Novel synthesis of Au nanoparticles using fluorescent carbon nitride dots as photocatalyst

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Abstract The present paper reports on a novel synthesis for Au nanoparticles (AuNPs) with the use of fluorescent carbon nitride dots (CNDs) as a photocatalyst. It suggests that the resultant CND-protected AuNPs (CNDs/AuNPs) exhibit good catalytic activity toward 4-nitrophenol reduction and that the CNDs enhance the catalytic activity via a synergistic effect.

Keywords Au nanoparticle · Carbon nitride dot · Fluorescence · Photocatalyst · 4-Nitrophenol reduction · Synergistic effect

Introduction

In the past few years, metal nanoparticles have been the focus of significant scientific research owing to their size-dependent

physical and chemical properties, and substantial effort has been invested into their synthesis and characterization [1, 2]. Among them, Au nanoparticles (AuNPs) are the most stable noble nanoparticles, and as key materials and building blocks for the twenty-first century [3], they represent one of the most widely studied nanomaterials [4]. Although the use of soluble Au dates back to the fifth to fourth century BC [3], the first report of the formation of stable gold colloids appeared as recently as 1857 [5]. After that, many preparative methods have been developed, including chemical reduction, photochemistry, sonochemistry, radiolysis, and thermolysis [1–3]. Among these methods, the photochemical one is unique due to its excellent spatial and temporal control. It has no rigorous temperature requirements and does not require the use of harmful strong reducing agents [6]. Indeed, the photochemical route has drawn great attention in synthesizing metal NPs [7–10]. Photocatalysts like polyoxometalates, porphyrin, and semiconductors have been applied to the photochemical synthesis of metal NPs [11–14]. However, most of the photocatalysts are either expensive or involve complex preparation. Accordingly, there is a strong desire to develop economical and simple photocatalysts for the synthesis of metal NPs.

Carbon nitride materials have been the focus of materials research because of their unique properties and wide applications in catalysis, sensors and corrosion protection, etc. [15–21]. More recently, photoluminescent carbon nitride dots (CNDs) have been easily prepared by the polymerization of CCl_4 and 1,2-ethylenediamine (EDA) under reflux, microwave, or solvothermal heating [22]. In this paper, we demonstrate a novel application of such CNDs as an effective photocatalyst to synthesize AuNPs for the first time, carried out by UV irradiation of an aqueous HAuCl_4 solution in the presence of ethanol and CNDs. It suggests that the resultant CND-protected AuNPs (CNDs/AuNPs) exhibit good activity in catalyzing the reduction of 4-nitrophenol

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(4-NP) by NaBH_4 . In addition, CNDs play a synergistic role in enhancing the catalytic activity of Au catalysts.

Experimental

The chemicals CCl_4 , EDA, and HAuCl_4 were purchased from Aladin Ltd. (Shanghai, China). 4-NP was purchased from Sinopharm Chemical Reagent Co. Ltd, and sodium borohydride (NaBH_4) was purchased from Tianjin Fuchen Chemical Corp. Gold sol solution (average, 15 nm) was purchased from Shanghai Jieyi Biotechnology Co., Ltd. All the chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

The photoluminescent CNDs were prepared following our previous work [22] by the polymerization of CCl_4 and EDA under reflux heating. CCl_4 and EDA are used as carbon and nitrogen sources, respectively. In a typical synthesis, 0.69 mL of EDA was added to 1 mL of CCl_4 solution. After that, the mixture was heated to 80°C for 60 min. The excess precursors and the resulting small molecules were removed by dialyzing against water using a dialysis membrane for 1 day. The resultant CNDs were dispersed in water for further characterization and use.

The synthesis of AuNPs was carried out in a quartz cuvette using CNDs as a photocatalyst. Twenty microliters of CNDs and 40 μL of HAuCl_4 (24.3 mM) were injected into 3 mL 30 % (volume ratio) ethanol aqueous solution in the quartz cuvette. The mixture was placed under a 50-W high-pressure mercury lamp ($\lambda=254\text{ nm}$) for 1 h to obtain AuNPs.

