

Electronic Supplementary Information (ESI) for
Reversible catalysis for the reaction between methyl orange
and NaBH₄ by silver nanoparticles

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Experimental details:

The preparation of citrate-stabilized silver nanoparticles (Ag NPs): 100 mL of 0.1 mM trisodium citrate was added into 100 mL of 0.1 mM AgNO₃ under stirring. Then 9 mg NaBH₄ was added rapidly into the above aqueous solution under vigorous stirring. This solution was further stirred for 2 h at room temperature. The resulting bright yellow colloidal silver nanoparticles were finally obtained.

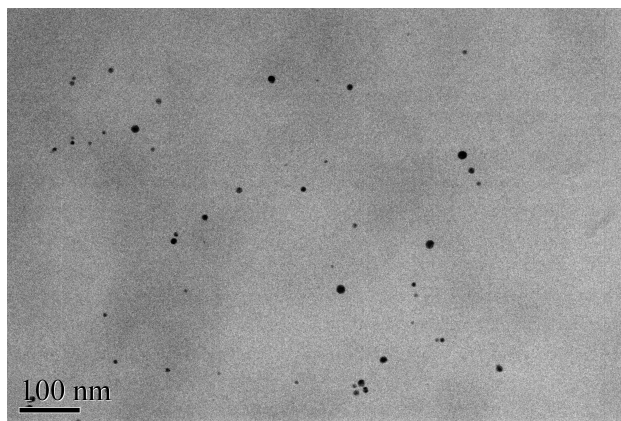


Figure S1. TEM image of citrate-capped Ag NPs

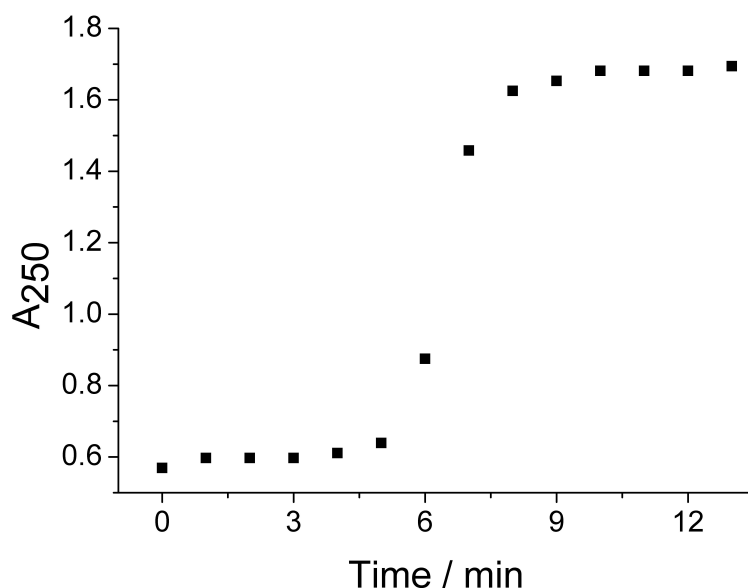


Figure S2. The time-dependent UV absorption at 250nm (A_{250}) of the MO solution containing NaBH_4 after adding aggregated Ag NPs induced by CTAB

The degradation of methyl orange (MO) catalyzed by Ag NPs: 300 μL of 0.25 mM MO solution mixed with 300 μL of 80 mM NaBH_4 solution in the 2 mL container, and then 200 μL of Ag NPs solution was added into the above solution. Finally, the color of solution changed from orange to colorless in 40 seconds.

UV spectra were recorded by UV-3600 spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) was recorded by a JEM-2100 electron microscope (JEOL, Japan) at 200 KV. All of the chemicals were of analytical grade. The water used throughout all experiments was purified by a Elix 5 Pure Water System (Millipore, USA).

LC-MS analyses were performed with Agilent 1290 Infinity LC/6460 QQQ MS system containing a Beckman Ultrasphere ODS column (4.6 mm \times 25 cm, 5 μm particle). The mobile phase was consist of acetonitrile and 0.01 mol/L ammonium acetate solution (v:v = 4:6). The flow rate was 0.7 ml/min and UV detection was performed at 260 nm. MS conditions: ESI ion source; positive ion mode.

