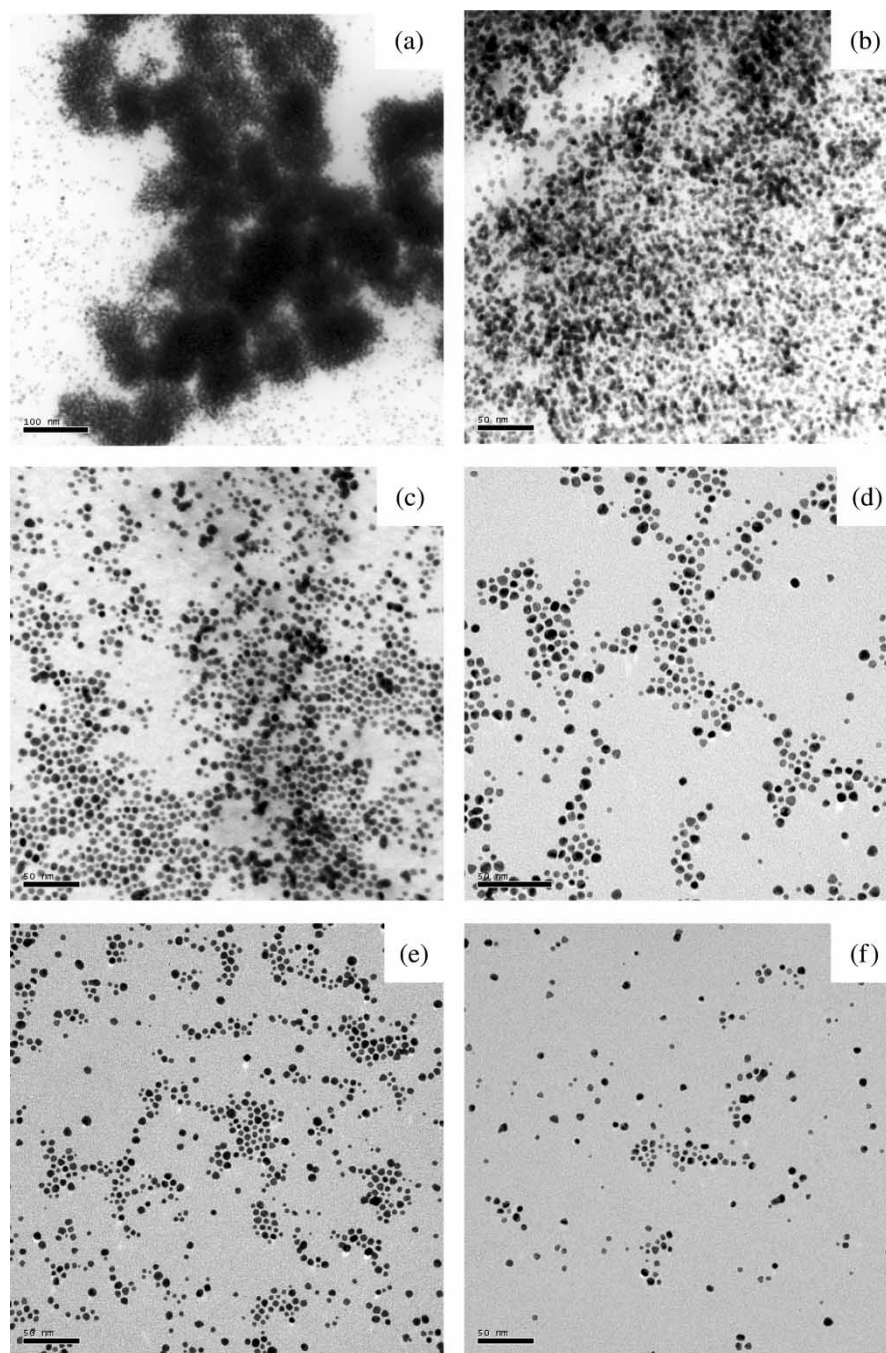
FIGURE 8 The effect of β-CD to II-modified gold nanoparticles clusters formed by put 2×10^{-5}M MG inio the II-modified gold nanoparticles aqueous solustion. The concentration of β-CD(10^{-5}M): (a) 0, (b) 1.0, (c) 2.0 (d) 10, (e) 50, (f) 100.

Guo *et al*. reported that β-CD can form 1:2 inclusion complex with methylene green (MG) [31]. Thus MG can be used as a linking bridge between two II-modified gold nanoparticles by forming inclusion complexes with two II modified gold nanoparticles, which will make the two nanoparticles connect to each other. Therefore, if MG was added into aqueous solution contained II-modified nanoparticles, the nanoparticles will aggregate and form clusters. Fig. 8a shows the TEM images of II-modified gold nanoparticles prepared at the conditions described in Fig. 7a when 2×10^{-5} M MG was

added. It is evident, because of the addition of MG, most of nanoparticles aggregate to each other and form spherical clusters with the diameter of about 100 nm, which confirms that II-modified gold nanoparticles has the ability of incorporating guest molecules. Moreover, it has been reported that free CDs are better at forming conclusion complex than immobilized CDs [32]. If a given amount of β-CD (much more compared to that modified on gold nanoparticles) was put into above solution, most free MG will be incorporated by β-CD, which will make the gold cluster dissociate to release the linker, MG,

because of the reaction competition. If the amount of free β-CD is large enough, it is reasonable to suppose that all clusters will dissociate. As shown in Fig. 8b to 8f, with addition of β-CD, the nanoparticles dissociated gradually, and at the end the single nanoparticles were obtained. Based on this typical experiment, it is clear that the II immobilized on the surface of gold nanoparticle reserves abilities of the well-known host-guest molecular recognition.

