



Preparation of gold nanostars and their study in selective catalytic reactions



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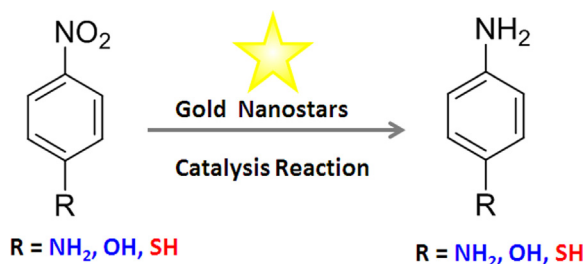
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HIGHLIGHTS

- Gold nanostars show catalytic and surface-enhanced Raman scattering (SERS) activity.
- They can catalyze the reduction of 4-nitrophenol and 4-nitroaniline efficiently.
- The different molecular orientations at surface were proved by SERS spectroscopy.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, gold nanostars (AuNSs) with size around 90 nm were prepared through an easy one-step method. They show excellent catalytic activity and large surface-enhanced Raman scattering (SERS) activity at the same time. Surprisingly, they exhibited different catalytic performance on the reduction of aromatic nitro compounds with different substituents on the para position. To understand such a difference, the SERS spectra were recorded, showing that the molecular orientation of reactants on the gold surface were different. We anticipate that this research will help to understand the relationship of the molecular orientation with the catalytic activity of gold nanoparticles.

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1. Introduction

In the past decades, gold nanoparticles (AuNPs) have received enormous attention due to their unique features like surface plasmon resonance, showing great practical or potential applications in numerous fields such as catalysis [1], surface-enhanced Raman

scattering (SERS) [2], biological sensing and imaging [3], diagnostics [4], photothermal therapy [5], nonlinear optics, solar cells and others [6]. The flourishing development of nanotechnology offers an impetus to fabrication of various AuNPs with different morphologies and geometries, as well as the corresponding attractive functions. The physicochemical properties of these AuNPs show a close dependency on their shapes, sizes, composition, capping agent, and aggregation state.

AuNPs attract considerable attention as a promising catalyst with high selectivity under mild conditions, like the reduction of nitro compounds, silane alcoholysis reaction [7], and CO oxidation at low temperature [8]. It is widely accepted that nanoparticles

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with small sizes exhibit higher catalytic activity due to their greater surface-to-volume ratio, while the AuNPs with diameter larger than 20 nm generally show limited catalytic ability [8,9]. Compared to spherical AuNPs, anisotropic AuNPs show better performance in catalysis without size limitation, demonstrated by experimental and theoretical calculations [10–12]. Up to now, AuNPs with different morphologies had been reported as efficient catalyst, including nanoprisms [13], nanocubes [14], octahedral [14], nanocages [15,16], nanoboxes [15], nanoflowers [17]. The increased exposed surface and number of low coordination atoms on their surfaces provide abundant activation sites for breaking the chemical bonds in catalysis [18]. Furthermore, these anisotropic AuNPs also exhibit other attractive advantages, such as their ultrahigh surface enhancement of Raman signals, which becomes a powerful technique to study heterogeneous catalysis.

The SERS technique has been well explored for chemical and biological measurements to derive fingerprint vibration information of molecules adsorbed on the metallic surfaces with ultrahigh sensitivity. Some detailed information on analytes can be acquired, such as their adsorption configuration and their interaction mechanism with the surfaces [19–24]. Through in situ SERS monitoring intermediates generated during the catalytic reaction were also captured [25], as well as the reaction kinetics [26].

Gold nanostars (AuNSs), as typical anisotropic AuNPs have attracted increasing interest due to their extraordinary field enhancement for SERS [27] and the high efficiency for photodynamic therapy [28]. With several sharp tips on their surfaces, AuNSs might show good performance in catalysis [12,29]. Here, we prepared AuNSs using a facile way, and examined their catalytic activity toward the reduction reaction of three aromatic nitro compounds with different substituent groups on the para position, showing different catalytic behavior. SERS was used to investigate the adsorption behavior of molecules on gold surfaces and explore the relationship of molecular orientation with catalytic activity of gold nanoparticles.

2. Experimental

2.1. Materials

Chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), silver nitrate (AgNO_3), 4-nitrothiophenol (4-NTP), 4-nitrophenol (4-NP), 4-nitroaniline (4-NA), sodium borohydride (NaBH_4), and L-ascorbic acid were purchased from Sigma-Aldrich. All chemical reagents were used as received without further purification. Ultrapure Millipore water (18.6 M Ω) was used throughout the experiments.

