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COMMUNICATION

Plasmonic swings during Fenton reaction: catalytic sensing of organics in water via fullerene-decorated gold nanoparticles

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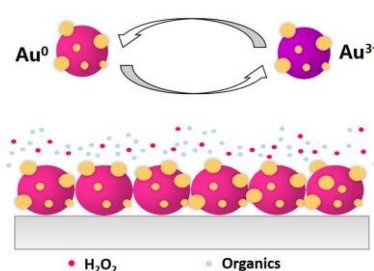
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Fullerene-decorated gold nanoparticles were used to catalyse the Fenton reaction and the electron transfer cycle of the catalyst shifts the gold surface plasmon resonance back and forth. The plasmonic swing frequency is in accord with the redox reaction rate and could be applied for detection of organics in water.

The Fenton reaction is well known for its green and strong oxidizability due to the production of highly aggressive hydroxyl radicals. It is widely applied for the oxidative degradation of organic pollutants in water at room temperature.¹⁻³ Surprisingly, up to now the Fenton reaction has not been used to determine the content of total organics in water as required for monitoring of water quality, which is also a very important application for environmental protection. In contrast, a number of attentions have been paid to the development of organics sensors based on another green method of photocatalytic degradation.⁴⁻⁶ The only reason we deduce is the lack of a sensitive and robust probe of the Fenton reaction under highly oxidizing conditions.

A catalyst, typically transition metal ions with variable valences such as iron(II), is usually required in the Fenton oxidation to promote the process. Recently, heterogeneous catalysts based on particles have been developed to overcome drawbacks of homogeneous catalysts, such as unreusability.⁷⁻⁹ In special, gold nanoparticles (AuNPs) dispersed on a porous, high-surface-area support material were found to behave the catalytic activity in Fenton reaction very effectively.¹⁰⁻¹³ On the other hand, an AuNP also exhibits the local surface plasmon (nanoplasmon), which is the light-driven oscillations of charge density confined to a metallic nanoparticle or nanostructure.¹⁴⁻¹⁷ The metallic nanoplasmon is characterised by a resonance absorption in the visible spectral region, and has been greatly utilised as a variety of chemical and biological sensors.¹⁸⁻²² Most of the nanoplasmonic sensors reported previously are based on that the wavelength of plasmon resonance



Scheme 1 Schematic illustration of plasmonic monitoring of the Fenton reaction. Cycle of electron transfer through the gold nanoparticle-based catalyst rocks plasma resonance frequency of the nanoparticle (indicated by colour change).

is sensitive to the dielectric property of the nanoparticle's surrounding medium.¹⁸ In addition, the nanoplasmon resonance is definitely determined by the electron 'cloud' density on the nanoparticle.²³ Mulvaney's group explored this issue in the catalysed oxidation of ascorbic acid by oxygen dissolved in solution on single gold nanocrystals.²⁴ The electron injection and extraction during a redox reaction was directly monitored with surface plasmon spectroscopy. Later, an indirect nanoplasmonic method was developed to probe catalytic reactions, in which a thin dielectric spacer was used to protect the sensing particles and support the catalytic particles.^{25,26} Not from the electron transfer, the plasmonic peak shift arises from changes in surface coverage of reactants during reaction in this way. Anyhow, these works opened up possibilities to follow heterogeneous catalysis in real time.

In this communication, we present the nanoplasmonic monitoring of the catalytic Fenton reaction for the first time. As illustrated in the Scheme 1, AuNPs were decorated by fullerene to endow the nanoparticles with catalytic activity for the Fenton reaction, in which hydroxyl radicals (HO[•]) were generated from H₂O₂ molecules by reduction with gold atoms. The AuNPs acted as an electron relay and the redox reaction taken place was tracked by the nanoplasmon resonance of the nanoparticles themselves. Similar to the work of Mulvaney's group,²⁴ the electron transfer on AuNPs was directly observed with optical extinction spectrum. But different from the previous work that displayed a shift cycle of plasmon resonance wavelength lasting for tens of minutes, the

