Can Plasmonic Effect Cause an Increase in the Catalytic Reduction of \( p \)-nitrophenol by Sodium Borohydride over Au Nanorods?

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**ABSTRACT:** The catalytic reduction of \( p \)-nitrophenol (4-NP) to 4-aminopyridine (4-AP) over Au nanoparticles can be increased by light illumination. Whether this is caused by the plasmonic effect remains unclear. The present research carried out a careful examination of the effects of light illumination and temperature on the catalytic conversion of 4-NP to 4-AP over Au nanorods. It was seen that light illumination has no effect on the apparent activation energy; this indicates that the catalytic mechanism is unchanged and the activity increase cannot be attributed to the effect of hot electrons. Based on the simulation of finite-difference time domain, the theoretical analysis also showed that plasmonic heating cannot play a major role. Thermographic mapping showed that the temperature of water solutions shows an increase under light illumination. By taking this temperature increase into consideration, the light-induced increase of the 4-NP to 4-AP conversion can agree well with dark catalysis, which cannot be attributed to the plasmonic effects of the Au nanorods.

1. INTRODUCTION

Materials with high densities of free electrons, such as noble metals (Ag and Au), have received much attention because of their strong optical absorption arising from localized surface plasmon resonance. Surface plasmons can decay through radiative and nonradiative pathways on a femtosecond timescale. The radiative decay can further lead to the generation of excited electrons in metal nanoparticles, which then relax as hot electrons via electron–electron and electron–lattice interaction in a short time. Hot electrons are able to drive catalysis by depositing excess energy in molecular orbitals of reactants through interfacial transfer; this is known as the nonthermal effect of surface plasmons. Over a longer timescale, hot electrons can undergo a further relaxation via electron–phonon interaction, thus finally resulting in an increase of lattice temperature, i.e., the photothermal effect, which can also cause an apparent increase of catalytic effect. It can be considered that the catalysis is caused by the hot electrons and the plasmonic heating results from surface plasmons in principle.

Plasmonic materials are also generally active in many catalytic reactions in the dark condition. For example, it has been reported that Au is the most efficient in CO oxidation when it is present in a nanoparticle form. Recently, selective reduction of \( p \)-nitrophenol (4-NP), a chemical pollutant of industrial and agricultural wastewater, as 4-aminophenol (4-AP), has attracted much attention. 4-AP can be used as an intermediate for many analgesics and antipyretics, such as paracetamol and phenacetin. The use of noble nanoparticles (Au or Ag) as catalysts to convert 4-NP to 4-AP in the dark has been studied. Because of the plasmonic effects, it is more attractive to make use of surface plasmons to increase the catalytic conversion. It has been reported that the 4-NP catalytic conversion can be increased by light illumination, which was in general ascribed to the plasmonic effect. For example, Hueso et al. reported that the 4-NP catalysis over Au-loaded hydrotalcite and calcined hydrotalcite was increased under LED illuminations; this was ascribed to the plasmonic effect of Au nanoparticles. Because the plasmonic heating is very low under normal sunlight illumination, the contribution of the increase in the 4-NP catalysis to the hot electrons seems plausible. For example, Zhu et al. reported a high selectivity in the 4-NP catalytic conversion over Au-Cu alloys/ZrO\(_2\) under a wide-spectrum halogen lamp and monochromatic LED light illuminations. They thought that the hot electron transfer to the N–O bond associated with the LUMO of 4-NP weakened the N–O bonds and activated the reduction of 4-NP.

However, we obtained a different result that the plasmonic effect may play a minor role in the light-induced 4-NP catalytic
conversion. To avoid the effect of metal−support interaction, Au nanorods were directly used as the catalyst in our research. We carefully examined the effects of some monochromatic light illuminations that matched well with the transverse and longitudinal plasmon modes, and wide-spectrum (420−800 nm) illumination that covers both transverse and longitudinal modes, on the catalytic conversion of 4-NP over the Au nanorods. It was found that, although light illumination can lead to an apparent increase in catalytic rates, it did not have an effect on the apparent activation energy (E_{app}), indicating that the light-induced effect cannot be attributed to the hole−electron transfer. Under careful correction with the light-induced increase in the solution temperatures and based on the theoretical analysis of the plasmonic heating, we concluded that the light-induced 4-NP conversion is not caused by the expected plasmonic effect of the Au nanorods, but results from an increase in the water temperature. This finding shows that the effect of light illumination on the environmental temperature, such as water temperature, should be carefully considered to give an accurate evaluation of the role of surface plasmonic effects in catalysis.

