Detection and degradation of environmental pollutants based on Fe$_3$O$_4$@Au nanoparticles as surface enhanced Raman scattering (SERS) substrates

J. Du and C. Jing*

*State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center of Eco-Environmental Sciences, Chinese Academy of Science, Beijing 100085, China, cyjing@rcees.ac.cn

ABSTRACT

Ever since the surface-enhanced Raman scattering (SERS) effect was discovered, it has played a significant role in the field of vibrational spectroscopy and is now finding increasing use in high-profile applications. Recently, many catalytic-active SERS substrates have been developed for in situ monitoring of environmental pollutants, which could provide new insights into the kinetics and mechanism of catalysis. Herein we developed a recyclable SERS substrate with Fe$_3$O$_4$ and Au constituents, which can also be used as active photocatalyst. Nitroaromatic compounds were chosen as the target pollutants due to their toxic and mutagenic effects towards organisms. The morphology and structure of Fe$_3$O$_4$@Au were characterized by multiple complimentary techniques including transmission electron microscopy, energy-dispersive X-ray spectroscopy, and vibrating sample magnetometry analysis. Under visible light or UV irradiation, the reduction of the nitro-group to amino-group was identified by observing the spectroscopic changes. The result indicates that the adsorption of nitroaromatic compounds on Fe$_3$O$_4$@Au substrate occurs via the nitro-group. Our study could extend the SERS application to the photodegradation monitor of environmental pollutants containing nitro-group.

Keywords: Fe$_3$O$_4$@Au substrate, pollutant, photocatalyst, nitro-group, SERS

1 INTRODUCTION

Ever since the surface-enhanced Raman scattering (SERS) effect was discovered, it has played a significant role in the field of vibrational spectroscopy and is now finding increasing use in high-profile applications. The sensitivity and reproducibility of SERS signal is based on the activity of SERS substrate. Recently, many catalytic-active SERS substrates have been developed for in situ monitoring of environmental pollutants, which could provide new insights into the kinetics and mechanism of catalysis [1]. Catalytic action typically occurs for small metal particles with diameters smaller than 10 nm, or on the surface of transition metals. It is difficult to acquire high Raman enhancement on these nanoparticles. Therefore, bifunctional materials composed of nanoparticles and one- or two-dimensional nanostructured support materials are demanded for the in situ SERS analysis taking advantage of their plasmonic and catalytic properties.

Our previous studies proved that by using Fe$_3$O$_4$ nanospheres as support materials, magnetic substrates could provide sensitive SERS response [2, 3]. Herein we developed a recyclable SERS substrate with Fe$_3$O$_4$ and Au constituents, which can also be used as active photocatalyst. P-nitroaniline (4-NA) was chosen as the target pollutants due to their toxic and mutagenic effects towards organisms. The objectives of this study were 1) to confirm the formation of Au nanoparticles on Fe$_3$O$_4$ magnetic microspheres, and 2) to explore the application potential of Fe$_3$O$_4$@Au in photocatalyst and detection of nitroaromatic compounds with SERS technique.

2 EXPERIMENTAL SECTION

2.1 Materials

All reagents were of analytical reagent grade and used without further purification. Ferric chloride, ferrous chloride, and absolute ethanol were obtained from Beijing Chemicals Corporation (China). Chloroauric acid tetrahydrate (HAuCl$_4$·4H$_2$O) and trisodium citrate dehydrate were purchased from Sinopharm Chemical Reagent Co., Ltd (China). 4-NA was purchased from J&K Scientific Ltd. (China). 3-aminopropyltrimethoxysilane (APTMS, 97%) was from Aldrich Chemicals Corporation (USA). Milli-Q water was used in all experiments.

2.2 Appatatus.

The size and morphology of Fe$_3$O$_4$ and Fe$_3$O$_4$@Au were characterized by transmission electron microscopy (TEM, JEM-1400 from JEOL Ltd.). The surface composition of Fe$_3$O$_4$@Au was analyzed by energy dispersive X-ray spectrometry (EDX, HITACHI S-3000N SEM with an Oxford energy dispersive X-ray analyzer.) X-ray photoelectron spectroscopy (XPS, ESCALab 220i-XL electron spectrometer from VG Scientific) was used to investigate the chemical properties of Fe$_3$O$_4$@Au. XPS data processing and peak fitting were performed using the XPSPeak software package. UV spectra were measured using UV-2550 Shimadzu spectrophotometer. Raman and SERS spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with 4 cm^{-1} resolution at 785 nm excitation energy.