The UV/Vis absorption spectra were recorded on a UV5800 spectrophotometer. The suspension was added into a quartz cuvette ($1\times 1\text{ cm}$, 4 mL) to obtain the UV/Vis absorbance data. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on a carbon-coated copper grid and drying at room temperature. Fluorescence emission spectra were recorded on a Shimadzu RF-5301 spectrofluorometer (Shimadzu Corporation, Kyoto, Japan). A 75-fold diluted solution was introduced to a quartz cuvette ($1\times 1\text{ cm}$, 2 mL) to obtain fluorescence emission data (excitation wavelength, 360 nm). Zeta potential measurements were performed on a Nano-ZS Zetsozer ZEN3600 (Malvern Instruments Ltd., UK). The dispersion was transferred to the test cell and measured by the device for three replicates. X-ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALAB MK II X-ray photoelectron spectrometer using $\text{Mg K}\alpha$ (1,253.6 eV) as the exciting source for approximately 14 h in a permanent working mode (12 kV, 20 mA). The sample for XPS characterization

was prepared by placing a drop of the dispersion on a bare indium tin oxide-coated glass substrate, which was air-dried at room temperature. All binding energies were determined after charge correction of the XPS data measured without the use of ion gun by setting, $C_{1s}=285.0\text{ eV}$.

Results and discussion

Figure 1 shows the UV/Vis absorption spectra of the aqueous dispersions of CNDs, HAuCl_4 , and CNDs– HAuCl_4 mixture before and after 1 h UV irradiation. It is seen that CND dispersion shows two peaks at 226 and 360 nm (curve a). The yellowish HAuCl_4 solution shows an intense absorption band at 320 nm (curve b) due to the metal-to-ligand charge transfer (MLCT) transition of the AuCl_4^- complex [23]. The CNDs– HAuCl_4 mixture before irradiation shows two peaks at 230 and 320 nm (curve c). In contrast, the mixture shows a new intense surface plasmon resonance (SPR) absorption band at 527 nm with the disappearance of the MLCT band at the same time after 1 h irradiation (curve d), suggesting that AuCl_4^- is reduced and AuNPs are generated [3]. Colloidal gold is known to have an intense SPR absorption in the visible region which generally occurs around an energy corresponding to 520 nm. The SPR is caused by light waves that are trapped on the surface due to the interaction with the free electrons of the metal, and the free electrons will oscillate in a collective fashion when the light wave meets the resonance conditions [24]. The color change of the mixture from yellow to purple before and after UV irradiation (inset) provides another piece of evidence to support the formation of AuNPs.

Fig. 1 UV/Vis absorption spectra of the aqueous dispersions of CNDs (a), HAuCl_4 (b), CNDs– HAuCl_4 mixture before (c) and after (d) 1 h of UV irradiation (inset, photographs of CNDs– HAuCl_4 mixture before and after UV irradiation)

Figure 2 shows the TEM images of the product thus formed, indicating the formation of nanoscale particles that are nearly spherical in shape. The corresponding particle size distribution histograms shown in Fig. 2c indicate that they have diameters ranging from 5 to 25 nm. The chemical composition of the product was further determined by the energy-dispersed spectrum, as shown in Electronic supplementary material (ESM) Fig. S1. The peaks of C, N, and Au elements are observed, indicating the existing of CNDs and AuNPs. The peaks of Si and Cu elements originate from the copper grid substrate used for TEM measurements, and the Cl element observed originates from Cl^- ions released from AuCl_4^- . The high-resolution TEM (HRTEM) image taken from one nanoparticle (see the inset in Fig. 2b) reveals clear lattice fringes with an interplane distance of 0.236 nm corresponding to the (111) lattice space of metallic gold [25], further suggesting that these particles are AuNPs. It is worth mentioning that these AuNPs can be very stable for several weeks without observation of any floating or precipitated particles. The zeta potential of AuNPs was measured as 8.35 mV as a positive net charge, which can be attributed to the adsorption of positively charged CNDs. The discrepancy of the zeta potential between AuNPs and CNDs (27.2 mV) [22] is due to the simultaneous adsorption of negatively charged counterions, i.e., Cl^- ions, on AuNPs [26]. The observation of zeta potential at charge stoichiometry being still positive of incomplete charge neutralization is due to the stabilized assembly charge caused by steric factors [27]. It is well established that AuNPs can quench fluorescence when fluorescent molecules and AuNPs are brought into close proximity with each other [28, 29]. Indeed, substantial fluorescence quenching is observed for the CNDs– HAuCl_4 mixture after UV irradiation (ESM Fig. S2), which can be attributed to the fact that some CNDs are associated with the AuNPs formed; subsequently, fluorescence quenching occurs with the fluorescence resonance energy transfer between CNDs and AuNPs

[30]. The residual fluorescence observed originates from free CNDs existing in the dispersion.