2. RESULTS AND DISCUSSION

Different amounts of silver nitrate solutions were added to change the size of the Au nanorods. Figure 1A−D shows the transmission electron microscopy (TEM) images of the as-synthesized Au nanorods. It is seen that the aspect ratio of the Au nanorods increases with the increase of the added silver nitrate amounts. The high-resolution TEM (HR-TEM) image of one Au nanorod in Figure 1B is also shown in Figure 1E, which shows clear (200) plane fringes of single crystallinity. The average widths and average lengths of the Au nanorods are listed in Table 1. The concentrations of the Au nanorods were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES), which are also summarized in Table 1. It is seen that the amounts of Au are almost the same in these samples, showing the good control of the experiment. Figure 2A shows the UV−vis absorption spectra and the color (inner) of the above four samples. The peak of transverse plasmonic oscillation absorption occurs at around 515 nm for all of the Au nanorods, while that of the longitudinal plasmonic oscillation absorptions shows an obvious red shift with an increase in the aspect ratio. The aspect ratios were also estimated by the empirical formula AR' = (\lambda_{max} - 420)/95, where \lambda_{max} is the wavelength of the strongest absorption. These values are also listed in Table 1, in good accordance with the TEM analysis. The Au nanorod with AR = 2.9 (Figure 1B) was used for catalytic reactions. Figure 2B shows a comparison between the optical absorption of this sample and some optical filters. Two band-pass optical filters were coupled with light sources to generate 520 and 650 nm monochromatic lights that can match the transverse and longitudinal modes of Au nanorod surface plasmons (Figure 2B, red and blue lines). A wide spectral optical filter was also used to generate light ranging from 420 to 800 nm (Figure 2B, green line).

Table 1. Summary of Average Widths (D), Average Lengths (L), Aspect Ratios, and Concentrations of Au Nanorods

| AgNO₃ amounts (mL) | D (nm) | L (nm) | AR | AR' | concentration (mg/L) |
|-------------------|--------|--------|----|-----|----------------------|
| 0.5               | 23.3   | 44.9   | 1.9 ± 0.1 | 1.63 | 111                  |
| 1.0               | 17.3   | 50.1   | 2.9 ± 0.3 | 2.68 | 118                  |
| 1.5               | 17.1   | 60.4   | 3.5 ± 0.2 | 3.77 | 117                  |
| 2.0               | 16.2   | 67.1   | 4.2 ± 0.4 | 4.50 | 123                  |

"AR−aspect ratios of Au nanorods determined from TEM images; AR’−aspect ratios of Au nanorods estimated from the UV−vis absorption spectra; the concentrations of the Au nanorods in aqueous solutions were determined by ICP-OES."
Au nanorods were used for the catalytic conversion of 4-NP by sodium borohydride. In the absence of the Au nanorods, 4-NP cannot be reduced, independent of light illumination or not. Figure 4 shows the UV–vis absorption of 4-NP solutions after different time intervals of reaction in the dark and under simultaneous illumination of different lights. The UV–vis absorption peaks around 400 and 300 nm are ascribed to the characteristic absorptions of 4-NP and 4-AP, respectively. Figure 3A shows that the UV–vis absorbance of 4-NP decreases during the dark catalysis in the presence of Au nanorods. The decrease in the absorption at 400 nm is accompanied with an increase in the absorption at 300 nm; this shows that 4-NP can be converted to 4-AP over Au nanorods, in accordance with other reports.26 Figure 3B,C shows that the catalytic conversions at the same set temperatures can be increased by 520 and 650 nm monochromatic light illuminations. The illumination with a wide-spectrum light (420–800 nm) leads to a higher increase in the catalytic conversion, as shown in Figure 3D.