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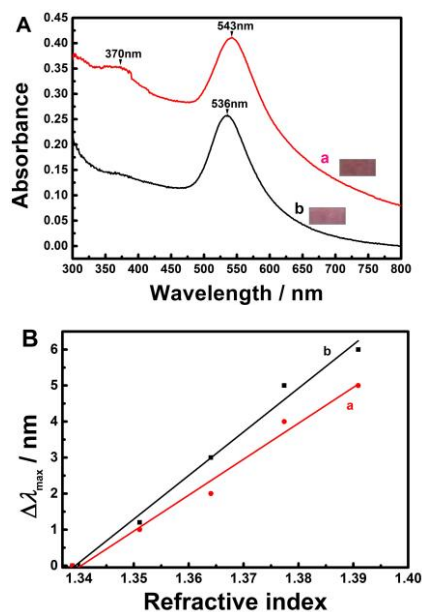


Fig. 1 (A) Extinction spectra of films of the fullerene-decorated gold nanoparticles (C₆₀@AuNPs, curve a) and the bare gold nanoparticles (AuNPs, curve b) in water. (B) Sensitivity of peak shift ($\Delta\lambda_{\max}$) of C₆₀@AuNPs (curve a) and AuNPs (curve b) films to refractive index changed by glycerol concentration in solution

peak location during the Fenton reaction shifted back and forth on a second timescale. We think the former is due to the slow interphase diffusion of atmospheric oxygen and the latter comes from the fast homogeneous supply of electron acceptor (H₂O₂). We termed this phenomenon 'plasmonic swing' and adopted the rock frequency as the sensor signal, which is totally different from the shift magnitude of peak wavelength measured before. Contrary to lower shift magnitudes (<10 nm) in a large base (ca. 550 nm for AuNP peak), the signal-to-noise of swing frequency measurement could be infinitely great due to a background equal to zero in response to none of catalytic reaction. In the presence of excess H₂O₂, the speed of Fenton reaction is determined by the concentration of organics, which ensures the catalytic sensing of organics in water to be successful with nanoplasmonic monitoring.

We constructed the catalytic sensor firstly through the multi-layered self-assembly of AuNPs (10 nm) on a glass slide with 3-aminopropyltriethoxysilane (APTES) to produce a thin film of AuNPs generating an obvious plasmonic peak (Fig. 1A). Then an ethanol solution of fullerene (1.0 mg/mL C₆₀) was spin-coated upon the AuNPs film. And the thin film was finally annealed at 500 °C to make it robust and have a good catalytic activity. Fullerene was chosen out from various carbon nanomaterials because it can be easily solution-engineered into regular nanoparticles.^{27,28} It was suggested from the scan electron microscopy of the film (Fig. S1-3†) that nano-fullerenes were decorated on a single AuNP (C₆₀@AuNP), other than deposition of smaller AuNPs on a single larger carbon nanomaterial as reported previously.¹¹⁻¹³ From the extinction spectrum of the C₆₀@AuNPs film in comparison with that of the bare AuNPs film (Fig. 1A), the fullerene decoration on AuNPs unobviously changed the plasmonic absorption of AuNPs besides a slight redshift in peak location. In addition, a weak absorption of

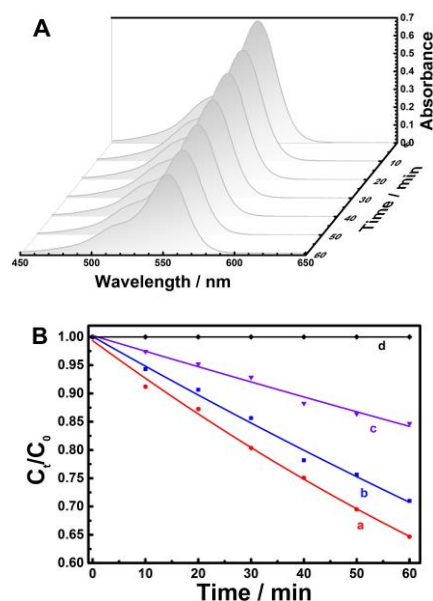


Fig. 2 (A) Absorption spectra of Rhodamine B (5.0 μM) during the Fenton reaction (30 mM H₂O₂, pH 3.0) catalysed by the C₆₀@AuNP film. (B) Fenton degradation activity of Rhodamine B (5.0 μM) using the C₆₀@AuNPs films annealed at different temperatures: 500 °C (curve a), 400 °C (curve b), 300 °C (curve c), 150 °C (curve d).

fullerene can be seen at the wavelength of 370 nm, indicating a micro amount of fullerene present in the film.²⁹ The effect of fullerene decoration on plasmonic sensing was also inquired by the sensitivity of peak shift ($\Delta\lambda_{\max}$) to refractive index change in solution (Fig. 1B). It was observed that the exterior fullerene lowered the sensitivity to environment from 121 nm/RIU to 50 nm/RIU.

