Effect of ligand structure on the catalytic activity of Au nanocrystals

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The surface coating-dependent catalytic activity of icosahedral Au nanoparticles (IAuNPs) for the reduction of 4-nitrophenol by NaBH\textsubscript{4} in aqueous solution was investigated. Cetyltrimethylammonium bromide (CTAB)-stabilized IAuNPs with average size of 50 nm were prepared by three-step seeding protocol. The CTAB was then exchanged with several amine derivatives such as pyrrole, pyridine, 2,2′-bipyridine, and 4,4′-bipyridine. The catalytic reaction rates of nanoparticles are in the order of IAuNPs@4,4′-bpy > IAuNPs@2,2′-bpy > IAuNPs@pyridine > IAuNPs@pyrrole > IAuNPs@CTAB, revealing that the catalytic activity of the nanoparticles highly depends on the type and structure of the ligand molecules.

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1. Introduction

In the past decades, tremendous research interest has been focused on the noble metal nanoparticles because of their unique optical and electrical properties [1] and their promising applications in catalysis [2], optics [3], sensors [4], and solar cells [5]. Particularly, Au nanoparticles (AuNPs) have potentially high catalytic activity although bulk Au is typically an ineffective catalyst [6]. In fact, stabilized AuNPs were frequently employed as active units in catalysis [7].

For preparing stable AuNPs, surface-stabilizers such as alkylthiolate, poly(vinyl pyrrolidone), and cetyltrimethylammonium bromide (CTAB) have been widely used. However, application of AuNPs to various fields such as catalysis, optics, and sensors can be potentially restricted owing to these stabilizers. For instance, Stowell and Korgel [2] and El-Sayed and coworker [8] demonstrated that ligand stabilization could decrease the catalytic activity of nanoparticles in some cases. On the basis of this fact, choice of an appropriate capping ligand which can enhance both stability and activity of the particles is crucial in the application of nanoparticles to catalysis.

Here we report on the surface coating-dependent catalytic activity of polyhedral metal nanoparticles, i.e., icosahedral AuNPs (IAuNPs). Due to their well-defined polyhedral morphology, there are a number of catalytic active sites such as corners and edges on the surfaces of the IAuNPs [9,10]. Although IAuNPs have many potentially active sites, they have weak catalytic activity due to the presence of many stabilizers on their surfaces. In fact, CTAB has been used as a stabilizer in the preparation of IAuNPs, which could decrease the catalytic activity of the particles owing to the inhibition of close contact between reactants and surface of catalysts. In this work, the surface of IAuNPs has been modified with various small organic amine additives such as pyrrole, pyridine, 2,2′-bipyridine, and 4,4′-bipyridine through ligand exchange reaction in order to improve the catalytic activity of IAuNPs, and ligand-dependent catalytic activity was investigated. Amine derivatives were chosen as ligand molecules because they can be bound strongly to the AuNPs surfaces through the Au–N bond and their adsorption structures have been well studied [11–14]. To investigate how the nature of the stabilizer has an influence on the catalytic activity of IAuNPs, the reduction of 4-nitrophenol (4-NP) by NaBH\textsubscript{4} has been chosen as a model reaction because this reaction is rapid and can be easily characterized [15–17]. Moreover, 4-NP is a typical contaminant of industrial wastewater and employed in a number of industrial processes such as the manufacture of explosives, drugs, dyes, insecticides, and pesticides [18].

2. Experimental

HAuCl\textsubscript{4}, CTAB, trisodium citrate, pyrrole, pyridine, 2,2′-bipyridine, and 4,4′-bipyridine were purchased from Aldrich. Other chemicals, unless specified, were reagent grade, and Milli-Q water...
with a resistivity greater than 18.0 MΩ cm was used in the preparation of aqueous solutions.

CTAB-stabilized IAuNPs with average size of ca. 50 nm were prepared by three-step seeding protocol [10]. In a typical ligand exchange reaction, 10 µL of 5.6 × 10⁻⁴ M aqueous solution of amine derivative (pyrrole, pyridine, 2,2'-bipyridine, and 4,4'-bipyridine) was added into a microtube containing 200 µL of aqueous solution of CTAB-stabilized IAuNPs, and the mixture was stored for overnight.

The catalytic reduction of 4-NP was studied as follows. In a standard quartz cuvette with a 1 cm path length, 2.745 mL of water, 0.030 mL of the surface-modified Au hydrosol, and 0.150 mL of 1.00 × 10⁻³ M 4-NP were mixed. Then, 0.0750 mL of 2.00 × 10⁻¹ M NaBH₄ was introduced into this mixture and time-dependent absorption spectra were recorded every 8 min in the range of 190–1000 nm at 25 °C.

