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A plasmon-driven selective surface catalytic reaction revealed by surface-enhanced Raman scattering in an electrochemical environment

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Plasmonic catalytic reactions of molecules with single amine or nitro groups have been investigated in recent years. However, plasmonic catalysis of molecules with multiple amine and/or nitro groups is still unknown. In this paper, plasmon-driven catalytic reactions of 4,4'-dinitroazobenzene (DNAB), 4,4'-diaminoazobenzene (DAAB) and 4-nitro-4'-aminoazobenzene (NAAB) are investigated using electrochemical surface-enhanced Raman scattering (SERS) spectroscopy. The results reveal that a plasmon-driven reduction reaction occurred for DNAB and NAAB in which the NO₂ group was reduced to NH₂, while the plasmon-driven oxidation reaction of NH₂ did not occur. This result demonstrates that plasmon-driven reduction reactions are much easier than plasmon-driven oxidization reactions in electrochemical environments. The molecular resonance may also play an important role in plasmon-driven catalytic reactions. These findings provide us with a deeper understanding of plasmon-driven catalytic reactions.

Plasmonic chemistry¹, which is based on catalytic reactions driven by surface plasmons, is an important applied field in the study of surface plasmons^{2–6}. It has been attracting increasing attention since the first reports that p-aminothiophenol (PATP) can be catalyzed to DMAB via surface plasmon resonance in 2010^{7,8}. Later, it was reported that 4NBT can also be catalyzed to DMAB by surface plasmon resonance^{9,10}, with hot electrons generated from plasmon decay taking part in this reduction reaction⁹. Such plasmon-driven catalyzed reactions of 4NBT and PAPT into DMAB were further confirmed in tip-enhanced Raman spectroscopy experiments in high vacuum and ambient environments, respectively^{2,10–12}. The mechanism of plasmon-driven catalytic reactions is mainly attributed to the density of state (DOS) of hot electrons generated from surface plasmon decay. Hot electrons with high kinetic energies play a key role in plasmonic chemistry¹⁰. This phenomenon is of significant interest in plasmon-driven catalysis, as discussed in several recent excellent reviews^{13–15}.

However, in practice, chemical reactions mostly occur in aqueous environments, while the above experimental works were predominantly performed in ambient or vacuum environments^{1–12,16}. Several experiments have been performed in aqueous environments that show similar catalytic reactions^{17,18},

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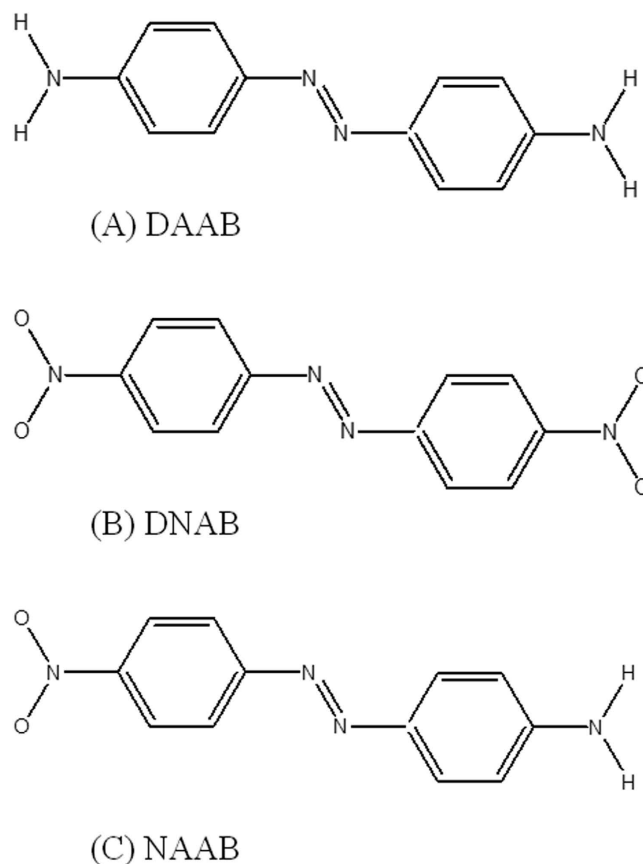


Figure 1. Molecular structures of DAAB, DNAB and NAAB.

