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In situ synthesis of easily separable Au nanoparticles catalysts based on cellulose hydrogels

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Abstract

Cellulose hydrogels are "green" reductants and supports for Au nanoparticles (Au NPs). Herein, we report a facile method for synthesizing Au NPs based on alkali/urea regenerated cellulose hydrogels. By controlling the precursor concentration and the reaction temperature, the size of the Au NPs can be adjusted. We successfully demonstrate that the Au NP/cellulose hydrogels can be used as efficient heterogeneous catalysts in the reduction of 4-nitrophenol (4-NP). Au NPs with smaller sizes have higher catalytic activity. The highest turnover frequency (TOF) of the Au NPs/cellulose hydrogels is 19.4 h^{-1} . The Au NP/cellulose hydrogels can be easily isolated after the catalytic reaction.

Introduction

Hydrogels are cross-linked 3D networks that are capable of retaining water or other fluids without disintegration [1]. Over the last few decades, hydrogels have been widely used in absorbents, biomedical devices, cosmetics, food, catalysts, and other application [2–4]. To date, cellulose and its derivatives are considered as one of the most promising building blocks for hydrogel preparation owing to their ecofriendly nature, biodegradability, and abundant sources [2]. In most cases, cellulose can be prepared as a hydrogel via dissolution-regeneration process, which has attracted increasing attention in both industry and in research [3]. Ionic liquids and alkali/urea aqueous systems are typical solvents in the dissolution procedure. 3D networks could be formed via the reconstruction of hydrogen bonds in the regeneration process. The formed hydrogel with cellulose II crystallinity has many useful features such as a high porosity, hydroxyl reactivity, excellent thermal, and mechanical stabilities.

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Xiaobo Lin linxiaobo@iccas.ac.cn Recently, Au NPs have been used in various applications including catalysis, biosensing, electronics, and information storage. To data, a variety of methods, including improved citrate reduction, the polyol process, and physical radiolytic synthesis have been studied for the synthesis of Au NPs [4–6]. With the growing concerns about environmental issues, considerable attention has been paid to the "green" synthesis of Au NPs using non-toxic reducing agents and "green" solvents [7, 8]. Cellulose biomass, the most abundant natural biopolymer on the earth, is renewable, biodegradable, and affordable. It has been reported that cellulose biomass such as cellulose microfibrils, as well as cellulose I nanolayers could be employed for the eco-friendly fabrication of noble metal NPs [9–12]. Until now, the synthesis of Au NPs using cellulose hydrogelshas been a challenge.

Owing to their large specific surface areas, Au NPs show enhanced catalytic reactivity compared to that of the bulk in many reactions [13–15]. At the same time, the recovery and recyclability of Au catalyst is crucial due to the low earth abundance and high cost of Au. To date, a variety of materials including oxides, mesoporous molecular sieves, and nanofibers have been employed as supports to prevent the aggregation of Au NPs [16–18]. Moreover, the deposition of Au NPs on the surface of supports form heterogeneous catalysts that can be easily separated from solution by centrifugal, filtration, or magnetic separation [19]. Up to now, nanocrystal, bacterial cellulose, and TEMPO oxidized bacterial have been studied as effective reducing agents and supports for Au NPs [20–22]. However, when used as catalysts, these cellulose/Au NPs

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nanocomposites were suspended in solution, making the facile and direct separation of the catalysts difficult. Until now, few separable heterogeneous catalysts using regenerated cellulose hydrogels as reductants and supports have been reported.

In this work, we report a relatively simple method for the in situ synthesis of Au NPs based on cellulose hydrogels. The protocol typically started from chloroauric acid and microcrystalline cellulose with cellulose I crystallinity, and then Au NP/hydrogel composite with cellulose II crystallinity could be obtained through the dissolution, coagulation, and reduction of chloroauric acid. The Au NP/ cellulose hydrogels could be used as heterogeneous catalysts and they showed excellent catalytic activities and recyclability in the reduction of 4-nitrophenol (4-NP).

Experimental procedures

Materials and chemicals

Microcrystalline cellulose (MCC) (AR) was supplied by Albert Tianjin Company, China. Sodium hydroxide (AR) was purchased from Tianjin Kermel Chemical Reagent Company, China. Urea (AR), ethanol (AR), sodium hydroxide (AR), and hydrochloric acid (AR) were purchased from Tianjin Yongda Chemical Reagent Company, China. Chloroauric acid (AR) was punchased from Shenyang Jinke Reagent Company, China.