Effect of II-modified Nanoparticles on the Electrochemical Reduction of Nitrobenzene

NB can be reduced by electrochemical method. A recent study was produced on the interaction of β-CD with NB [33]. It was found that the electrochemical reductive current decreased with increasing β-CD because of the formation of an inclusion complex between β-CD and NB. Therefore, the electrochemical behavior of NB will be affected by II-modified gold nanoparticles because of the inclusion complex formed between II and NB. Electrochemical experiments were performed with CHI660a electrochemical work station (Shanghai Chenhua, China) equipped with a three-electrode jacked cell. A glassy carbon disc electrode (diameter: 3 mm) served as the working electrode. Reference and counter electrodes were saturated calomel electrode (SCE) and platinum wire electrode, respectively. All experiments were carried out at $25 \pm 0.1°C$. The working electrode was polished to a mirror with $0.05\,\mu m$ alumina aqueous slurry, and rinsed with double distilled and sterilized water before each experiment. The supporting electrolyte was $0.1\,M$ KNO_3. Fig. 9 shows the different cyclic voltammograms of NB with different amounts
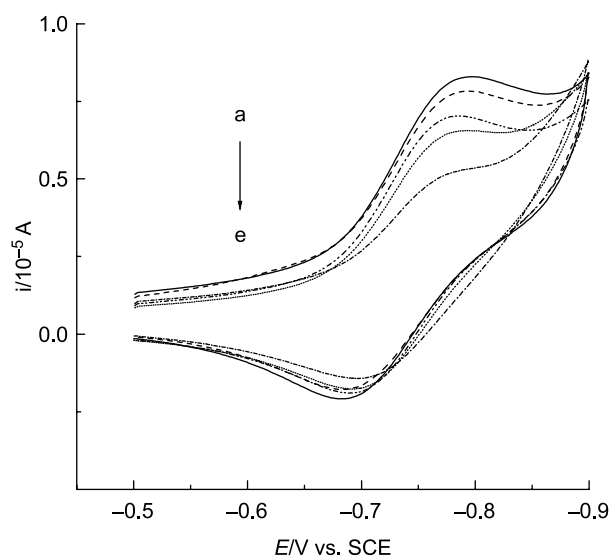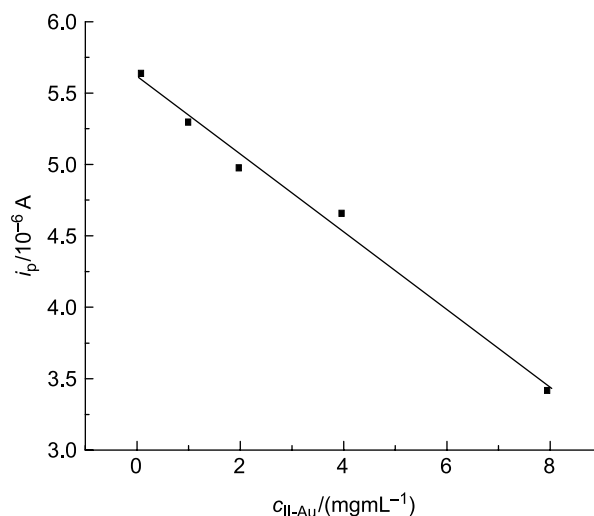

FIGURE 10   The peak current measured from Fig. 9 decreases with the concentration of II-modified Au nanoparticles.

of II-modified gold nanoparticles. It is clear that the electrochemical current decreased with an increase of II-modified gold nanoparticles. As shown in Fig. 10, the cathodic peak current decreased linearly with the concentration of II-modified nanoparticles, which confirms that II-modified gold nanoparticles can adsorb NB by formation of inclusion complex between NB and II modified on gold nanoparticles. In fact, at given concentration of NB and II-modified gold nanoparticles, the cathodic peak current is proportional to the square root of scan rate, which means that the electrochemical reaction of NB is also controlled by diffusion even the addition of II-modified gold nanoparticles.

CONCLUSIONS

II can be capped on gold nanoparticles. At high concentration of II (for example, [II]/[HAuCl_4] ≥ 0.93), a stable gold nanoparticle with uniform distribution and diameter of 6.0 ± 0.9 nm can be prepared. II-capped gold nanoparticles have an ability of host-guest molecular recognition. However, at low concentration of II (for example, [II]/[HAuCl_4] < 0.93), the nanoparticles are not uniform due to less capping efficiency of II.

II-modified gold nanoparticles are of the recognition to some organic guest molecules. In this article, nitrobenzene and methylene green were used as guest molecule. The experimental results show that the addition of II-modified gold nanoparticles into nitrobenzene aqueous solution, the electrochemical current of nitrobenzene will decrease because some nitrobenzene in the electrolyte solution was incorporated by II-modified gold nanoparticles. On the other hand, because of the formation of 1:2 inclusion complex between MG and β-CD, MG can be used as a linking bridge to make the

FIGURE 9   At 30°C and 0.1 Vs^{-1}, the cyclic voltammograms of 2.58×10^{-3} M NB + 0.1 M KNO_3 at different concentrations of II-modified Au nanoparticles, c_{II-Au}/mg· or ·mL^{-1}: a. 0.1; b. 1.01; c. 1.99; d. 3.98; e. 7.96.

nanoparticles aggregate in three-dimensional. The assembly of multidimensional nanoparticle arrays is a present topic of active research work [34].

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