and the electrochemical mechanism can work synergistically with plasmon catalysis. The target molecules were NH_2 or NO_2 groups in the previous experiments in aqueous environments. If molecules with both NH_2 and NO_2 groups are in an aqueous environment, what type of plasmon-driven chemical reaction will occur (i.e., reduction or oxidation)? If the target molecules have two NH_2 or NO_2 groups, can the target molecules form dimers via one NH_2 (or NO_2) or polymers via two or more NH_2 (or NO_2) groups? These questions are very interesting and need to be answered. 4,4'-Diaminoazobenzene (DAAB), 4,4'-dinitroazobenzene (DNAB) and 4-nitro-4'-aminoazobenzene (NAAB) are three good candidates for investigating the above issues, as they possess combinations of these two groups (Fig. 1). DNAB has two NO_2 side groups, which can be used to study the plasmon-driven reduction reaction; DAAB has two NH_2 side groups, which can be used to study the plasmon-driven oxidation reaction; and NAAB has both an NH_2 and an NO_2 group, so it can be used to study the priority of the plasmon-driven oxidation and reduction reactions.

In this paper, the electrochemical surface-enhanced Raman scattering (SERS) spectra of DNAB, DAAB and NAAB were experimentally studied. We attempt to answer the above questions experimentally and provide an interpretation of the findings based on theory. Plasmon-driven reduction of the NO_2 groups occurred, i.e., NO_2 was reduced to NH_2 , while plasmon-driven oxidation of NH_2 did not occur. Our study provides experimental evidence that the plasmon-driven reduction reaction occurs more easily than the plasmon-driven oxidation reaction in an aqueous environment.

Results

To have a clear picture of the plasmon catalytic reaction, we must first identify the characteristic Raman peaks of these three molecules (DAAB, DNAB and NAAB). The experimental and calculated Raman spectra of DAAB, DNAB and NAAB powder are shown in Fig. 2. As shown in Fig. 2(a,b), the Raman peak of DAAB at 1398 cm^{-1} is the strongest, representing the $-\text{N}=\text{N}-$ stretching mode of DAAB. The two Raman peaks (one weak and one strong) at approximately 1152 cm^{-1} are attributed to the asymmetric and symmetric vibrations of H on the two benzyls. The two weak Raman peaks at approximately 1600 cm^{-1} are the asymmetric and symmetric scissor vibrations for the H of the two NH_2 groups. Figure 2(c,d) reveal that the Raman peak of DNAB at 1350 cm^{-1} is the two symmetric $-\text{NO}_2$ stretching mode of DNAB. The strongest Raman peak at 1334 cm^{-1} in Fig. 2(e,f) is the $-\text{NO}_2$ stretching mode of NAAB.