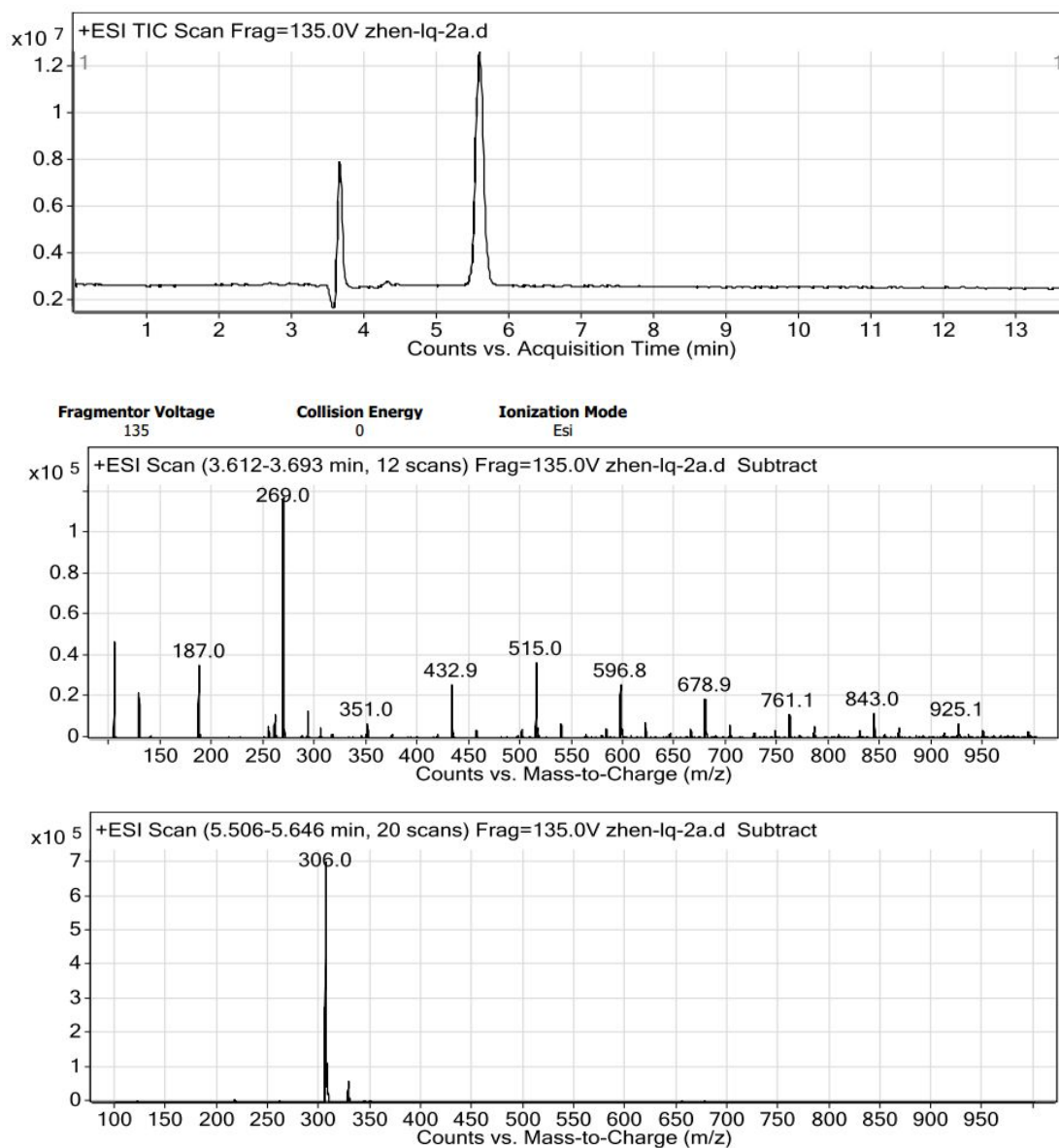
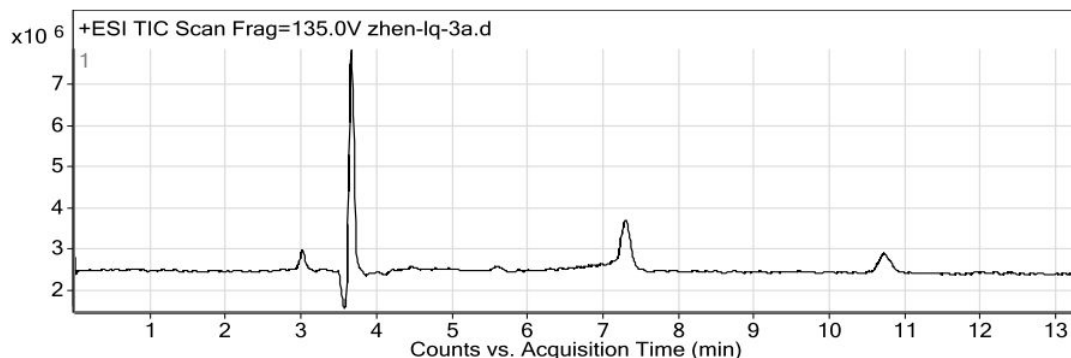
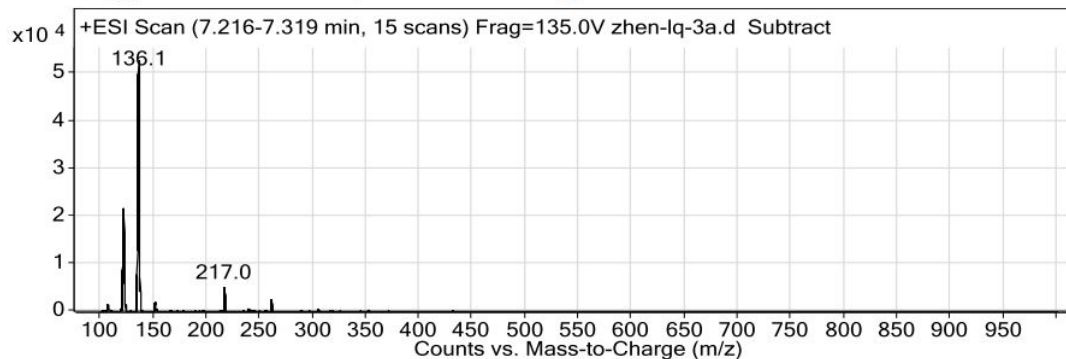