The surface composition and elemental analysis for the resultant nanoparticles were characterized by the XPS technique. The XPS spectra of the nanoparticles are shown in Fig. 3. The five peaks at 56.8, 85.2, 334.2, 353.0, and 546.3 eV in Fig. 3a are attributed to Au_{5p3} , Au_{4f} , Au_{4d5} , Au_{4d3} , and Au_{4p3} , respectively. Another three peaks at 285.0, 398.8, and 531.8 eV associated with C_{1s} , N_{1s} , and O_{1s} are also observed. The XPS results show that the nanoparticles obtained are mainly composed of C, N, and Au and limited amounts of O element. O atoms may come from the O_2 , H_2O , or CO_2 adsorbed on the surface of particles [22]. The Au_{4f} , C_{1s} , and N_{1s} regions were analyzed using the peak deconvolution method. The spectrum of Au_{4f} shows two peaks at 83.9 eV for $4f_{7/2}$ and 87.5 eV for $4f_{5/2}$ (Fig. 3b). The position and difference between the two peaks (3.8 eV) exactly match the value reported for Au^0 [31]. The absence of a binding energy at 84.9 eV, corresponding to Au^{3+} , further indicates that the gold atoms exist as Au^0 (AuNPs) [32]. Furthermore, the C_{1s} spectrum of the nanoparticles (Fig. 3c) exhibits three peaks at 284.6, 285.8, and 288.1 eV, which are attributed to C–C, C–N, and C=N, respectively. The N_{1s} spectrum of such nanoparticles (Fig. 3d) exhibits three peaks at 398.5, 399.4, and 400.6 eV, which are associated with the C–N–C, N–(C)₃, and N–H groups, respectively [33]. The XPS spectrum data are consistent with that of CNDs reported by our previous work [22] and prove the existence of CNDs in the product. The XPS data further confirm the formation of CNDs/AuNPs [34].

In light of the total absence of any specific reducing agent in the solution, the formation of the AuNPs is quite surprising and can be ascribed to a photoinduced reductive pathway with the use of CNDs as a photocatalyst. Scheme 1

Fig. 2 a, b Typical TEM images at different magnifications of the AuNPs thus formed. c Corresponding particle size distribution histograms. *Inset* in (b) shows a HRTEM image of one single AuNP

Fig. 3 **a** XPS spectrum of AuNPs thus formed. **b** Au_{4f} spectrum. **c** C_{1s} spectrum. **d** N_{1s} spectrum of AuNPs thus formed (red line, the sum of all peaks)

illustrates the proposed mechanism for the photochemical synthesis of AuNPs. The fluorescent CNDs have a strong UV absorption before 360 nm (a in Fig. 1). Electron and hole pairs are generated in the CNDs upon UV excitation (reaction 1) [35, 36]. The photogenerated electrons reduced the surrounding $AuCl_4^-$ (reaction 2), while the holes were scavenged by the alcohols (reactions 6) [37]. Au^0 atoms are generated after the fast disproportionation of Au_2^+ (reaction 3) and the disproportionation of Au^+ and Au_2^+ (reaction 4) [38]. After the start of the photocatalytic reaction, the concentration of Au^0 atoms steadily increases with elapsed time as $AuCl_4^-$ is reduced. When the concentration reaches the point of supersaturation, the Au^0 atoms start to form small clusters, i.e., nuclei by diffusion-limited aggregation (reaction 5), and then finally grow into CND-protected nanocrystals [39]. As reported previously, $AuCl_4^-$ itself can be

photochemically reduced to Au^0 atoms [40]. To confirm the catalytic effect of CNDs in synthesizing AuNPs, control experiments were conducted by the UV irradiation of an equal amount of $HAuCl_4$ in aqueous solution of ethanol for 1 h, in the absence of CNDs. The solution color changed from clear light yellow to colorless due to the photoinduced reduction of Au^{3+} to Au^+ [41]. However, no AuNPs were obtained. Also, keeping the CNDs- $HAuCl_4$ mixture with the presence of ethanol in the dark for several days or under visible light irradiation for several hours failed to produce AuNPs. All these observations indicate that CNDs indeed serve as an effective photocatalyst for the photoreduction of $AuCl_4^-$.