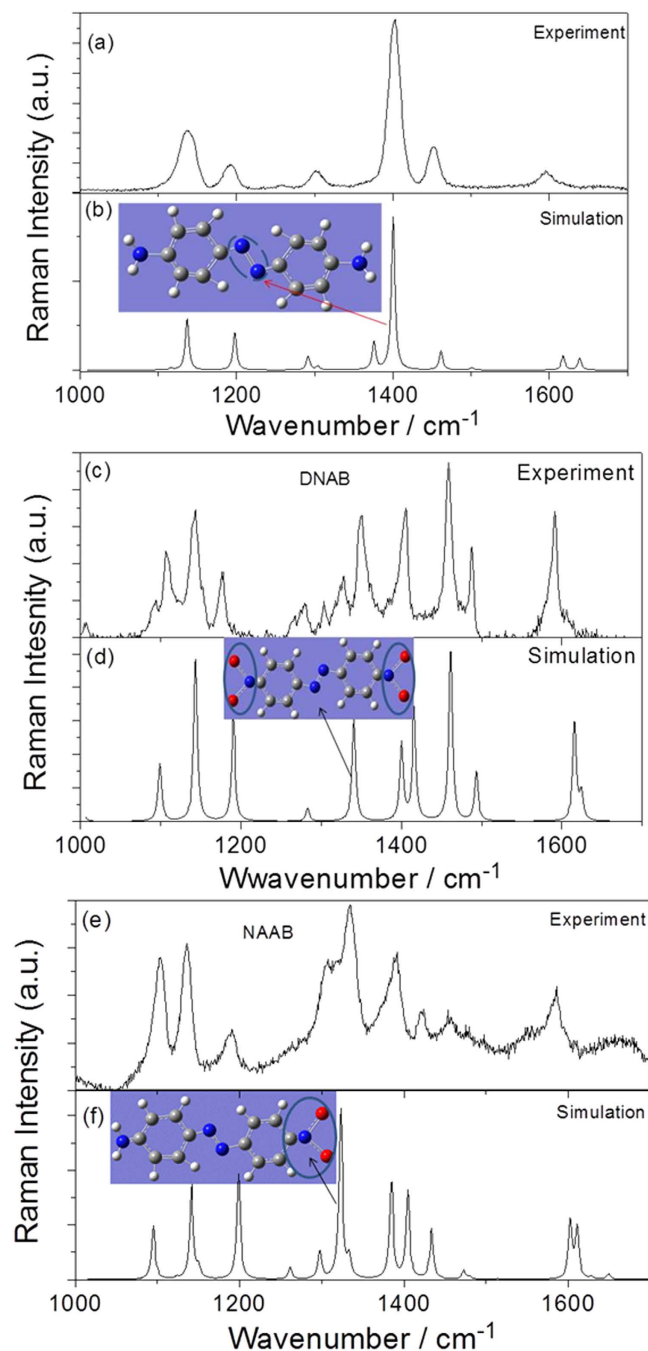


Figure 2. Experimental and theoretical Raman spectra. (a) and (b) experimental and theoretical DAAB Raman spectra; (c) and (d) experimental and theoretical DNAB Raman spectra; and (e) and (f) experimental and theoretical NAAB Raman spectra.

Figure 3 shows the potential-dependent electrochemical SERS spectra of DAAB. The Raman profiles are stable, and they do not change with the variation in the external electric voltage. The weak Raman peak to the left of 1152 cm^{-1} (the asymmetric vibrations of H on the two benzyIs) gradually increased as the potential increased, and its Raman strength is comparable to another Raman peak at approximately 1152 cm^{-1} . The two weak Raman peaks from the asymmetric and symmetric scissor vibrations of the H atoms in the two NH_2 groups at approximately 1600 cm^{-1} decreased owing to the increase in the width of the Raman peak. The results show that no reduction or oxidation reaction occurs during the measurement. For further confirmation of this result, please see Supporting Information Fig. S1.

Figure 4(a,b) are the potential-dependent electrochemical SERS spectra of DNAB measured with a 532 nm laser. From Fig. 4(a), we can see that the Raman peak at 1350 cm^{-1} gradually decreased as the potential increased, indicating that the two NO_2 groups of DNAB were reduced by the surface plasmon

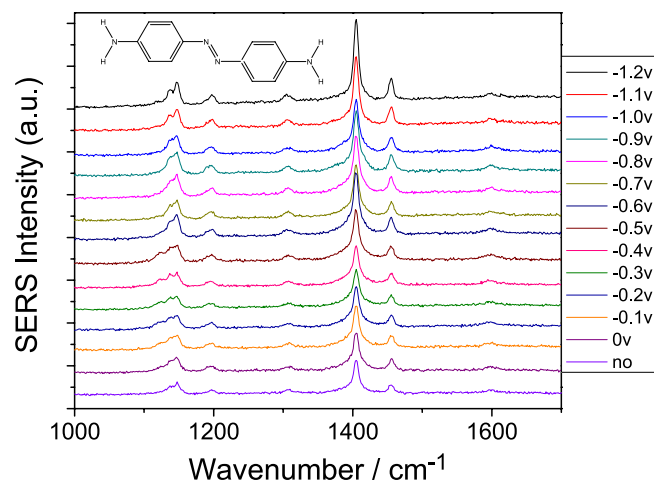


Figure 3. Electrochemical SERS spectra of DAAB at different potentials, excited by a 532 nm laser.