The kinetics of the catalytic conversions is in accordance with a quasi-first-order reaction. The concentrations of the 4-NP aqueous solutions are proportional to the corresponding UV–vis absorbances according to the Lambert–Beer law. Therefore, the quasi-first-order reaction is described as formula 1.

\[
\ln \frac{A_0}{A_t} = k_{app} t
\]  

where \(k_{app}\) is defined as the apparent rate constant, \(A_0\) is the absorbance at 400 nm at the starting of the reactions, and \(A_t\) is the corresponding absorbance after reaction for \(t\) min. Figure 4A shows the dependence of \(\ln(A_0/A_t)\) on time in the course of the catalytic conversions in the dark and under light illumination. \(k_{app}\) was estimated by fitting these lines with eq 1 and is shown in Figure 5B. The catalytic conversion is increased by 1.74, 1.86, and 5.22 times under illuminations of 520, 650, and 400–800 nm lights, respectively. Figure 4C shows the dependence of \(\ln(A_0/A_t)\) on time in the catalytic conversions under the illumination of 520 nm light with different intensities. As shown in Figure 4D, \(k_{app}\) almost shows a linear increase with light intensity. Based on these observations, it seems that the light-induced increase in the catalytic conversions of 4-NP over Au nanorods might be attributed to the plasmonic effect because of the good match between the light illumination and plasmonic absorption.

It is difficult to carry out direct measurement under the plasmonic heating effect. Many studies used theoretical analysis to estimate the caused increase of temperature. It has been widely reported that plasmonic heating cannot cause an increase in the temperature of the Au nanorod under low-intensity light illumination. In reference to these studies,11,28 the temperature difference (\(\Delta T\)) between the Au nanorod solutions before and after light illumination, caused by the plasmonic heating effect, was estimated by the following formula

\[
\Delta T = \sigma_{abs} I / (4 \pi R_c^2 \beta \kappa_{water})
\]  

where \(\sigma_{abs}\) is the absorption cross section, \(I\) is the irradiance of the incoming light (100 mW/cm²), \(R_c\) is the radius of a sphere with the same volume as the particle, \(\beta\) is the thermal capacitance coefficient depending on the nanoparticle aspect ratio (\(\beta = 1 + 0.96587 \ln(2AR)\)), and \(\kappa_{water}\) is the thermal conductance of water (0.6 W/(m K)). The absorption cross section of Au nanorods was simulated using the FDTD method, as shown in Figure 5A,B. The \(\sigma_{abs}\) value of the Au nanorod at 520 nm (transverse mode) is 560 nm². In the case of the present experimental condition, the temperature difference (\(\Delta T\)) caused by the surface plasmons under the 520 nm light illumination is about 2.83 \(\times\) 10⁻⁶ K, so it is
confirmed that the plasmonic heating effect cannot lead to a change in the solution temperature; this is also in accordance with other studies. Therefore, a plausible conclusion may be obtained that the nonthermal effect of surface plasmons, i.e.,

Figure 5. Absorption cross sections obtained from the finite-difference time domain (FDTD) simulations for the Au nanorods with a diameter of 17 nm and an aspect ratio of 2.7. (A) Directions of E (electric field) and k (wave vector) of the lights are perpendicular and parallel to the axial direction of the Au nanorod, respectively. (B) Directions of E and k of the lights are parallel and perpendicular to the axial direction of the Au nanorod, respectively.

Figure 6. (A) Dependence of ln(\(A_0/A_t\)) on time in the course of the catalytic conversions in the dark at different set temperatures. (B) Dependence of ln(\(A_0/A_t\)) on time in the course of the catalytic conversions under the illumination of 89 mW/cm² by 520 nm monochromatic light at different set temperatures. (C) Arrhenius dependence of \(k_{app}\) on the set reaction temperatures. (D) Arrhenius dependence of \(k_{app}\) on the corrected temperatures based on the measurement of infrared thermography.

Figure 7. (A) Infrared thermographic images of Au nanorod solutions in the dark and after 12 min illumination of 520 nm monochromatic light, 650 nm monochromatic light, and 420−800 nm wide-spectrum light. (B) Infrared thermographic images of pure water in the dark and after 12 min illumination. (The light intensities were the same as that used in Figure 4A.)
the hot electron interfacial transfer, might assist the catalytic reduction of 4-NP.

Figure 6A,B shows the dependence of ln($A_0/A_t$) on time in the dark and under 520 nm light illumination at different set temperatures, respectively. It is seen that the catalytic conversions of 4-NP are highly sensitive to temperature, independent of light illumination. The $E_{\text{app}}$ values of these reactions were obtained, and the Arrhenius dependence of $E_{\text{app}}$ on the set temperatures is shown in Figure 6C, which shows that light illumination increases the catalytic rates at all temperatures. The $E_{\text{app}}$ values of dark catalysis and catalysis under light illumination are determined to be 98 and 105 kJ/mol, respectively. Such a small difference between the $E_{\text{app}}$ values indicates that light illumination might not change the mechanism of the catalytic conversion of 4-NP over Au nanorods. Therefore, the photoinduced increase in the catalytic conversion in principle belongs to thermocatalysis and the nonthermal effect of surface plasmons should play a minor role.