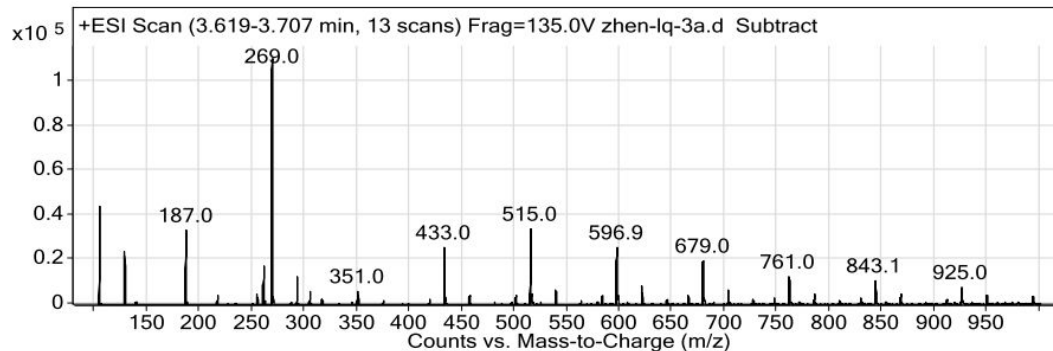
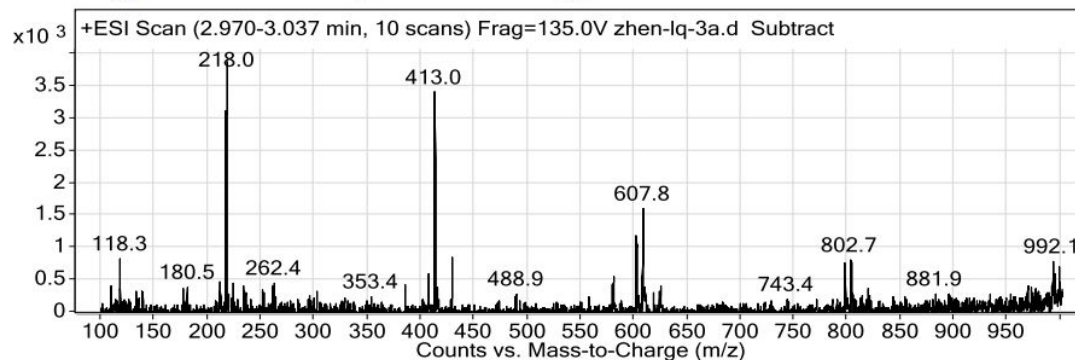