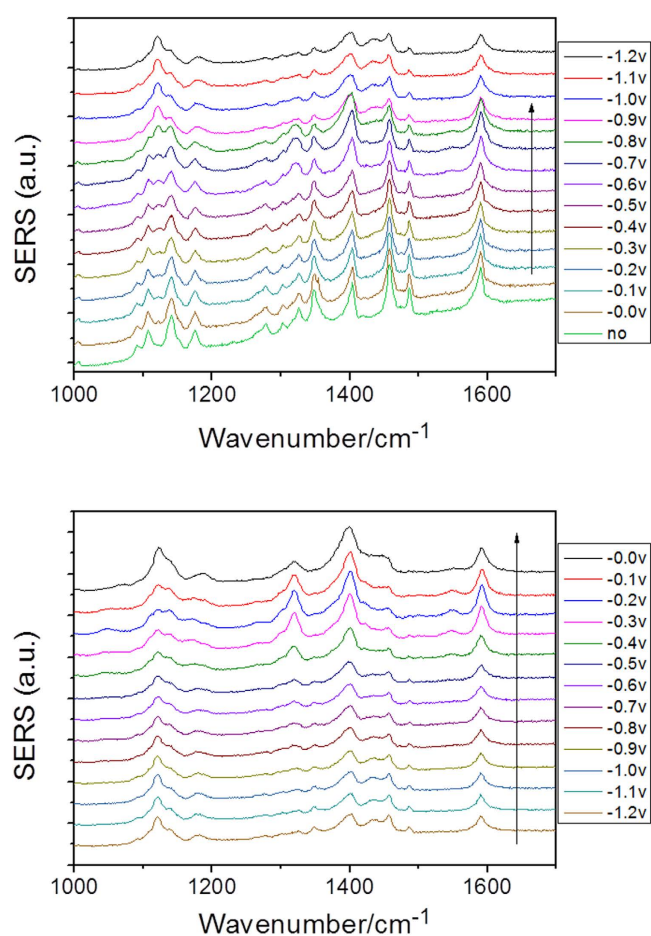


Figure 4. Electrochemical SERS spectra of DNAB at different potentials, excited by a 532 nm laser.

catalytic reaction. The results indicate that the plasmon-driven chemical reaction occurred during the measurement with the variation of the external electric voltage. The SERS spectra as the external electric voltage returned from -1.2 V to 0 V are shown in Fig. 4(b). The spectra had very similar features during the return of the potential. A comparison is made between the reacted DNAB and the original DAAB (Fig. 5). From the figure, we can see that, at 0 V , there was no chemical reaction, but once the potential increased to -1.2 V (and when it returned to 0 V), the SERS profiles were significantly different. The reacted Raman spectrum of DNAB is the same as the Raman spectrum of DAAB, which indicates that plasmon-driven chemical reactions occurred because of the variation in the external electric voltages,

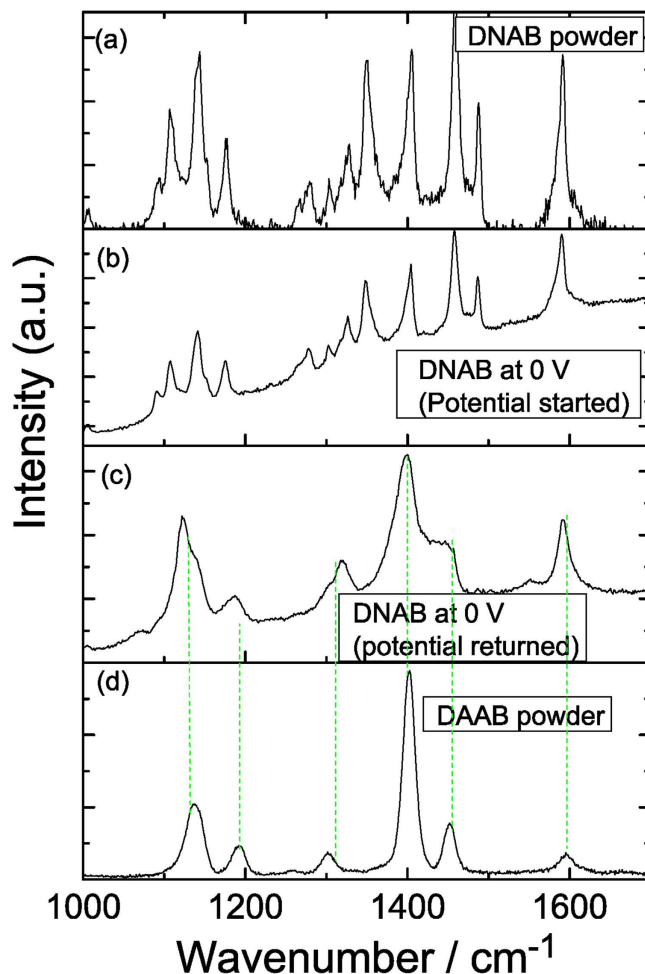


Figure 5. Comparison of the experimental and theoretical Raman spectra of DNAB.