Due to the high $E_{\text{app}}$, even a small increase of the reaction temperature can have a non-negligible effect on catalytic conversion rates. Although the plasmonic heating effect is unable to increase the reaction temperatures, it is still possible for the light illumination to generate an increase in the solution temperature due to other causes. Infrared thermography was used to measure the temperature change before and after light illumination. The emissivity of the Au nanorod aqueous solution was set as that of pure water (0.98) because the concentration of the Au nanorods is too low. First, at a constant set temperature (~17 °C), the effects of 520, 650, and 400–800 nm light illuminations on the temperature of the Au nanorod solution were determined, as shown in Figure 7A. After 12 min light illumination, the temperatures are increased by 1.7, 1.6, and 11.9 °C, respectively, while the temperature of the Au nanorod solution in the dark is almost unchanged, showing that even the monochromatic visible light illumination can cause a rise in temperature. Figure 7B shows that illumination of pure water with a 520 nm monochromatic light can also lead to a 1.5 °C increase of temperature. Therefore, the light-induced increase of temperature of Au nanorod solutions is caused by the increase of water temperature, not by the plasmonic heating effect; this is also in accordance with the above theoretical analysis.

Then, based on the above observation, is the light-induced catalytic conversion of 4-NP caused by the increase of water? The real temperatures among the different set temperatures at which the catalytic experiments were conducted (Figure 6A,B) were also checked by infrared thermography in the dark and under light illumination, as shown in Figure 8. Under 12 min illumination, the temperatures of the Au nanorod solutions are increased by about 2 °C for all set temperatures. After corrections with these temperature differences, the Arrhenius dependence of $k_{\text{app}}$ of the reactions under light illumination was further plotted in Figure 6D, which shows that catalytic conversions under light illumination mostly locate in the line of dark catalytic conversions. Based on these observations, we confirmed that the plasmonic effects of the Au nanorods cannot contribute to the increase of the 4-NP catalytic conversion.

To further confirm that the light-induced increase in the 4-NP catalytic conversions is attributed to the increase in water temperature, additional experiments were also done as follows. At the set temperature of 30 °C, the catalytic reactions were performed in the dark and under 420–800 nm light illuminations. The infrared thermography measurement showed that the temperature of the solution was increased to about 40 °C and the catalytic reaction was also done at the set temperature of 40 °C in the dark. Figure 9A shows the dependence of ln($A_0/A_t$) on time in the course of 4-NP catalytic conversions in the dark at set temperatures of 30 and 40 °C and under 420–800 nm light illumination at the set temperature of 30 °C and (B) the corresponding $k_{\text{app}}$ values of the above reactions.

3. CONCLUSIONS

In summary, we carefully studied the effect of light illumination on the catalytic conversion of 4-NP over Au nanorods and the temperature of the Au nanorod aqueous solution. The results showed that light illuminations did not change the catalytic conversion rates. Although the plasmonic heating effect is unable to increase the reaction temperatures, it is still possible for the light illumination to generate an increase in the solution temperature due to other causes. Infrared thermography was used to measure the temperature change before and after light illumination. The emissivity of the Au nanorod aqueous solution was set as that of pure water (0.98) because the concentration of the Au nanorods is too low. First, at a constant set temperature (~17 °C), the effects of 520, 650, and 400–800 nm light illuminations on the temperature of the Au nanorod solution were determined, as shown in Figure 7A. After 12 min light illumination, the temperatures are increased by 1.7, 1.6, and 11.9 °C, respectively, while the temperature of the Au nanorod solution in the dark is almost unchanged, showing that even the monochromatic visible light illumination can cause a rise in temperature. Figure 7B shows that illumination of pure water with a 520 nm monochromatic light can also lead to a 1.5 °C increase of temperature. Therefore, the light-induced increase of temperature of Au nanorod solutions is caused by the increase of water temperature, not by the plasmonic heating effect; this is also in accordance with the above theoretical analysis.

Figure 8. Infrared thermographic images of Au nanorod solutions in the dark and after 12 min illumination of 520 nm monochromatic light (89 mW/cm²) at different set temperatures.