The extinction spectra were recorded with a SINCOS S-3100 UV–vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained with a FEI Technai G2 F30 Super-Twin transmission electron microscope operating at 300 kV.

3. Results and discussion

IAuNPs stabilized with amine derivatives were prepared by substitution of CTAB ligand with pyrrole, pyridine, 2,2'-bipyridine (2,2'-bpy), and 4,4'-bipyridine (4,4'-bpy). The ligand desorption kinetics depend on the binding strength between the ligand functional group and the inorganic nanocrystal surface. Since the Au–N bond is considerably more covalent than Au–N⁺ bond owing to charge donation/back-donation mechanism, Au–N bond has a larger binding energy than Au–N⁺ [19]. Therefore, CTAB which has a relatively weak binding strength to Au can be easily stripped from the nanocrystal surfaces by ligand exchange reaction with amine additives. The functionalization of the AuNPs with amine compounds was verified by UV–vis spectroscopy. It is well-known that the AuNPs exhibit strong plasmon resonance absorption that is dependent on their size and shape [20,21]. The surface plasmon band is also influenced by the surrounding media, especially by the nature of surface capping agent [22]. Fig. 1 shows the UV–vis absorption spectra of the as–prepared CTAB- and amine derivatives-stabilized IAuNPs. Each spectrum exhibits a single strong surface plasmon peak at ~530 nm which can be assigned to dipole plasmon resonance [9,23]. It is noticeable that plasmon peaks of all the amine derivatives-stabilized IAuNPs are narrower than that of CTAB-stabilized IAuNPs, revealing the effective exchange of CTAB with amine compounds. Such the variation of bandwidth of surface plasmon absorption has been frequently observed for ligand exchange processes [24].

The particle structures and size distributions can be determined by TEM measurements. Fig. 2 shows the TEM images of CTAB- and amine-coated IAuNPs. As shown in the figure, the prepared particles have hexagonal morphology which is a typical projected image of icoshedral particles [9]. All the particles have well-defined edges and corners, and they have generally sharper surface features than spheres. Furthermore, size and shape distributions are very narrow. The measured mean particle sizes were mostly around 50–51 nm; IAuNPs@CTAB (50.4 ± 1.2 nm) (Fig. 2a), IAuNPs@pyrrole (50.8 ± 1.2 nm) (Fig. 2b), IAuNPs@pyridine (50.4 ± 1.8 nm) (Fig. 2c), IAuNPs@2,2'-bpy (50.5 ± 1.4 nm) (Fig. 2d), and IAuNPs@4,4'-bpy (50.9 ± 1.5 nm) (Fig. 2e). These results clearly show that the structural properties of IAuNPs are same among the samples regardless of the type of stabilizers. On the basis of this fact, catalysis experiments with these particles might exclusively demonstrate the effect of stabilizers on the catalytic activity of nanoparticles.

To investigate the effect of stabilizer on the catalytic activity of IAuNPs, the catalytic reduction of 4-NP by NaBH₄ was examined. 4-NP is inert to NaBH₄ if it is used alone. However, the metal nanoparticles can effectively catalyze the reduction of 4-NP by acting as an electron relay system; electron transfer takes place between 4-NP and NaBH₄ through the metal particles. The reaction can be readily monitored by using UV–vis spectroscopy. In NaBH₄ medium, the peak corresponding to 4-NP at 317 nm is red-shifted to 400 nm due to the formation of 4-nitrophenolate. The reduction can be visualized by the disappearance of the 400 nm peak with the concomitant appearance of a new peak at 300 nm after the catalytic reaction. This peak has been attributed to 4-amino phenol (4-AP) [15–17]. Fig. 3 shows successive UV–vis absorption spectra of the reduction of 4-NP in the presence of IAuNPs@CTAB, IAuNPs@pyrrole, IAuNPs@pyridine, IAuNPs@2,2'-bpy, and IAuNPs@4,4'-bpy. In the absence of IAuNPs, the peak associated with the 4-nitrophenolate remained unaltered. The addition and proper mixing of an aliquot of IAuNPs to the reaction mixture cause the fading and ultimate bleaching of the yellow color of the 4-NP solution. This was reflected in the UV–vis spectra (Fig. 3); the intensity of the 400 nm peak decreases while a new peak at 300 nm corresponding to 4-AP appears. This shows that the IAuNPs catalyze the reduction reaction. Because the amount of the nanoparticles added is very small, the absorption spectra of 4-NP is hardly interfered with that of the AuNPs. Since the concentration of borohydride ion (BH₄⁻) used for the reaction largely exceeded the concentration of 4-NP and the IAuNPs, pseudo-first-order kinetics with respect to the concentration of 4-NP could be applied to estimate the rate constant. Fairly good linear relationships were found between ln A and reaction time (see insets of Fig. 3). Here, A represents the absorbance at 400 nm at any reaction time. The pseudo-first-order rate constants determined from these plots are 8.00 × 10⁻³, 2.16 × 10⁻², 2.42 × 10⁻², 2.54 × 10⁻², and 4.30 × 10⁻² min⁻¹ for the reaction in the presence of IAuNPs@CTAB, IAuNPs@pyrrole, IAuNPs@pyridine, IAuNPs@2,2'-bpy, and IAuNPs@4,4'-bpy, respectively (Fig. 4). The reaction rate highly depends on the type of stabilizer on metal surface; the catalytic activities of nanoparticles are in the order of IAuNPs@4,4'-bpy > IAuNPs@2,2'-bpy > IAuNPs@pyridine > IAuNPs@pyrrole > IAuNPs@CTAB. The reaction with IAuNPs@4,4'-bpy was fastest and its reaction rate was about 5 times higher than that of IAuNPs@CTAB. A still doubtful point is whether surface-bound or free ligands can reduce 4-NP or not. To check this possibility, 4-NP reduction reactions in the presence of amine compounds were carried out under identical experimental conditions without IAuNPs. The absorbance at 400 nm of 4-nitrophenolate was not changed by free ligands, indicating that added amine additives themselves could not reduce
the 4-NP. As shown in Fig. 3, the overall reduction process is rather slower than those observed in the previous studies [16,17]. This may be ascribed to the relatively larger particle size of IAuNPs than those of the other AuNPs. In fact, we have chosen IAuNPs with average size of 50 nm due to their excellent homogeneity in particle shape and size and also to their invariant structural properties regardless of the type of stabilizers (Fig. 2).