and DNAB was catalyzed to form DAAB by surface plasmon resonance. To reveal the contribution of the surface plasmons to the catalytic reaction, potential-dependent SERS spectra were also measured using a 785 nm laser (see Fig. 6). No reaction occurred during excitation by the 785 nm laser. This means that surface plasmons play a significant role in the reaction, indicating that it is a plasmon-driven chemical reaction because 785 nm is far from the surface plasmon resonance, as shown in the spectrum of the surface plasmon resonance in Fig. 1(d) in reference¹⁸.

The above experiments show the plasmon-driven reaction conditions of DAAB (or DNAB), which has two NH_2 (or NO_2) groups. However, for NAAB, which has both NH_2 and NO_2 groups, what will happen? The potential-dependent electrochemical SERS spectra of NAAB were measured using a 532 nm laser (see Fig. 7) and a 785 nm laser (see Fig. 8). As shown in Fig. 7, the profiles of the potential dependent SERS spectra are significantly different at the different electric voltages when excited by the 532 nm laser, which reveals that a chemical reaction occurred. Figure 9(a) is the Raman spectrum of NAAB powder, and Fig. 9(b) is the SERS spectrum of NAAB at 0 V excited by a 785 nm laser. Upon comparing Fig. 9(a,b), we can see that their profiles are almost the same. Figure 9(c,d) are the SERS spectra of NAAB measured at 0 V and -1.2 V, excited by the 532 nm laser. By comparing Fig. 9(b,c), we can see that even at 0 V, upon excitation by the 532 nm laser, the plasmon-driven chemical reaction occurred due to the strong SPR peak at approximately 532 nm, as the Raman peak at 1350 cm^{-1} ($-\text{NO}_2$ vibration) significantly decreased, although it did not completely disappear. By comparing Fig. 9(d,e), we can see that the SERS spectrum at -1.2 V is almost the same as that of the DAAB powder, indicating that NAAB was catalyzed to DAAB in this system by surface plasmon resonance.

Discussion

In the sequences of the potential-dependent electrochemical SERS spectra, we can see that, for DNAB, the reaction occurs between -0.8 and -0.9 V, which means that the surface plasmon energy associated with the applied potential can allow the electrons to overcome the barrier and drive the reaction upon excitation with a 532 nm laser. For NAAB, the reaction can occur at 0 V, which means that the reaction has a much lower barrier; upon excitation with the 532 nm laser, the energy of the surface plasmon is

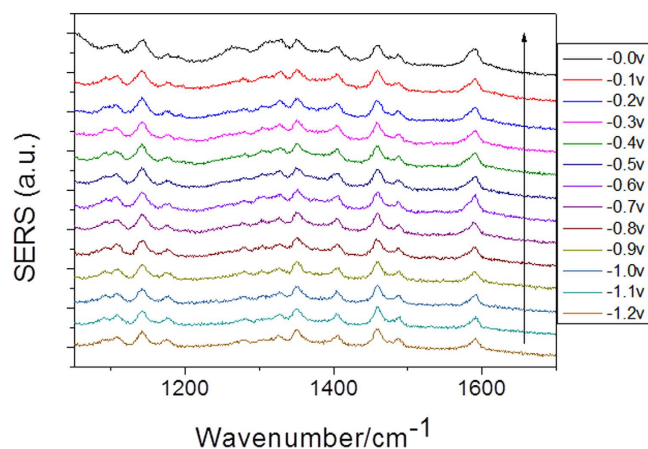
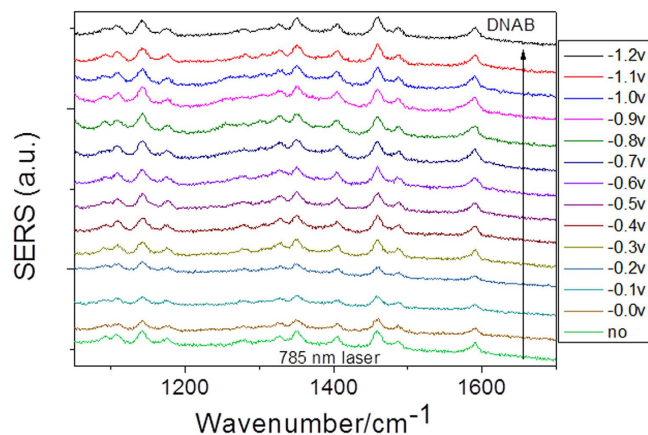