2.3 Synthesis of Fe₃O₄@Au particles.

Fe_3O_4 were prepared following our previous work. About 0.1 g of the as-prepared Fe_3O_4 particles were washed by ethanol three times and dispersed in 100 mL ethanol in a three neck flask. With constant stirring, 1 mL APTMS was slowly added to the above solution. The mixture was sonicated for 30 min, and stirred at room temperature for 3 h. The product was washed with ethanol and water several times to remove the excess APTMS. The APTMS-coated Fe_3O_4 was dispersed in 23 mL water in a three neck flask, under mechanical agitation, 1 mL $HAuCl_4 \cdot 4H_2O$ (2% wt.) solution was added. The mixture was heated to 100 ℃ in an oil bath. Then, 1 mL of 50 mg/mL sodium citrate was added to the above solution and reacted for 20 min. The mixture was allowed to cool to room temperature and the final product was washed with DI water (18.2 ΩM) until the supernatant turned clear. The final Fe_3O_4@Au particles were stored in 25 mL DI water before using.

2.4 Photodegradation of 4-NA on Fe₃O₄@Au

The Fe_3O_4@Au particles (4 mg/mL, 100 μL) were added to 2 mL 4-NA solutions (0.025 mM), followed by the addition of 10 μL $NaBH_4$ (8% wt.). About 10 μL above mixture was placed on the silicon wafer, and exposed to the laser for 5 s to collect the SERS signal. The SERS spectra were collected at regular intervals up to 2 min in the first10 min and then at 5 min interval during the rest of adsorption experiment. For UV analysis, the above solution was mixed at room temperature for 10 min. The solution was filtered through a 0.22 μm membrane and the dye concentration was measured using a spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Characterization of Fe₃O₄@Au

Recently, micrometer-sized bimetallic SERS-platforms have been developed. Compared with nanoparticles, microparticles with a high order of roughness could provide an inhomogeneous distribution of local plasmon resonance surfaces over the whole particle surface, causing a local increase in the electromagnetic field density. Apart from the SERS activity, the bimetallic assemblies also show good surface reaction activity compared to their parent metals, which offers the opportunity to obtain new catalysts. Inspired by the above facts, presented herein is Fe_3O_4 magnetic microspheres decorated with Au NPs. The morphology and structure of Fe_3O_4@Au were first characterized by scanning electron microscopy (SEM). The SEM image in Figure 1(a) indicated the high density of Au on Fe_3O_4 surface. Energy dispersive X-ray spectrometry (EDX) confirmed the presence of atomic Au and the Fe_3O_4 particles (Figure 1(b)). High-resolution (HR) TEM in Figure 1(c) verified the presence of Fe_3O_4@Au particles. Fringe patterns in spacings of 0.236 nm and 0.301 nm were

corresponding to the distances between the (1 1 1) crystal planes of Au and the (3 2 0) planes of Fe_3O_4. The XPS analysis of Au4f for Fe_3O_4@Au is presented in Figure 1(e). The $4f_{7/2}$ level located at 84.05 eV and the $4f_{5/2}$ level at 87.75 eV, with a splitting width of 3.7 eV, demonstrate the successful formation of Au. The magnetism of Fe_3O_4@Au was retained in the presence of Au on Fe_3O_4. The saturated magnetization of Fe_3O_4@Au was 43 emu g^{-1} (data not shown), which enables instantaneous magnetic separation.
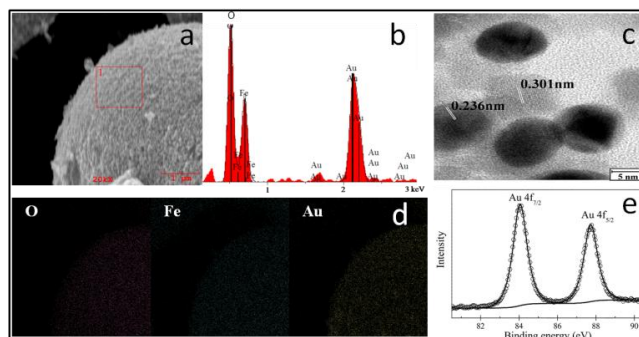

Figure 1: The SEM image (a), EDX spectra (b), and HR-TEM image (c) of Fe_3O_4@Au. The EDX mapping of O, Fe, Au on surface of Fe_3O_4@Au (d). The XPS spectra of Au 4f peaks of Fe_3O_4@Au (e).