2.2. Preparation of gold nanostars

200 μL of 10 mM aqueous HAuCl_4 was mixed with 10 mL of water, added to 20 μL of 10 mM aqueous AgNO_3 . After the solution had been thoroughly mixed, 40 μL of 100 mM ascorbic acid was quickly added, and the mixture was stirred vigorously for 20 s at room temperature. It changed from colorless to blue, indicating the formation of AuNSs. Then the particles were washed with water and collected through centrifugation three times to remove the small nanoparticles and impurities.

2.3. Catalytic reaction monitored by UV–vis absorption spectroscopy

In a typical catalysis reaction, 10 μL of 0.01 M 4-NP (or 4-NA, or 4-NTP) ethanol solution was mixed with 870 μL of water, followed by the addition of 20 μL of AuNSs colloids. Then, 100 μL of freshly prepared NaBH_4 solution (0.1 M) was added to the mixture and

initiate the reaction. The whole process was monitored by UV–vis absorption spectroscopy, and each curve was recorded every min.

2.4. Characterization

Standard and high-resolution transmission electron microscopy (TEM and HRTEM) were performed with a JEOL JEM-2100 transmission electron microscope, equipped with an energy-dispersive X-ray spectrometer (EDX, Horiba EMAX Energy EX-350) operated at acceleration voltage of 200 kV, for which samples were placed onto the carbon coated copper grids. The X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance X-ray diffractometer. The particle size and size distribution were measured by a ZetaSizer Nano ZS (Malvern Instruments). Extinction and absorption spectra were recorded on a Cary 500 Scan UV–vis–near-infrared (UV–vis–NIR) spectrophotometer. The Raman spectra were obtained using a confocal Raman microscope (alpha 300, WITec, Ulm, Germany) equipped with laser excitation at a wavelength of 785 nm (I_2 laser). The laser beam was focused through a 60 \times water immersion (Nikon, NA=1.0) microscope objective. The spectra were acquired with a thermoelectrically cooled CCD detector (DU401A-BV, Andor, UK) placed behind the spectrometer (UHTS 300; WITec, ULM, Germany) with a spectral resolution of 3 cm^{-1} .

3. Results and discussion

Gold nanostars (AuNSs) were synthesized through a one-step seedless method at ambient temperature according to the method in literature [28]. Briefly, a small amount of AgNO_3 as the structure director was mixed thoroughly with the gold precursor, HAuCl_4 aqueous solution. After ascorbic acid as reducing and stabilizing agent was added into the mixture, the blue AuNS colloids were formed quickly without any obvious incubation time. To eliminate the interference of small AuNPs, the colloids were washed with water through centrifugation several times. Most of the synthesis of AuNSs in literature required a multi-step procedure, gold seeds and additional stabilizing agents [30]. Here, the preparation was quite easy, time- and energy-saving. More importantly, it generated a relatively rough and clean gold surface, which is favorable for catalysis and SERS.

Fig. 1a and b shows the morphology of the obtained AuNSs nanoparticles. Star-like shapes of the nanoparticles with several tips on their surfaces were revealed by TEM. The average size of the AuNSs is around 90 nm with a narrow size distribution (Fig. 1c). Energy dispersive X-ray (EDX) spectroscopy (Fig. 1f) of the AuNSs confirms the existence of Au-M at 2.1 keV, Au-L α at 9.7 keV and Au-L β at 11.4 keV, together with a small fraction of Ag at 3.0 keV [17,31]. The maxima of the X-ray diffraction (XRD) pattern (Fig. 1d) are identified as the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) Bragg reflections of Au. The peak width corresponds to a crystallite size of about 10 nm, implying its polycrystalline nature. The diffraction peaks match well the standard data for gold nanoparticles. The ratios of the peak intensities of the (1 1 1) plane relative to the (2 0 0) and (2 2 0) planes are 3.2 and 4.5, respectively, which is larger than the common spherical Au nanoparticles (1.9 and 3.1) [31]. This suggests that the face-centered cubic (fcc) Au crystal is predominant in the AuNSs.

The extinction spectrum (Fig. 1e) of the AuNSs displayed two distinct bands. The first band at 646 nm is attributed to the collective electron oscillation of the core, and its position usually depends on the size of the core. The second band at 900 nm is assigned to the electron oscillation along the tip-to-tip axis, and it would red-shift to longer wavelength if the number of tips branched on the gold core increases [28,32]. Both peaks are broadened due to the size distribution present in the colloidal solution.

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