The catalytic activity of the C₆₀@AuNPs film was addressed by the Fenton oxidation of organic dye, Rhodamine B (RhB), in water. As shown in Fig. 2A, 5 μM RhB was degraded up to 40% in 60 min with the aid of the C₆₀@AuNPs film in contrast to no degradation of the dye with the use of AuNPs film. The latter result is coincident with the common knowledge in gold catalysis that the particle larger than a threshold size (ca. 8 nm) hardly exhibits activity.^{30,31} And the former indicates an exception that larger AuNPs behave active as composited with carbon materials, which was also proved by the previous reports using other carbon-supported AuNPs.¹¹⁻¹³ It was also found in our experiment that the annealing temperature is crucial to the catalytic activity (Fig. 2B). The C₆₀@AuNPs film was inactive if annealed below 150 °C, and was more active with higher annealing temperature, which suggests that the chemical bonding between gold and carbon is necessary to catalyse the Fenton reaction. The C₆₀@AuNPs film annealed at 500 °C exhibited a catalytic activity which may be not highly efficient for organics degradation but is appropriate for sensing application (see below).

Nanoplasmons of AuNPs enable us to monitor the catalytic Fenton reaction in real time and then to detect the total organics in water. Oxidation of phthalate was selected as a model following the calibration used in determination of chemical oxygen demand (COD) by the standard dichromate method. The glass slide covered by the C₆₀@AuNP film was immersed into the phthalate solution and then

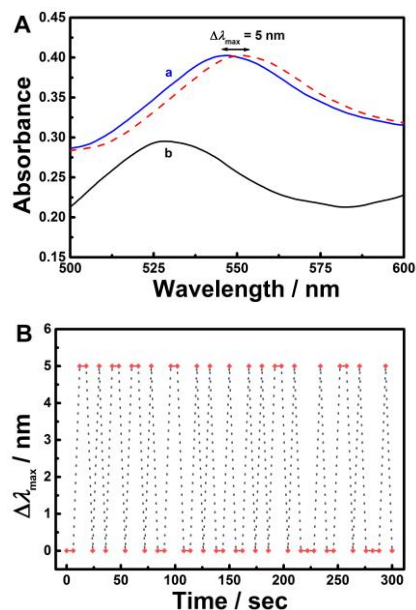


Fig. 3 Plasmonic swing during the initial period of the Fenton reaction catalysed by C_{60} @AuNPs film. (A) Extinction spectra of C_{60} @AuNPs film (curve a) and AuNPs film (curve b). (B) Shift in plasmonic peak wavelength ($\Delta\lambda_{\max}$). Fenton reaction solution: 5.0 μM phthalate, 30 mM H_2O_2 , pH 3.0.

H_2O_2 was added. Meanwhile the plasmonic spectroscopy was collected every 6 second to track the initial phase of process (0-300 sec) (Fig. 3A), in which the redox rate would be well proportional to the concentration of phthalate (≤ 0.01 mM) using a great excess amount of H_2O_2 (30 mM). In experiments that Fenton degradation took place, it was observed that the plasmonic peak of gold nanoparticle redshifted forth ($\Delta\lambda_{\max} = 5$ nm) and blueshifted back to the initial position within tens of seconds repeatedly (Fig. 3B). In contrast, when no oxidation of organics occurred using the bare AuNPs film or using the C_{60} @AuNPs film in the absence of phthalate, the swing of the peak location was less than 1 nm and was considered as the spectral noise. By increasing phthalate amount up to 1 mM in the absence of H_2O_2 , the peak location was also not rocked, although the peak height was somewhat lowered. It indicates that the dielectric change caused by adsorption of phthalate on gold NPs is too small to be resolved by the plasmonic peak shift with a wavelength resolution of 0.1 nm. Consequently, it is suggested that the swing of plasmonic peak is only contributed by the electron transfer through gold NPs.