Figure 6. Electrochemical SERS spectra of DNAB at different potentials excited at 785 nm.

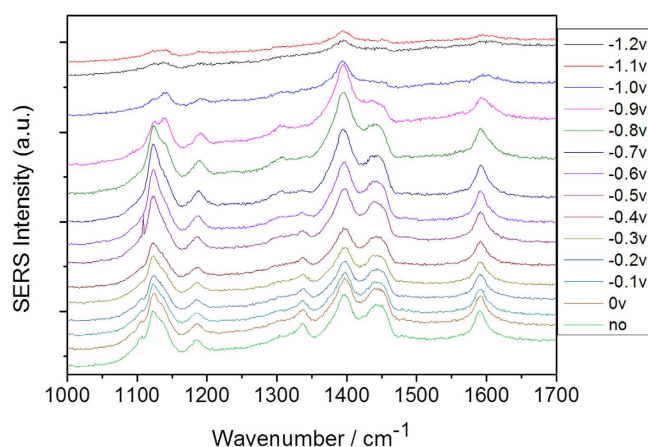


Figure 7. Electrochemical SERS spectra of NAAB at different potentials, excited by a 532 nm laser.

enough for the catalytic reaction. All of the experiments show that DAAB has a stable structure. One reason may be that the surface plasmon decayed hot electrons have a higher energy to overcome the barrier, while the surface plasmon decayed holes cannot diffuse to the molecule (i.e., the electrons in the molecule transfer back). Therefore, reduction can occur much more easily than oxidation. The nitro groups of DNAB and NAAB can be reduced to amine NH_2 groups by plasmon-driven catalysis.

When the potential was 0V, the plasmon-driven chemical reaction occurred for NAAB when excited by the 532nm laser, while for DAAB, such a chemical reaction did not occur. The reason for this is that the molecular resonance may play an important role (Fig. 10). Figure 10(a) shows the absorption

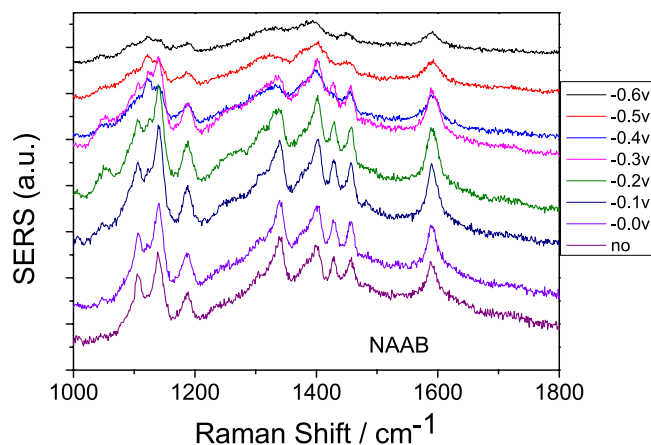


Figure 8. Electrochemical SERS spectra of NAAB at different potentials, excited by a 785 nm laser.