The mophology of Au was further confirmed through SEM. Figure 2 shows that a uniform Au layer was coated on the Fe_3O_4 surface. The SEM analysis resolved the average size of Au NPs at 25 nm (Figure 2e). It should be noted that the Au NPs with 10 nm average gap were closely packed but not aggregated (Figure 2f). This array ensured the high SERS enhancement due to the plasmon resonance of the closely connected Au NPs with the field enhancement within them.
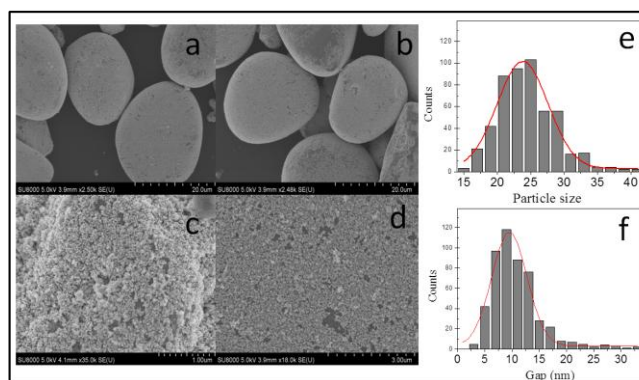

Figure 2: (a-d) SEM micrographs of Fe_3O_4@Au particles. (e, f) The size distribution and particle gap of Au on Fe_3O_4.

3.2 Photodegradation of 4-NA by Fe₃O₄@Au

The photocatalytic activity of Fe_3O_4@Au was investigated. The mechanism of transformation from aryl nitro amine compound to aryl amine product has been

reported to follow a probable direct route, where the BH_4^- serves as the hydrogen source and $Fe_3O_4@Au$ acts as the electron donor [4]. Under light irradiation, the reduction of the nitro-group to amino-group occurred according to the reaction:

$$R\text{-}NO_2 + 4H^+ + 6e^- \rightarrow R\text{-}NH_2 + 2OH^-$$
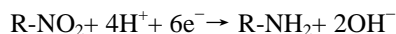
As shown in Figure 3, the UV-visible absorbance spectrum of 4-NA dissolved in water showed the maxima at 380 nm, which can be assigned to the π-π^* transition (Figure 3). In the absence of the $Fe_3O_4@Au$ catalyst or $NaBH_4$ solution, the absorption peak (λ_{max}) of 4-NA remained over several days, suggesting that the reduction did not occur. When a small amount of $Fe_3O_4@Au$ and $NaBH_4$ were added, the peak centered at 380 nm gradually decreased at room temperature (Figure 4). Meanwhile, a new absorption peak centered at ~240 nm ascribed to the characteristic absorption of p-phenylenediamine (PPD) appeared. The $Fe_3O_4@Au$ acted as a catalyst to transfer electrons from BH_4^- to 4-NA during the entire process. It should be noted that the same photocatalytic activity for $Fe_3O_4@Au$ was observed under UVA/Vis light irradiation.

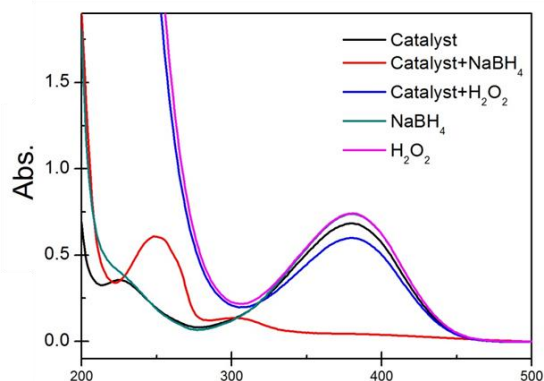Figure 3: UV-adsorption spectra of 4-NA in different reducing conditions.

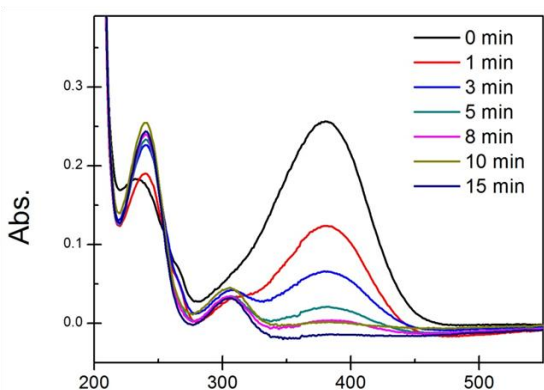Figure 4: Absorption spectra of 4-NA with $NaBH_4$ in the presence of $Fe_3O_4@Au$ with time up to 15 min.