In the previous studies on the catalytic activity of metal nanoparticles, it was established that the catalytic activity was related to binding strength between metal surface and ligand [25,26], capping ligand stabilization [8,27], and surface-to-volume ratio [28]. The enhanced catalytic activities of the amine derivatives-stabilized IAuNPs can be attributed to their surface characteristics. The diffusion of anionic reactants, i.e., 4-
Fig. 3. Successive UV–vis absorption spectra (8 min interval) of 4-NP by NaBH₄ in the presence of (a) IAuNPs@CTAB, (b) IAuNPs@pyrrole, (c) IAuNPs@pyridine, (d) IAuNPs@2,2′-bpy, and (e) IAuNPs@4,4′-bpy. The insets show the pseudo first-order plots of −ln A vs time for each sample.

Fig. 4. Plot of rate constant for the reduction of 4-NP vs type of stabilizer.

nitrophenolate and borohydride, to the surface of catalyst particles can more readily proceed in the case of amine ligand than in the case of CTAB because the long alkyl chains of CTAB should hinder the incorporation of ions onto the surface of IAuNPs, whereas amine stabilizer should induce the close contact between reactant metal surface. Since the rate-determining step in the electron-transfer reaction catalyzed by metal nanoparticles is the approach of reactants to the particle surface [29,30], the different ligand chemistry could differentiate the catalytic activities between nanocatalysts. On the other hand, the highest catalytic activity of IAuNPs@4,4′-bpy among the amine derivative-stabilized IAuNPs can be ascribed to the structure of adsorbates on the surface of the particles. Due to the strong affinity of nitrogen to Au surfaces, pyrrole, pyridine, and 2,2′-bpy take upright orientations on the particle surfaces with all nitrogen atoms pointing towards the Au surface [11–13]. In the case of 4,4′-bpy, the molecules adsorb on the Au surface vertically via only one N atom, with the other N atom pointing outward.
with respect to the Au surface [14]. As a result, the outermost surface of the 4,4′-bpy-stabilized particles should provide more polar environment than other amine compound-stabilized particles, thus facilitating the approaching of ionic reactant species onto the nanoparticle surfaces, and consequently enforcing the catalytic activity. All the above experimental results demonstrate unambiguously that the molecular structure of the capping molecule plays a decisive role for the efficient AuNPs-mediated electron transfer between charged reactants.

4. Conclusions

We have investigated the effect of stabilizers, i.e., CTAB, pyrrole, pyridine, 2,2′-bpy, and 4,4′-bpy, on the catalytic activity of the Au nanoparticles for the reduction reaction of 4-NP with NaBH₄. The reaction occurs faster in the presence of amine derivative-stabilized AuNPs than in the presence CTAB-stabilized particles. The reaction with AuNPs@4,4′-bpy was fastest and its reaction rate was about 5 times higher than that of AuNPs@CTAB. These experimental results show that the structure of the capping ligands plays a crucial role for the efficient nanoparticle-catalyzed electron transfer reactions.

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