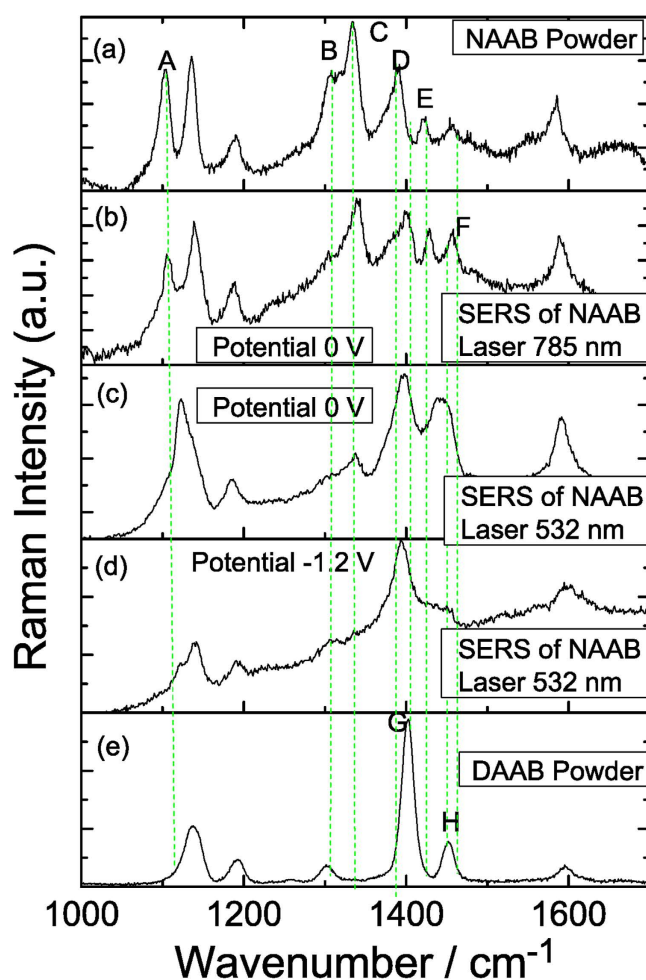


Figure 9. Comparison of the experimental and theoretical Raman spectra of NAAB.

spectrum of DAAB, which reveals that the SERS excited at 532 nm is the normal Raman scattering. By contrast, Fig. 10(b) demonstrates that the SERS of DNAB excited at 532 nm is a pre-resonance Raman scattering, while the SERS of NAAB is a resonance Raman scattering excited at 532 nm (see Fig. 10(c)). Therefore, molecular resonance can also significantly enhance plasmon-driven chemical reactions. To further reveal the contributions of the molecular resonance absorptions to the plasmon-driven chemical reactions, we measured the electrochemical SERS spectra of NAAB (see Fig. 8) excited at 785 nm, where 785 nm is far from the SPR resonance of the roughened substrate (see Fig. 1d in Reference¹⁷); there was

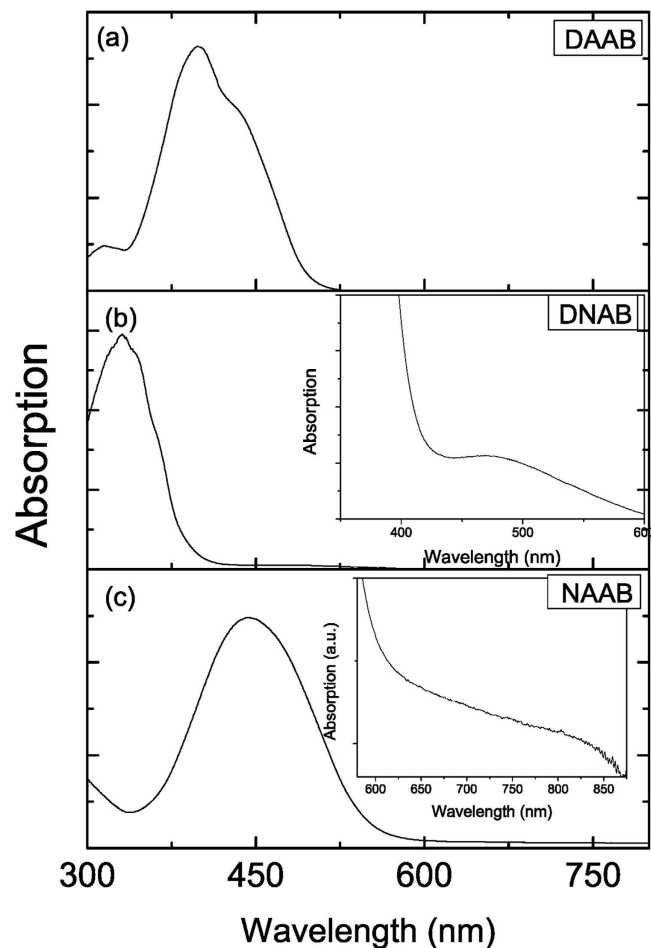


Figure 10. Absorption spectra of (a) DAAB, (b) DNAB, and (c) NAAB.