Figure S3. HPLC-MS result of MO solution containing NaBH₄.

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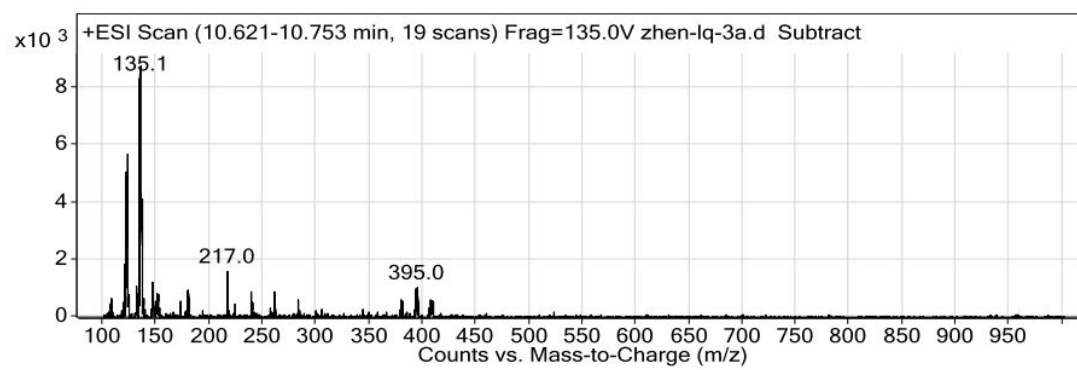


Figure S4. HPLC-MS result of the MO solution containing NaBH₄ upon the addition of Ag NPs.