Preparation

In a typical procedure, microcrystalline cellulose was dissolved in a NaOH/urea (5 wt%) solution (pre-cooled to -12 °C) to form a 5 wt% cellulose solution. After removing air bubbles by centrifugation, 1 g cellulose solution (pre-cooled to 6 °C) was transferred to a circular mold (3 cm in diameter) without removing the residual NaOH and urea. Next, $500 \,\mu$ L of chloroauric acid (0.0002 to 0.005 mol/L) was added into the solution, which was stirred for 1 min. Then, the mixtures were coagulated by ethanol (3 mL) to give cellulose hydrogels (settled for 4 h). After thorough washing with deionized water, the mixtures were heated for 1 h at a certain temperature (in the range from room temperature to $100 \,^{\circ}$ C). The formed Au NPs/cellulose hydrogels were subjected to catalytic tests.

Characterization

The UV-vis absorption of the Au NPs/cellulose hydrogel was measured using a U-4100 UV spectrophotometer (Hitachi, Japan). The morphologies of the Au NPs/cellulose hydrogels were observed using a Jem-2100 (JEOL, Japan)

transmission electron microscope (TEM) operating at 100 keV. Specimens for TEM observations were prepared by depositing a drop of the hydrogel suspension (obtained by crushing the hydrogel in water) onto a carbon-coated copper grid and subsequent drying. The number-averaged diameters of the Au NPs were determined by measuring the diameters of more than 100 particles in the TEM images. The products were freeze-dried, and the X ray diffraction peaks of the product were determined by a D8-Advance (Bruker AXS, Germany) X-ray diffractometer (XRD). Inductively coupled plasma atomic emission spectrometry (ICP AES, Varian 710-ES, USA) was used to determine the concentrations of Au atoms.

Catalytic activity

For all catalytic experiments, the initial concentrations of 4nitrophenol (4-NP) and NaBH₄ were kept at 1.6 mmol/L and 0.42 mol/L, respectively. First, 16 mL of water, 2 mL of 4-NP, and 2 mL of NaBH₄ were added to a flask. The Au NPs/cellulose hydrogels (prepared from 1 g of regenerated cellulose solution) were added to the mixtures without stirring. The addition of the Au NPs/cellulose hydrogels to the mixtures caused a decrease in the intensity of the peak of 4-NP. To a quartz cuvette with a 1 cm path length, were added 2 mL of water and 1 mL of reaction mixture and the absorption spectrum was recorded on a U-4100 UV spectrophotometer (Hitachi).

Results and discussion

In the procedure, MCC was dissolved in aqueous NaOH/ urea. Then, chloroauric acid was added into the cellulose solution, which was stirred for 1 min at room temperature. The mixtures were coagulated by ethanol to give cellulose hydrogels. After the removal of ethanol, the mixtures were heated to give the final products. In our procedure, the Au ions could be reduced by the cellulose solution during the Au ions addition step and by the cellulose hydrogels during the heating step. Typically, the reducing group in cellulose is the hydroxy group. It has been reported that NaOH/urea aqueous system could dramatically weaken the hydrogen bonding of cellulose and thus dissolve cellulose. In solution, more activated hydroxyl groups could be liberated from the hydrogen bonding interactions in cellulose, which is great advantageous for the reduction of metal ions [2]. Before heating, colored cellulose hydrogels could be seen, which provides evidence for the reduction of Au ions by the cellulose solution. After heating, the color of the cellulose hydrogel deepened. Since Au ions were added into the cellulose solution, the Au ions would be confined in the cellulose hydrogels during gelation. During the ethanol removal step, part of the Au ions was removed, but some Au ions remained in the cellulose hydrogel due to the difficulty of diffusion. In another test, blank cellulose hydrogels were prepared and then immersed in a $HAuCl_4$ solution. After heating, only the surface of the cellulose hydrogels showed color changes (the formation of Au NPs). This result illustrates that the diffusion of Au ions inside the hydrogels is difficult. In our procedure, the trapped Au ions were reduced by the cellulose hydrogels to give the final products in the heating step.

Typically, the reducing group of cellulose is the hydroxy group [18]. It can be inferred that a small amount of hydroxy group could be oxidized by $AuCl_4^-$ during the reduction of $AuCl_4^-$ to Au^0 . Since the cellulose crystallinity is based on the reconstruction of hydrogen bonds, it is possible that the change in the hydroxy content may influence the degree of cellulose crystallinity in the gelation process. Moreover, with addition of the HAuCl₄, the salting-out effect may increase the hydrophobic interchain interactions which may decrease the cellulose crystallinity [23]. To investigate the crystallization of the regenerated cellulose, XRD patterns of the Au NP/cellulose hydrogels with different initial $AuCl_4^-$ concentration were measured.