no chemical reaction at 0 V. With the increase of the external electric voltage, it is closer to the SPR peak¹⁷. Although the SPR is still weak at -0.6 V (see Fig. 6 in Ref. 17), the plasmon-driven chemical reaction for NAAB still occurred, reducing it to DAAB (see Fig. S2). This is direct evidence for molecular resonance in the plasmon-driven chemical reaction. At 785 nm, it is pre-resonant for NAAB, as shown in the inset in Fig. 10(c).

The plasmon-driven selective surface catalysis in our experiment is driven by three factors: the applied potential, the resonance of the surface plasmons and the resonance of the molecules. The applied potential will raise the Fermi level of the metal surface and will allow the electrons to overcome the meta-molecule junctions. The resonant plasmons will decay to hot electrons that can also overcome the junction barrier. The plasmon-decayed hot electrons should have higher energy (in our experiment, the measured range is approximately 1.3–2.7 eV) than the applied voltage ($0 \sim -1.2$ V). Thus, the surface plasmon plays the main role. Under some conditions, the applied voltage is not even necessary. However, they are associated with each other¹⁶. The resonance of the molecules overlapping with the surface plasmon resonance may increase the electron tunneling and transition because a Förster resonance energy transfer occurs, and the excited states of the molecules may be more easily reduced. The underlying mechanism still remains to be determined.

In summary, plasmon-driven selective surface catalytic reactions have been revealed by surface-enhanced Raman scattering in an electrochemical environment. Our experimental and theoretical evidence revealed the reduction of nitro groups to amine groups under plasmon conditions using electrochemical SERS spectra. However, the plasmon-driven oxidation of amine groups to nitro groups does not occur. The results reveal that the molecular resonance electronic absorption also plays an important role in the plasmon-driven chemical reaction. Our results are very interesting for plasmon chemistry and are of significant importance in elucidating the competition between reduction and oxidation in plasmon-driven chemical reactions in aqueous environments. Our results also provide us with a deeper understanding of plasmon-driven catalytic reactions. This method can be applied to other similar molecules and reactions.

Methods

The Ag electrode (a single-crystal silver rod of 99.99% purity) was polished with emery paper and cleaned with Milli-Q water in an ultrasonic bath. Next, the electrode was placed in a typical electrochemical cell containing a solution of 0.1 M Na₂SO₄ for roughening. A double potential step was used to roughen the surface by applying a voltage of +0.25 V for 8 s and then applying a voltage of −0.35 V. This roughening treatment was performed to enhance the Raman intensity for the convenience of spectral recording¹⁸.

The DAAB and NAAB were purchased from Aldrich Chemical Co., Alfa Co. and Sigma Co. The DNAB was synthesized by Beijing Kaida Co. according to the customer's requirements, and their NMR spectrum can be observed in Figures S3–S5 in the supporting information. The Raman spectra of the DNAB, DAAB and NAAB powders and their SERS spectra were recorded using a microprobe Raman system RH13325 (R-2000) spectrophotometer. For the SERS measurements, the applied voltage of the working electrode was controlled by a CHI619B electrochemical instrument. The samples were excited with 532 nm and 785 nm lasers with an effective power of 0.3 mW.

The theoretical calculations of the molecular Raman spectra and their vibrational modes were performed using Gaussian 09 software with density functional theory¹⁹, the pw1pw91 functional²⁰, and the 6-31G(d) basis set. The pw1pw91 functional is the best functional for the calculation of the Raman spectra of azo compounds²¹.

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Author Contributions

M.S. and P.W. supervised the project, and M.S. designed the experiments. L.C. experimentally measured the SERS spectra. M.S. and L.C. analyzed the data. M.S. wrote the paper. L.C., P.W., Y.F. and Y.L. discussed and revised the manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

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