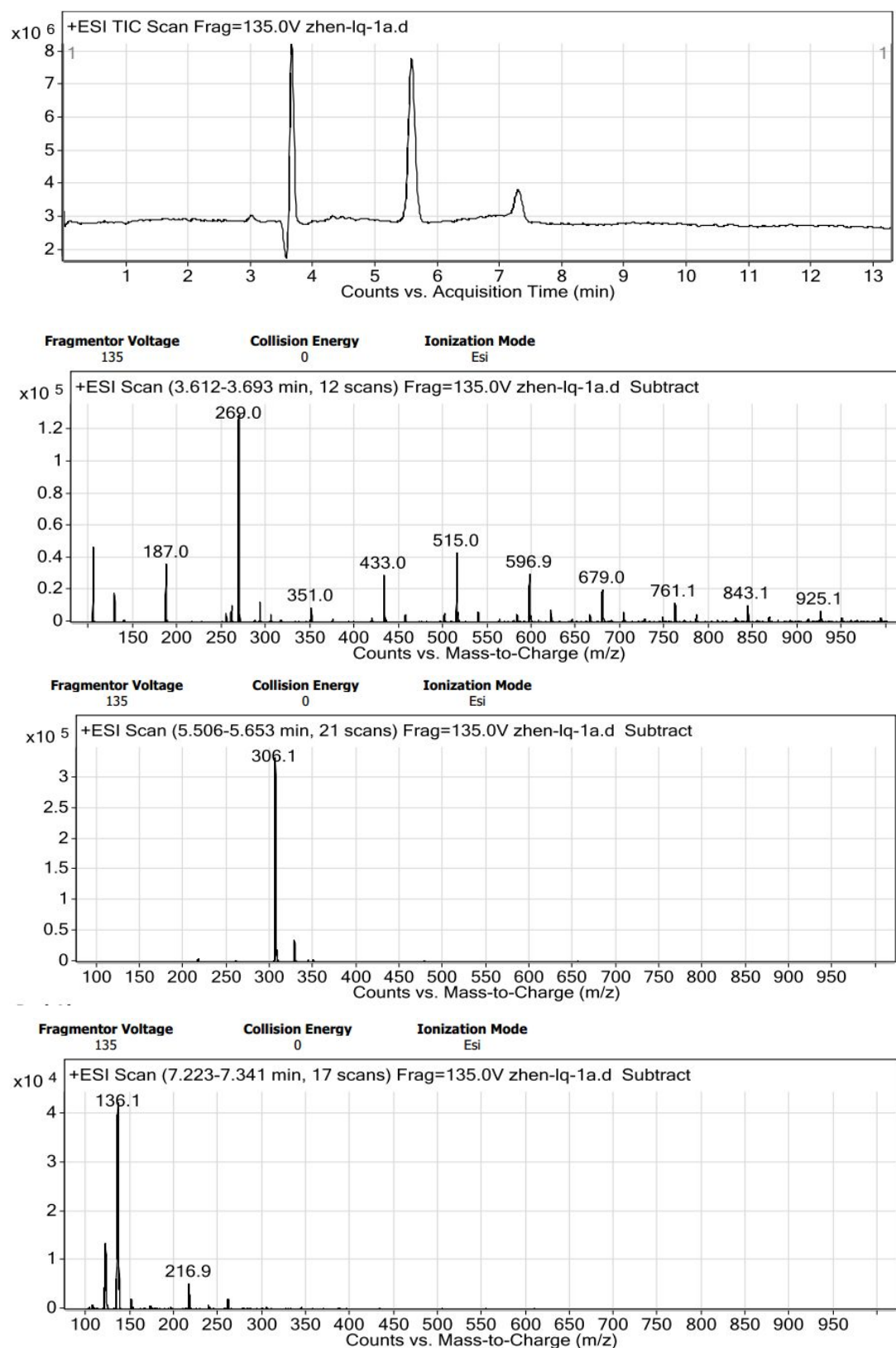


Figure S5. HPLC-MS result of the MO solution containing NaBH_4 and Ag NPs upon the addition of $5 \mu\text{M}$ CTAB

Experimental details:

The separation and purification of the reduction products of MO: 3.88 g NaBH₄ was added into 20 mL of 0.15 M MO solution under stirring, and then 50 mL of Ag NPs solution was added. The above solution was further stirred for 24 h at room temperature. Finally, the color of solution changed from orange to black. The solution was extracted by CH₂Cl₂ because sodium sulfanilate could not dissolve in CH₂Cl₂ and N,Ndimethyl-1,4-phenylenediamine dissolved well in CH₂Cl₂. After extraction, the aqueous phase contained sodium sulfanilate, NaBO₂ and MO, so the powdered activated carbon was added into the aqueous phase to remove MO. The pKa of sulfanilic acid was 3.01 and pKa of HBO₂ was 9.20. Therefore, sulfanilic acid and NaBO₂ could be separated by strong base anion ion exchange column. The SAX SPE Column was used to collect sulfanilic acid. The eluent was ultrapure water to remove NaBO₂ first, and then 1 M HCl was used for elution. Finally, the solvent of the obtained solution was removed under reduced pressure. The residue was solved by D₂O for the characterization of NMR.

In addition, the organic phase was further treated with Column Chromatography to get N,Ndimethyl-1,4-phenylenediamine. An alumina column was prepared and the concentrated solution was loaded into the column. The ethyl acetate was used as eluent to remove other impurities first, then methanol was used for elution. The solvent of the obtained solution was removed under reduced pressure. The residue was solved by DMSO-D6 for the characterization of NMR.