Scheme 1 Scheme (not to scale) illustrating the proposed mechanism for the photochemical synthesis of AuNPs

Fig. 4 **a** UV/Vis absorption spectra of 4-NP and time-dependent absorption spectra for the catalytic reduction of 4-NP by NaBH₄ in the presence of CNDs/AuNPs (**b**) and AuNPs (**c**). **d** Plot of $\ln(C_t/C_0)$ of 4-NP against time for the catalysts. Conditions: [4-NP]=3.5 mM; [Catalyst]=30 mg/L; [NaBH₄]=80 mM

It is well known that 4-aminophenol (4-AP) is very useful and important in many applications that include analgesic

and antipyretic drugs, photographic developer, corrosion inhibitor, anti-corrosion lubricant, and so on [42, 43]. The reduction of 4-NP by NaBH₄ in the presence of noble metal nanoparticles as catalysts has been intensively investigated for the efficient production of 4-AP [44, 45]. Therefore, the reduction of 4-NP to 4-AP with an excess amount of NaBH₄ was used as a model system to quantitatively evaluate the catalytic activities of CNDs/AuNPs. As indicated in Fig. 4a, pure 4-NP shows a distinct spectral profile with an absorption maximum at 316 nm. When a NaBH₄ solution was added into the 4-NP, a new absorption peak was observed at 400 nm, corresponding to the 4-NP ions in alkaline conditions [46]. The absorption intensity of 4-NP ions at 400 nm decreased quickly with time, accompanied with the appearance of the peak of 4-AP at 300 nm, indicating successful conversion of 4-NP to 4-AP.

Scheme 2 Scheme (not to scale) illustrating the proposed mechanism of synergistic enhancement in CNDs/AuNPs

The total reduction reaction is summarized by the following equation:

It should be noted that the reduction of 4-NP by NaBH_4 was finished within 50 min upon the addition of CNDs/AuNPs (Fig. 4b), with the observation of a fading and ultimate bleaching of the yellow green color of the reaction mixture in aqueous solution. However, a longer reaction time of 90 min was required to achieve the full reduction using gold sol solution (AuNPs stabilized by sodium citrate, about 15 nm in diameter) as a catalyst which contained equivalent Au atoms (Fig. 4c). The reproducibility of the result was tested for three replicates to confirm the enhanced catalytic activity of CNDs/AuNPs than AuNPs. Without the addition of a catalyst, the reduction did not proceed, and the absorption peak centered at 400 nm remains unaltered over time. However, due to the presence of a large excess of NaBH_4 compared to 4-NP, the rate of reduction is independent of the concentration of NaBH_4 . ESM Fig. S3 presents the analysis of the experimental data using different kinetic models, indicating that the first-order reaction model is the most precise for the 4-NP catalytic reduction system [47]. Hence, $\ln(C_t/C_0)$ versus time can be obtained based on the absorbance as a function of time, and good linear correlations are observed, as shown in Fig. 4d, suggesting that the reactions follow first-order kinetics. Then, the kinetic reaction rate constants (defined as k_{app}) are estimated from the slopes of the linear relationship to be $5.25 \times 10^{-2} \text{ min}^{-1}$ (AuNPs) and $9.43 \times 10^{-2} \text{ min}^{-1}$ (CNDs/AuNP), respectively.

These results clearly indicate the CNDs/AuNPs have a higher catalytic activity for the reduction of 4-NP than the AuNPs only. The π -rich nature of CNDs adsorbed on the surface of AuNP may play an active part in the catalysis, yielding a synergistic effect. The synergistically enhanced catalytic activity may be explained as follows: it is expected that 4-NP can be adsorbed onto CNDs via π - π stacking interactions. Such adsorption provides a high concentration of 4-NP near to the CNDs/AuNPs, leading to a highly efficient contact between them (Scheme 2a). In contrast,

without the presence of CNDs on the nanoparticle surface, 4-NP must collide with AuNPs by chance and remains in contact for the catalysis to proceed. When this is not achieved, 4-NP will pass back into the solution and can only react further when it collides with AuNPs again (Scheme 2b) [48, 49].

Conclusions

In summary, AuNPs were synthesized using fluorescent CNDs both as an effective photocatalyst and a stabilizer to protect the synthesized AuNPs from aggregation. Such CNDs/AuNPs are found to exhibit good catalytic performance toward 4-NP reduction, and the synergistic effect of adsorbed CNDs enhances the catalytic activity of Au catalysts. We believe that these studies will provide a general CND-based synthesis strategy and lead to the development and design of simple chemical synthesis of metal nanoparticles methodologies.

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