As shown in Fig. 1, the diffraction peaks at 14.5, 16.3, and 22.4° can be assigned to the (11(-)0), (110), and (200) planes of cellulose I of MCC. The XRD pattern of the freeze-dried cellulose hydrogel regenerated from aqueous NaOH/urea shows diffraction peaks at 12.2, 20.1, and 21.7°, corresponding to (11(-)0), (110), and (200)planes of cellulose II [24]. For the Au NP/cellulose hydrogels, the pattern shows apparent changes in the intensity of the diffraction peaks. With higher AuCl₄⁻ concentrations, the intensities of the diffraction peaks at 20.1 and 21.7° decrease, which can be attributed to the lower degree of crystallinity of cellulose II. Therefore, we believe that the addition of AuCl₄-before the gelation process may decrease the crystallinity of cellulose II. However, it was difficult to illustrate that the decrease in the crystallinity of cellulose II was caused by the oxidation-reduction reaction or the presence of AuCl₄⁻. Further work is required to clarify this phenomenon and the mechanism remains to be established.

As shown in Fig. 2a, after dissolution, coagulation and in situ synthesis, purple and black Au NPs/cellulose hydrogels were formed, and the color darkened with increasing AuCl₄⁻ concentration. Figure 2a shows the UV-vis absorbance spectra of the Au NP/cellulose hydrogels with AuCl₄⁻ concentrations of 0.001, 0.003, and 0.005 mol/L. There are clear peaks centered at 523, 531, and 548 nm, respectively, which correspond to the characteristic plasmon resonance band of Au NPs, implying the formation of Au NPs. The redshift in the absorption peak with higher AuCl₄⁻ concentration can be



Fig. 1 XRD pattern of MCC, the blank cellulose hydrogel, and the Au NP/cellulose hydrogels with $AuCl_4^-$ concentrations of 0.001, 0.003, and 0.005 mol/L. The heating temperature was 70 °C

attributed to the presence of large Au NPs. Moreover, in Mie theory, monodispersed spherical Au nanocrystals show a single narrow and symmetrical absorption peak; thus, the considerably wide peaks in the UV-vis spectra suggest that Au NPs in the cellulose hydrogels are not uniform in shape and size [6].

TEM and HRTEM studies were carried out to study the formed Au NPs/cellulose hydrogels with different AuCl₄ concentrations. It can be seen from Fig. 2 that for a AuCl₄⁻ concentration of 0.001 mol/L, nearly spherical Au NPs with a mean diameter of 4.0 nm are formed (the corresponding statistical histograms are shown in the supporting information). The particles are anchored on the surface of the cellulose networks without apparent aggregation. The reason for this result can be attributed to the "small size effect". In general, the surface energy of Au NPs is significantly higher than that of the bulk. Small Au NPs are unstable and are inclined to adsorb to a medium or aggregate to decrease the surface energy by balancing the surface and migration energies. From the results of this study, it can be demonstrated that the cellulose hydrogels could act as loading media for the formed Au NPs. The HRTEM observations (Fig. S1) show that the lattice fringe spacing is measured to be 0.23 nm, which corresponds to the (111) plane of the face-centered cubic (fcc) structure of Au NPs. The increase in the precursor concentrations from 0.001 to 0.005 mol/L caused apparent changes in the particle sizes, which varied from 4.0 to 22.6 nm (Fig. S2). As shown in Fig. 2d, for a $AuCl_4^-$ concentration of 0.005 mol/L, large Au NPs approximately 70 nm in diameter began to form. Moreover, as shown in Fig. S2c, the histogram of the Au



Fig. 2 a UV-vis spectra of the Au NP/cellulose hydrogels with $AuCl_4^-$ concentrations of 0.001, 0.003, and 0.005 mol/L. TEM images of the Au NP/cellulose hydrogels with different $AuCl_4^-$ concentration: (b) 0.001 mol/L, (c) 0.003 mol/L, and (d) 0.005 mol/L. The heating temperature was 70 °C

NP size showed some small particles, as well as some large particles. The fact that Au ions can be reduced by the cellulose solution and by the cellulose hydrogels is likely to be the major reason for this phenomenon. These data are consistent with the results of the UV-vis measurement.

It is well documented that the reaction temperature is crucial in the nucleation and growth of metal NP, and determines the morphology of the Au NPs [19, 25]. Fig. 3 shows the UV-vis spectra and TEM images of the Au NP/ cellulose hydrogels prepared at different temperature (25 to 100 °C). As shown in Fig. 3a, the UV-vis absorption peak of the Au NPs obtained at 100 °C was observed at 511 nm and this peak moved to 536 nm with a redshift of 25 nm for the Au NPs obtained at 25 °C.