Figure 9. (A) Dependence of ln($A_0/A_t$) on time in the course of 4-NP catalytic conversions in the dark at set temperatures of 30 and 40 °C and under 420–800 nm light illumination at the set temperature of 30 °C and (B) the corresponding $k_{\text{app}}$ values of the above reactions.
mechanism because $E_{pp}$ is almost the same as that in the dark. By combining the theoretical analysis of plasmonic heating effect and the temperature correction with the temperatures measured with infrared thermography, it was revealed that both the plasmonic heating and nonthermal effects of the Au nanorods cannot contribute to the catalytic conversion of 4-NP. The light-induced increase of the water temperature leads to the photoinduced increase of 4-NP catalytic conversion. Although our result did not reveal that the increase of the 4-NP catalytic conversion is not an expected photocatalytic process caused by surface plasmons, we thought that this finding is also important to clarify the catalytic pathway that may be misdetermined in some studies.

4. EXPERIMENTAL SECTION

4.1. Gold Nanorod Preparation. Au nanorods were synthesized by the seed-mediated growth method.$^{29}$ The seed solution was first prepared by the addition of a freshly prepared, ice-cold 1.2 mL solution of 0.01 M NaBH₄ (Shandong XiYa Chemical Industry Co., Ltd.) into a mixture of 1 mL of 5 mM HAuCl₄ (Sinopharm Chemical Reagent Co., Ltd.) and 19 mL of 0.1 M hexadecyl trimethyl ammonium bromide (CTAB, Beijing Biotopped Science & Technology Co., Ltd.), which was kept at 30 °C for 2.5 h for further use. The growth solution was prepared as follows: different amounts of 4 mM AgNO₃ solution (Sinopharm Chemical Reagent Co., Ltd.) were mixed with 3.65 g of CTAB dissolved in 85 mL of deionized water under stirring for 15 min. A HAuCl₄ solution (10 mL, 5 mM) and ascorbic acid solution (0.9 mL, 80 mM; Sinopharm Chemical Reagent Co., Ltd.) were then added and stirring was continued for 30 s until the solution became colorless. Subsequently, 2.25 mL of 1 M HCl solution and 0.2 mL of the seed solution were added, which was then kept at 30 °C for 16 h to obtain the aqueous solution containing Au nanorods.

4.2. Characterization. Transmission electron microscopy (TEM) images of the Au nanorods were taken on a transmission electron microscope (JEM−2100F, JEOI, Japan) operated at 200 kV. UV−vis diffusion spectra were obtained on a UV−vis spectrophotometer over the wavelength range of 200−900 nm (UV-2600, Shimadzu, Japan). The content of gold nanorods in the aqueous solution was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Prodigy 7, Leeman Labs).

4.3. Catalytic Activity Measurement. The as-prepared Au nanorod solution (10 mL) was washed by centrifugation three times and redispersed into 2 mL of deionized water. The catalytic reduction of 4-NP under light illumination was performed in a (10 × 10 × 45 mm³) cuvette, which was placed in a water bath at set temperatures. Water (2.7 mL), 10 mM 4-NP (60 µL), 0.1 M NaBH₄ solution (0.4 mL, with 0.01 M NaOH), and 100 µL of concentrated gold nanorod solution were successively added to the cuvette. A 300 W Xe arc lamp (PLS-SXE300UV, Beijing Perfect Light Co., Ltd.) equipped with different optical filters was used as the light source. The catalytic activities were evaluated by recording the UV−vis absorption spectra of the A-NP aqueous solution at different reaction intervals with a UV−vis spectrophotometer (UV-2600).

4.4. Finite-Difference Time Domain (FDTD) Simulation. FDTD simulation was used to obtain the cross section of Au nanorod surface plasmons with commercial FDTD software (Canadian Lumerical Solutions 7.5). The Au nanorod was modeled with a cylinder in the middle and hemispheres at both ends, with a length of 50 nm and a diameter of 17 nm. The dielectric functions were taken from the Johnson and Christy measurement and corrected for size effect (surface scattering and radiation damping).$^{30}$ The refractive index (n) of the surrounding environment is set as the n of water (1.333). The whole wavelength scattering field source (TFSP) was used to calculate the absorption cross section with the wavelength range being 400−1000 nm. The grid resolution was set as 1 nm to obtain accurate results.

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Notes

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