¹H NMR results of two reduction products of MO:

¹H NMR (500 MHz, D₂O): 6.80 (d, 2H), 7.50 (d, 2H). (Figure S6)

¹H NMR (500 MHz, DMSO-D6): 2.70 (s, 6H), 4.40 (s, 2H), 6.55 (s, 4H). (Figure S7)

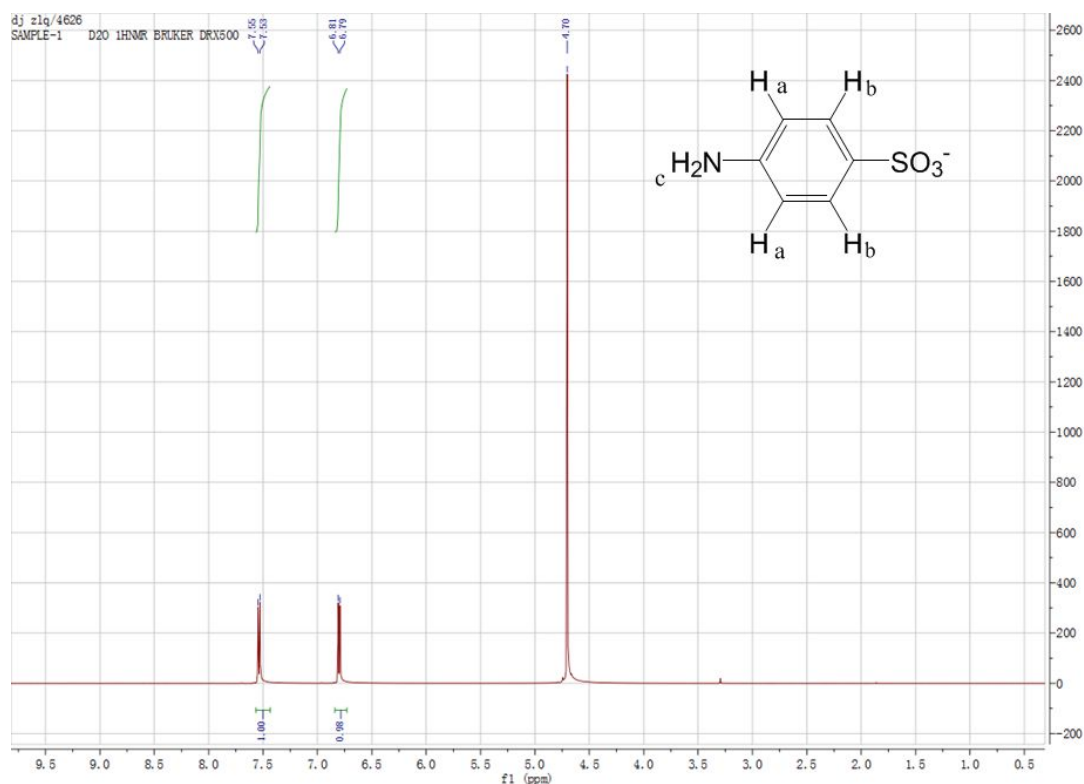


Figure S6. ^1H NMR spectrum of one of the reduction products of MO

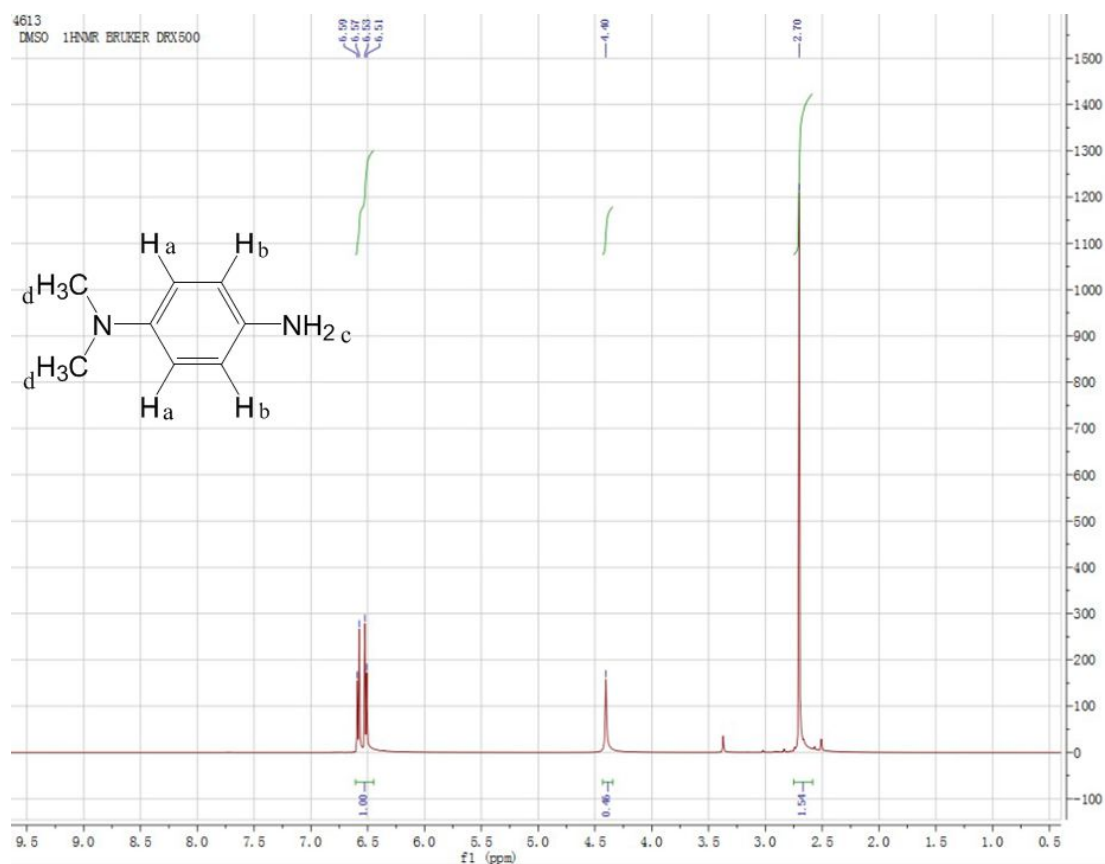
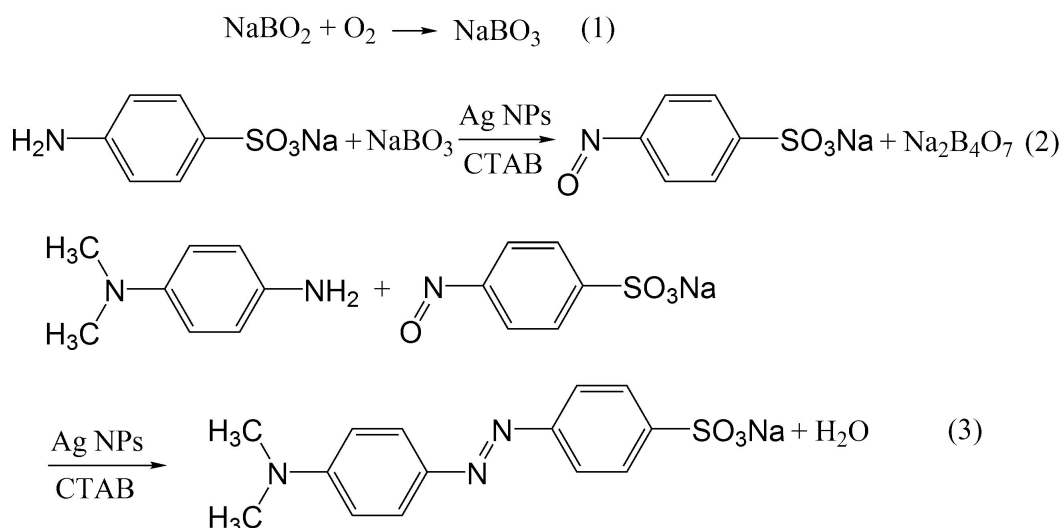


Figure S7. ^1H NMR spectrum of the other the reduction products of MO

As shown in Figure S6, the resonance signal at around $\delta = 6.80$ ppm corresponded to Ha of aromatic ring and $\delta = 7.50$ ppm was Hb of aromatic ring. There was no NMR response signal of the amino group was ascribed to the replacement of hydrogen by deuterium. In Figure S7, the resonance signal at around $\delta = 2.70$ ppm corresponded to Hd of methyl group, $\delta = 4.40$ ppm was Hc of amino group and $\delta = 6.55$ ppm was H of aromatic ring.