As derived by Mulvaney et al.,²³ the store electrons alter the plasmon resonance frequency of the metal, leading to a blue-shift in the extinction spectrum of the particle. The plasmonic redshift in our experiments reveals that the neutral C_{60} @AuNP loses electrons to H_2O_2 to become positive, similar to the mechanism of the Fenton reaction catalysed by nanodiamond-supported AuNPs.¹¹ In return, the positive gold ion obtains electrons to be back to the neutral state, corresponding to the plasmonic back blueshift. The phthalate or both of phthalate and H_2O_2 might act as the donor of electrons to reduce the gold cation in this process (the standard redox potential of $\text{Au}^{3+}/\text{Au} = 1.8$ V), and the exact pathway would be discerned out in the future study. Within the initial reaction period, the plasmonic

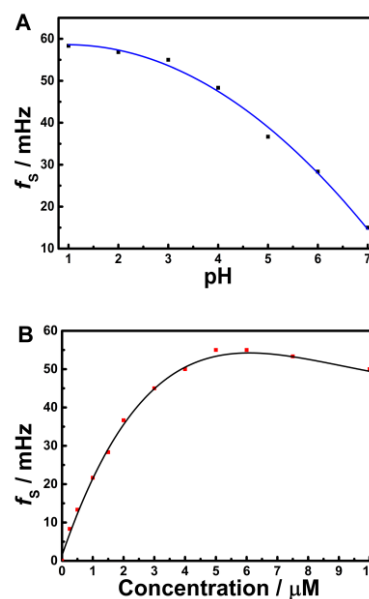


Fig. 4 (A) Dependence of the plasmonic swing frequency (f_s) on solution pH (Fenton reaction solution: 5.0 μM phthalate, 30 mM H_2O_2). (B) Relationship of the plasmonic f_s with the phthalate concentration (Fenton reaction solution: 30 mM H_2O_2 , pH 3.0).

swing is unobservable when phthalate is absent and is significant when phthalate is present. It is suggested that the redox reaction of the AuNPs was too slow to be detected in the absence of organics and was speeded up by the presence of organics. This phenomenon was also observed in the work of Garcia's group, in which the rate of H_2O_2 disappearance was higher in the presence of organics than when it is absent.¹¹ Very importantly, the observed swings between the two extreme plasmonic positions suggests that the rate-determined step of the Fenton reaction was the interfacial electron transfer on gold, rather than the diffusion process of electron acceptor or donor. In other words, there existed enough amounts of reactant molecules on the particle's surface. And the donor/acceptor in excess led to that all the AuNPs contacting the solution were set to be either in the positive charge state or in the neutral state to cause the swings.

Obviously, the swing number of plasmonic peak per unit time (swing frequency) is in accord with the cycle rate of electron transfer on gold NPs or the reaction rate. As the Fenton reaction is strongly influenced by the medium pH, we also investigated the reaction under different pH (1-7). It can be seen from Fig. 4A that the swing frequency (redox rate) was higher with lower pH, which is also suggested by that electron acceptance of H_2O_2 forms $\cdot\text{OH}$ radical and HO^- ion (see Scheme 1). The dependence of the swing frequency on phthalate concentration is shown in Fig. 4B. It illustrates that the rate speeded up from zero to a plateau (swing frequency = 55 mHz) and then slowed down when phthalate was present from zero to higher concentrations (0-10 μM). The reaction rate might be limited by the diffusion of the generated CO_2 from oxidation of phthalate, and even the catalyst maybe poisoned by the product on its surface, which will numb its activity. This assumption will be tested in the ongoing research, and if it holds

true, the clean out of the particles coincident with the reaction, by stirring for example, would be a key to improve the upper detection limit. On the other hand, the lower detection limit (here is ca. 0.25 μM) is only relied on that how many phthalate molecules is at least required to result in a single swing cycle within the period of measurement, since the swing frequency has a background of zero. It should also be noted that the minimal amount of phthalate to produce a complete swing is correlated with the amount of Au present in the sensor. Furthermore, the zero background will lead to a much better precision and accuracy of determination than usual nanoplasmonic sensors. In the present experiment, the relative standard deviation ($n=5$) was 6.95 % and the recovery was 99.5 % for 1.0 μM phthalate, respectively.

In summary, a catalyst of fullerene-decorated gold nanoparticles is active for Fenton chemistry. We for the first time monitored the Fenton reaction with plasmonic spectra of the catalyst. The cycles of electron transfer on the particles results in synchronous swings of the plasmonic peak, and the swing frequency directly indicates the redox rate. It makes a green detection of organics in water be possible at room temperature. The key feature of our system is the use of plasmonic swing frequency, leading to a highly accurate and sensitive sensing of microlevels of organics with a background signal of zero.

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