The TEM images (Fig. 3b-d) show that at higher reaction temperatures, more small particles formed, and the average particle size varied from approximately about 46.8 to 17.6 nm. Since nucleation occurs through the movement and reduction of AuCl₄⁻, it is likely that the diffusion of AuCl₄⁻ that is confined in the space of the cellulose gels requires more time. This confined diffusion would decrease the quantity of Au crystal nucleus formed at lower temperatures. Accordingly, fewer small particles could form inside the cellulose hydrogels at lower temperatures. This result is consistent with the UV-vis measurements. Additionally, it has been reported that metal NPs with smaller sizes show higher catalytic activities in a number of reactions [15]. In



Fig. 3 a UV–vis spectra of the Au NP/cellulose hydrogels at temperatures of 25, 70, and 100 °C. TEM images of the Au NP/cellulose hydrogels prepared at different temperatures: (b) 25 °C, (c) 70 °C, and (d) 100 °C. The concentration of HAuCl₄ was 0.004 mol/L

our experiment, we could utilize a high reaction temperature to obtain catalysts with a smaller particle size.

The reduction of 4-NP by NaBH₄ was used as a model reaction for evaluating the catalytic activity of the Au NPs/ cellulose hydrogels. It is well documented that the reduction reaction does not proceed without catalyst. The addition of the Au NP/cellulose hydrogels to the reaction mixture caused gradual fading of the yellow color. This color change was used to monitor the reaction kinetics on the basis of spectroscopic measurements. Figure 4a shows a typical change in the UV-vis spectrum caused by the reduction of 4-NP by NaBH₄ in the reaction catalyzed by the Au NP/cellulose hydrogels. The absorption by 4-NP at 400 nm gradually decreases, concomitant with the appearance of a new band at 300 nm, which can be assigned to the production of 4-aminophenol (4-AP).

It can be inferred that higher reaction temperature and lower precursor concentration is beneficial for the preparation of Au NPs with smaller size. Herein, Au NPs/cellulose hydrogels were prepared at 100 °C with AuCl₄⁻ concentrations of 0.0002 (the TEM observation and the statistical histograms are shown in Fig. S4) and 0.004 mol/L. The average diameter of the Au NPs in the composite was 3.0 and 17.6 nm, respectively, and the yield of Au NPs was 54.1 and 57.5% (Table S1). As shown in Fig. 4b, the catalytic activities of the Au NP/cellulose hydrogels obtained with AuCl₄⁻ concentrations of 0.0002 and 0.004 mol/L are depicted according to the changes in the absorbance at a wavelength of 400 nm versus the reaction time. The

Fig. 4 a Time-dependent UV-vis spectra for the reduction of 4-NP catalyzed by 0.004 mol/L AuCl₄-(containing 1.15 µmol Au). Time course: 0, 16, 24, 36, 48, 60, 72, 84, 96, and 108 min. b Catalytic activities of the Au NP/cellulose hydrogels with initial AuCl₄ concentration of 0.0002 and 0.004 mol/L. c Photograph of the reaction and schematic illustration of the recycling of the catalyst with an initial AuCl₄ concentration of 0.004 mol/L. d TOF of 4-NP during the cyclic test for the catalyst with an initial AuCl₄⁻ concentration of 0.0002 mol/L



catalytic efficiency was estimated by turnover frequency (TOF), which is defined as

$$TOF = n_p / n_c t \tag{1}$$

where n_p and n_c are the moles of for product formed during a reaction time t and the moles of the catalyst, respectively. Herein, n_c is the number of Au atoms in the Au NP/cellulose hydrogels, which was calculated by ICP measurements (total amount of Au minus the amount of Au in the liquid, as summarized in Table S1). The TOF values of the Au NPs/cellulose hydrogels could be calculated from Fig. 4b. The highest TOF values of the Au NPs/cellulose hydrogels with AuCl₄⁻ concentrations of 0.0002 and 0.004 mol/L are 19.4 and 0.03 h⁻¹, respectively. The catalytic activity is negatively dependent on the particle size. This result agrees with the fact that Au NPs with larger accessible surfaces are more active [26]. The highest TOF value of the Au NP/cellulose hydrogels in this work is 19.4 h⁻¹, which is lower than some cellulose supported Au NPs, such as the bacterial cellulose supported Au NPs and nanocrystalline cellulose supported Au NPs [26, 27], but higher than some Au NP catalysts in the literature such as polymer supported Au NPs [28]. (Table 1). It has been reported that $_4$ NP reduction is postulated to follow the Langmuir-Hinshelwood mechanism. First, borohydride ions react with the metal surface of Au NPs with the concurrent adsorption of nitrophenolate ions. Then, electrons are transferred from the borohydride ion to the 4-NP ion through the Au NPs surface to reduce the 4-NP ion to 4-AP, which is the rate determining step. After that both H^+ and 4-AP ions desorb from the Au surface to produce 4-AP [29]. In our system, since the Au NPs are confined in the spaces within the cellulose hydrogels, it is likely that the contact between 4-NP, NaBH₄, and the Au NPs, as well as the dissociation of 4-AP would be blocked by the cellulose network, which would decrease the catalytic efficiency of the Au NPs in the reduction reaction.