Therefore, ^1H NMR spectroscopy studies further demonstrated that the reduction products of MO were sodium sulfanilate and N,N-dimethyl-1,4-phenylenediamine.



Scheme S1. The reaction process of N,N-dimethyl-1,4 phenylene diamine and sodium sulfanilate to form MO.

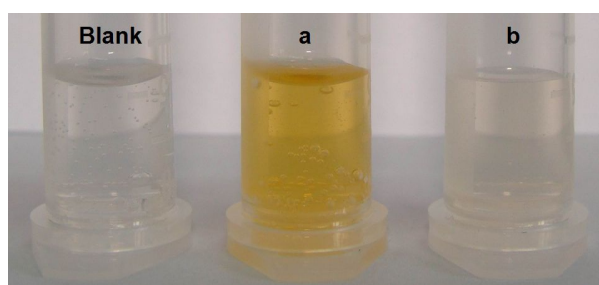


Figure S8. Images of the MO solutions containing NaBH_4 and Ag NPs (Blank) upon the addition of $5 \mu\text{M}$ CTAB before (a) and after saturated with N_2 for 10 min (b).

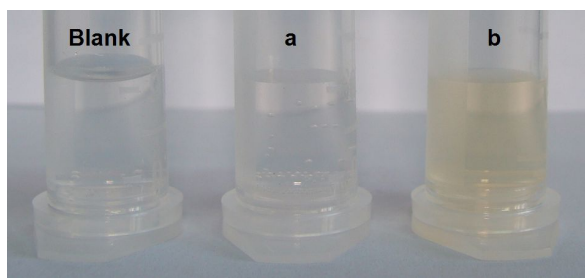


Figure S9. Images of the MO solutions containing NaBH_4 and Ag NPs (Blank) upon the addition of $5 \mu\text{M}$ CTAB after saturated with N_2 for 10 min (a), solution a was saturated with O_2 for 10 min (b).

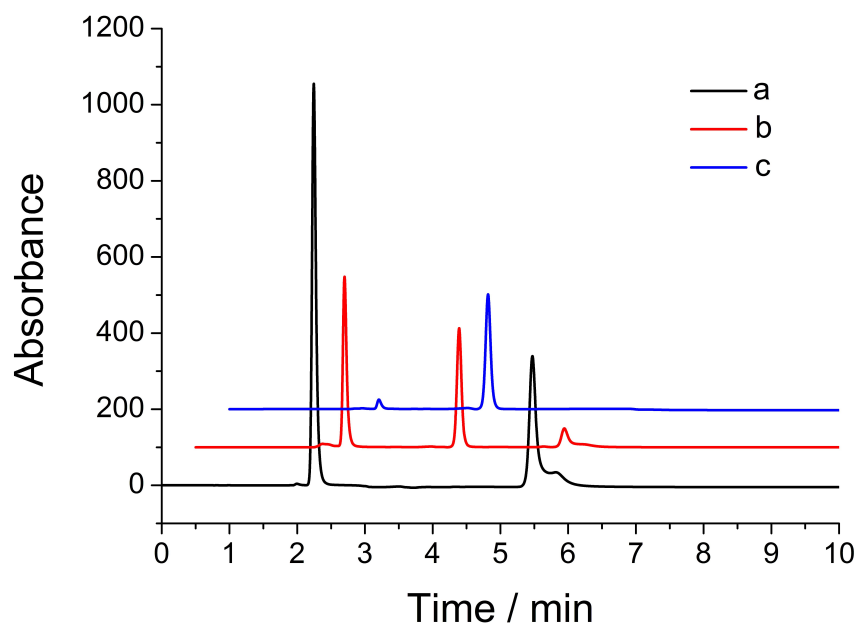


Figure S10. HPLC chromatograms. (a) sodium sulfanilate and N,Ndimethyl-1,4-phenylenediamine solution containing Ag NPs with the addition of CTAB after saturated with O_2 ; (b) sodium sulfanilate and N,Ndimethyl-1,4-phenylenediamine solution containing Ag NPs and NaBO_2 with the addition of CTAB after saturated with O_2 ; (c) 0.25 mM MO solution.