When employing magnetic properties to prepare the catalyst, the recycled properties as a catalyst must be validated. Figure 5 shows the photo-degradation percentages of 4-NA by $Fe_3O_4@Au$ for repeated use in the photocatalytic process. The catalyst was reused 5 times. In each process cycle, the same $Fe_3O_4@Au$ was mixed with a fresh solution of 4-NA for 30 min. The photodegradation percentage of R6G was only slightly reduced by 8-10%. The results indicated that $Fe_3O_4@Au$ was very stable in physical strength.

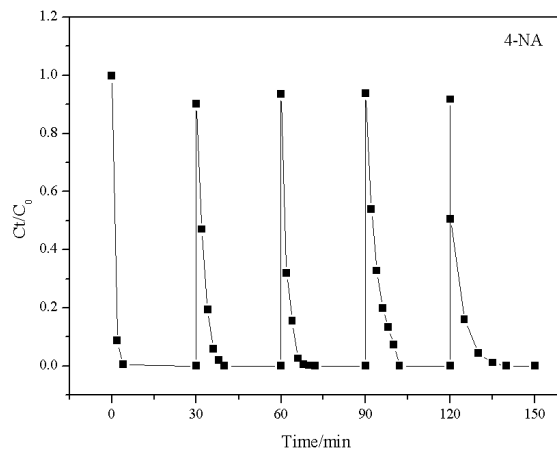Figure 5: The recyclability test of the photocatalytic decomposition rate of 4-NA in the presence of $Fe_3O_4@Au$.

3.3 SERS detection of 4-NA on $Fe_3O_4@Au$ substrates

Considering that 4-NA is a widespread pollutant, we examined the use of $Fe_3O_4@Au$ for 4-NA detection. As shown in Figure 6, the Raman peak at 859 cm^{-1} and 1320 cm^{-1} are the $N\text{-}O_2$ and $C\text{-}NO_2$ stretching modes of 4-NA, respectively. The resluts indicated the substrates can achieve SERS sensing of 10^{-7} M 4-NA.
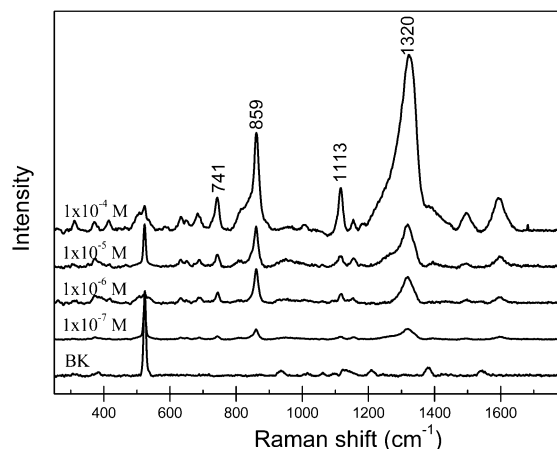

Figure 6: SERS spectra of 4-NA with different concentrations of 10^{-4}, 10^{-5}, 10^{-6}, and 10^{-6} M on $Fe_3O_4@Au$ substrate.

The Fe$_3$O$_4$@Au exhibited both catalytic and SERS activities, which enables the in situ SERS monitoring of the surface catalytic reaction. The SERS spectra taken during the reduction of 4-NA catalyzed by Fe$_3$O$_4$@Au in the presence of NaBH$_4$ were shown in Figure 7. The reduction was identified by observing the spectroscopic changes. The intensity of nitro-group stretching bands at about 1320 cm^{-1} and 859 cm^{-1} decreased and became indiscernible after 3 min irradiation, indicating the adsorption of nitroaromatic compounds on Fe$_3$O$_4$@Au substrate occurs via the nitro-group. The new bands at 811 cm^{-1} and 1160 cm^{-1} were assigned to the vibration modes of the PPD product. The drastic decrease of the SERS enhancement after reduction can be explained by considering that PPD does not strongly interact with the Fe$_3$O$_4$@Au substrate, which insteadly occurs when the electron-drawing nitrogroup is present.
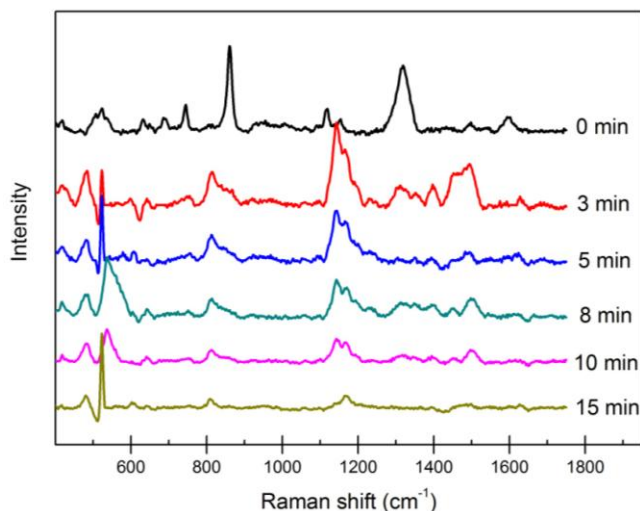

Figure 7: SERS spectra recorded during the reduction of 4-NA on Fe$_3$O$_4$@Au at different reaction times. From top to bottom: SERS spectra recorded at 0, 3, 5, 8, 10, and 15 min after addition of NaBH$_4$ solution.