The recovery and recyclability of the Au catalyst is crucial due to the low earth abundance of Au. Au NPs catalysts can be recovered through dialysis, filtration, centrifugation, or magnetic removal [26-28, 30, 31]. Our protocol demonstrated that the cellulose hydrogels could be used as eco-friendly supports for Au catalyst in the reduction of 4-NP with facile isolation. The catalyst could be easily recovered by removing it from the mixture, and its activity was nearly retained. Only a slight decrease in the TOF of approximately 6.2% was observed in the 4th cycle (Fig. 4d, Table S2). A possible cause of this deterioration is the release of Au particles from the cellulose hydrogels [18]. Further work is required to clarify this degradation of the catalytic activity in the present system. The Au NP/ cellulose hydrogels obtained in our experiment could be stored for several months without apparent changes. This phenomenon demonstrates that regenerated cellulose hydrogels could serve as excellent stabilizers for Au NPs with good swelling resistance. Moreover, as could be predicted, Au NP/cellulose aerogels could be formed via

Table 1 Reduction of 4-NP over Au nanocatalysts

Catalyst support	Temp. (K) ^a	Au NPs size (nm)	NaBH ₄ /4-NP/Au (mole ratio)	TOF (h ⁻¹) ^b	Recovery method	Ref.
Cellulose hydrogels	298	3.0	15503/59/1	19.4	Taking out	This work
PNIPAP-b-P4VP	298	167/5/1	167/5/1	15.5	Dialysis	[28]
PDMAEMA-PS	298	4.2	28/0.14/1	0.7	_ ^c	[<mark>30</mark>]
PDDA/NCC	298	3.09 ± 0.1	36585/ 37/1	212	Filtration	[27]
AOBC	298	10.6 ± 2.9	244444/280/1	1198	_d	[26]
Chitosan/ iron oxide	303	3.14	20/6/1	50	Magnetic field	[31]
Wood nanomaterials	298	2.5	466.6/1.4/1	75.9	Centrifugation	[18]

^a Reaction temperature

^b TOF estimated using the data in corresponding references

^c No data available

^d A reaction column with filter paper pulp and sea sand was prepared

supercritical drying of the hydrogels and were used as a catalytic membrane [2]. We would keep that in focus in our group.

Conclusions

We demonstrated here that regenerated cellulose can be effectively applied as a reducing agent and support for Au NPs. The size of the formed Au NPs could be adjusted by varying the reaction parameters. With higher AuCl₄⁻ concentrations, the average diameter of the Au NPs increased dramatically. At the same time, the crystallinity of cellulose II decreased with the increase of precursor concentration. Moreover, it was found that the average diameter of the Au NPs decreased remarkably with increasing reaction temperature. The resultant Au NP/ cellulose hydrogels showed excellent catalytic activity in the reduction of 4⁻NP by NaBH₄. The catalytic activity of the Au NP/cellulose hydrogels negatively depended on the particles size. Moreover, the heterogeneous catalysts could be easily isolated and reused after the catalytic reaction. The procedure developed here offers a potentially useful route for utilizing regenerated cellulose as a functional material.

Supporting information

HRTEM images of the Au NP/cellulose hydrogels with a $AuCl_4^-$ concentration of 0.001 mol/L. Statistical histograms of the Au NP/cellulose hydrogels with $AuCl_4^-$ concentration of 0.001, 0.003, and 0.005 mol/L, prepared with a reaction temperature of 70 °C. Statistical histograms of the Au NP/cellulose hydrogels prepared at different

temperatures: (a) 25 °C, (b) 70 °C, and (c) 100 °C, with a HAuCl₄ concentration of 0.004 mol/L. TEM image of the Au NP/cellulose hydrogels prepared with a AuCl₄⁻ concentration of 0.0002 mol/L and a reaction temperature of 100 °C. Loading amount of Au in the Au NP/cellulose hydrogels. Recycle ability of the Au NP/cellulose hydrogels in the reduction of 4–NP.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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