3.4 SERS monitor of nitroaromatic compounds on Fe$_3$O$_4$@Au substrates

To justify our hypothesis that Fe$_3$O$_4$@Au could be applied in monitor of catalytic reaction for nitroaromatic pollutants, SERS spectra of typical nitraromatic compounds were recorded during the catalytic reduction. As shown in Figure 8, Fe$_3$O$_4$@Au particles exhibit surface plasmon resonance and could be used as substrate in SERS detection of organic pollutants such as 2,6-DC-NA, 2-NA, and 4-NP. The Fe$_3$O$_4$@Au possesses not only highly sensitive and stable SERS properties, but also stable catalytic performance. Under UV irradiation, the SERS spectrum undergoes significant changes. The nitrogroup stretching band disappearing, along with marked new Raman bands of the overall SERS enhancement. The results extend the \application of Fe$_3$O$_4$@Au to the photodegradation monitor of environmental pollutants containing nitro-group.
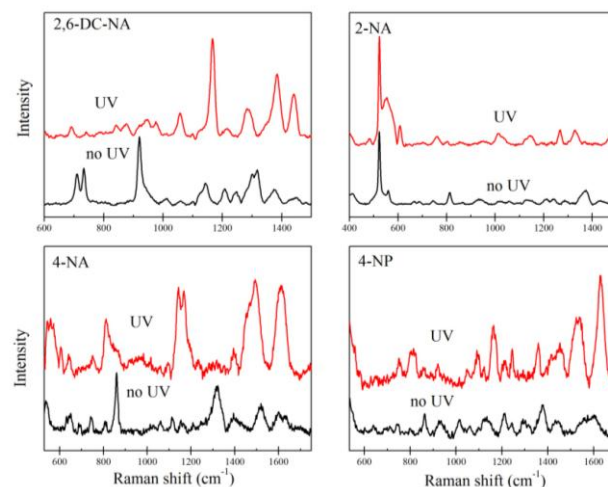

Figure 8: SERS spectra recorded during the reduction of 2,6-DC-NA, 4-NA, 2-NA, and 4-NP on Fe$_3$O$_4$@Au with addition of NaBH$_4$ solution.

4 CONCLUSION

In conclusion, we present a Fe$_3$O$_4$@Au material with core-shell sructure. Examination of Fe$_3$O$_4$@Au using SEM, EDX mapping, XPS, and HR-TEM provided complementary identification and characterization. In Fe$_3$O$_4$@Au- NaBH$_4$ system, nitraromatic compounds could be photo-degradated under UVA/Vis light irradiation. Fe$_3$O$_4$@Au exhibit surface plasmon resonance and can be used as substrate for SERS detection of environmental pollutants containing nitro-group. With the high catalytic and SERS activities, the Fe$_3$O$_4$@Au could be applied for the in situ SERS monitoring of the surface catalytic reaction. Our results could extend the SERS investigation to the photodegradation processes of pollutants by catalytic activity of bimetallic substrates.

REFERENCES

[1] Muniz-Miranda, M., SERS monitoring of the catalytic reduction of 4-nitrophenol on Ag-doped titania nanoparticles. Appl. Catal. B-Environ. 2014, 146, 147-150.

[2] Du, J.; Jing, C., Preparation of Fe$_3$O$_4$@Ag SERS substrate and its application in environmental Cr(VI) analysis. J. Colloid Interface Sci. 2011, 358 (1), 54-61.

[3] Du, J.; Cui, J.; Jing, C., Rapid in situ identification of arsenic species using a portable Fe$_3$O$_4$@Ag SERS sensor. Chem. Commun. 2014, 50 (3), 347-349.

[4] Chiu, C.-Y.; Chung, P.-J.; Lao, K.-U.; Liao, C.-W.; Huang, M. H., Facet-Dependent Catalytic Activity of Gold Nanocubes, Octahedra, and Rhombic Dodecahedra toward 4-Nitroaniline Reduction. J. Phys. Chem. C 2012, 116 (44), 23757-23763.