

Electronic Supplementary Information

One-pot Solvent-free Synthesis of Sodium Benzoate from the Oxidation of Benzyl Alcohol over Novel Efficient AuAg/TiO₂ Catalysts

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Catalyst Preparation

Monometallic Au/TiO₂ (commercial Degussa P25) catalysts were prepared by deposition-precipitation method. HAuCl₄·3H₂O was dissolved in 100 mL of deionized water (24.3 mmol/L). Urea was used as precipitation agent, with a gold/urea molar ratio of 1/200. Then 0.6 g of TiO₂, 10 ml of HAuCl₄, 2.92 g of urea and 48 ml of H₂O was added. The mixture was stirred for 2 h at 80°C, during which the pH value gradually increased from 3 to 8. The as-received precipitate was collected by filtration, washed three times with deionized water, and dried in air overnight at 100°C, followed by calcining in air for 4 h at 300°C.

Monometallic Ag/TiO₂ catalysts were prepared by a wet impregnation method. 1.0 g of TiO₂ was added to mixture of 8.5 ml of AgNO₃ (aqueous solution, 47.6 mmol/L) and 85 ml of H₂O, and then the resulting slurry was vigorously stirred at 60°C under atmospheric pressure until the complete evaporation of water. The solid materials were dried at 100°C, followed by calcining in air for 4 h at 500°C.

AuAg/TiO₂ catalysts were synthesized as following. Firstly, Ag/TiO₂ was prepared by impregnation method; then AuAg/TiO₂ was prepared by homogeneous deposition-precipitation method with Ag/TiO₂ as the support. The total metal loading was controlled as 8 wt.%. For the recycling test, the used catalyst was washed with dilute HCl aqueous solution three times, then calcined at 300°C in a muffle oven for 4 h.

Catalyst Characterization

The XRD patterns were recorded on a Bruker D8 advance spectrometer with Cu K α radiation ($\lambda = 0.154$ nm), operated at 40 mA and 40 kV. The XPS spectra were recorded under vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV on a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source using an Mg K α (1253.6 eV) anode and a hemi-spheric energy analyzer. All binding energies were calibrated using contaminant carbon (C 1s = 284.6 eV) as a reference. TEM micrographs were obtained on a JOEL JEM 2010 transmission electron microscope. The UV–Vis. DRS spectra were collected using a Shimadzu UV-2450 spectrophotometer from 200 to 800 nm using BaSO₄ as the background. The gold loadings were determined by the inductively coupled plasma (ICP) method. The ¹H NMR spectrum of the as-prepared product was recorded on a DMX 500. FT-IR spectra were taken on a Nicolet-NEXUS 470 FT-IR spectroscopy.

Activity Measurements

All the experiments were carried out in a magnetically stirred glass flask provided under reflux and a mercury thermometer. Reaction temperature of oil bath was maintained at 200°C. A pre-determined quantity of benzyl alcohol (1.08 g) was added in the reactor, and then AuAg/TiO₂ (0.1 g) and NaOH (0.5 g) was added at atmospheric pressure. This reaction was carried out under solvent-free condition and was maintained at a fixed temperature (200°C) with the stirring rate of 800 rpm for 10 h. After that 12 ml of H₂O was added, and the reaction mixture was centrifuged to remove the solid catalyst. The filtrate was evaporated and crystallized. White solid of sodium benzoate was obtained with purity >99%. In addition, after acidification by HCl aqueous solution until the pH value was gradually decreased to 2.0, the mixture was filtered and then white solid of benzoic acid was obtained with purity >99%. It should be mentioned that, after 10 hours, there was no liquid drop dripped, meaning the benzyl alcohol was completely transformed. Thus, the conversion of benzyl alcohol is 100% and the selectivity is the same as the yield.

The white solid was dried in air, and then weighed.

$$\text{Yield\%} = [\text{n}(\text{benzoic acid})/\text{n}(\text{benzyl alcohol})] * 100\%$$

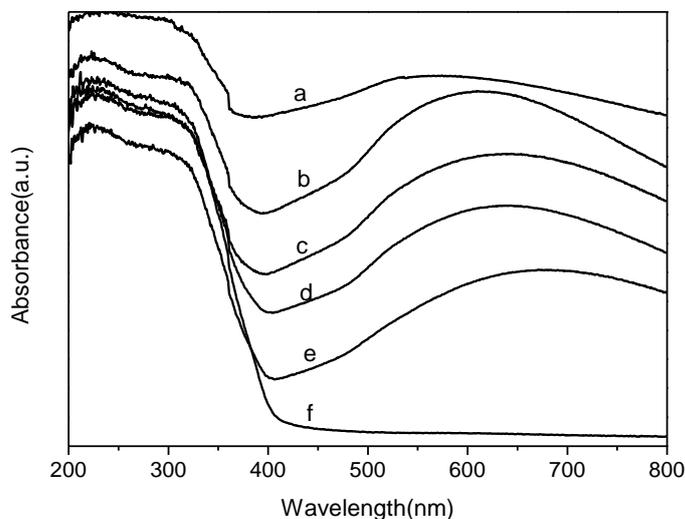


Figure S1 UV-Vis. DRS spectra of AuAg/TiO₂ with different Au/Ag molar ratios: (a)4/0, (b)3/1, (c)2/2, (d)1/3, (e)0.5/3.5, (f)0/4.

Fig. S1 shows the UV-Vis. DRS spectra of AuAg/TiO₂ with different Au/Ag molar ratios. Au-Ag bimetallic catalysts show the absorption peaks due to their surface plasma resonance band. For the monometallic Au/TiO₂, absorption bands with maxima were observed at 525 nm. All Au-Ag bimetallic catalysts show absorption peaks with a red shift compared to the monometallic Au one, and the absorption peaks shift to the higher end with an decrease in Au/Ag molar ratios.

Fig. S2 shows Au 4f_{7/2} and Au 4f_{5/2} of XPS spectra in AuAg/ TiO₂ with different Au/Ag molar ratios. In monometallic Au/TiO₂, the gold exists in the metallic state. In bimetal catalyst there is a negative shift for the Au 4f BE, which suggests that a negative charge is deposited on Au clusters. Fig. S3 shows Ag 3d_{5/2} and 3d_{3/2} XPS spectra in AuAg/ TiO₂ with different Au/Ag molar ratios. In monometallic Ag/TiO₂, the silver exists also in the metallic state. In the bimetallic catalysts there is a also negative shift of the Ag 3d_{5/2} BE, which suggests that a positive charge is deposited on Ag clusters because the BE of Ag 3d_{5/2} shifts negatively if the silver was positively charged. Table S1 lists the surface composition and bulk composition of those catalysts.

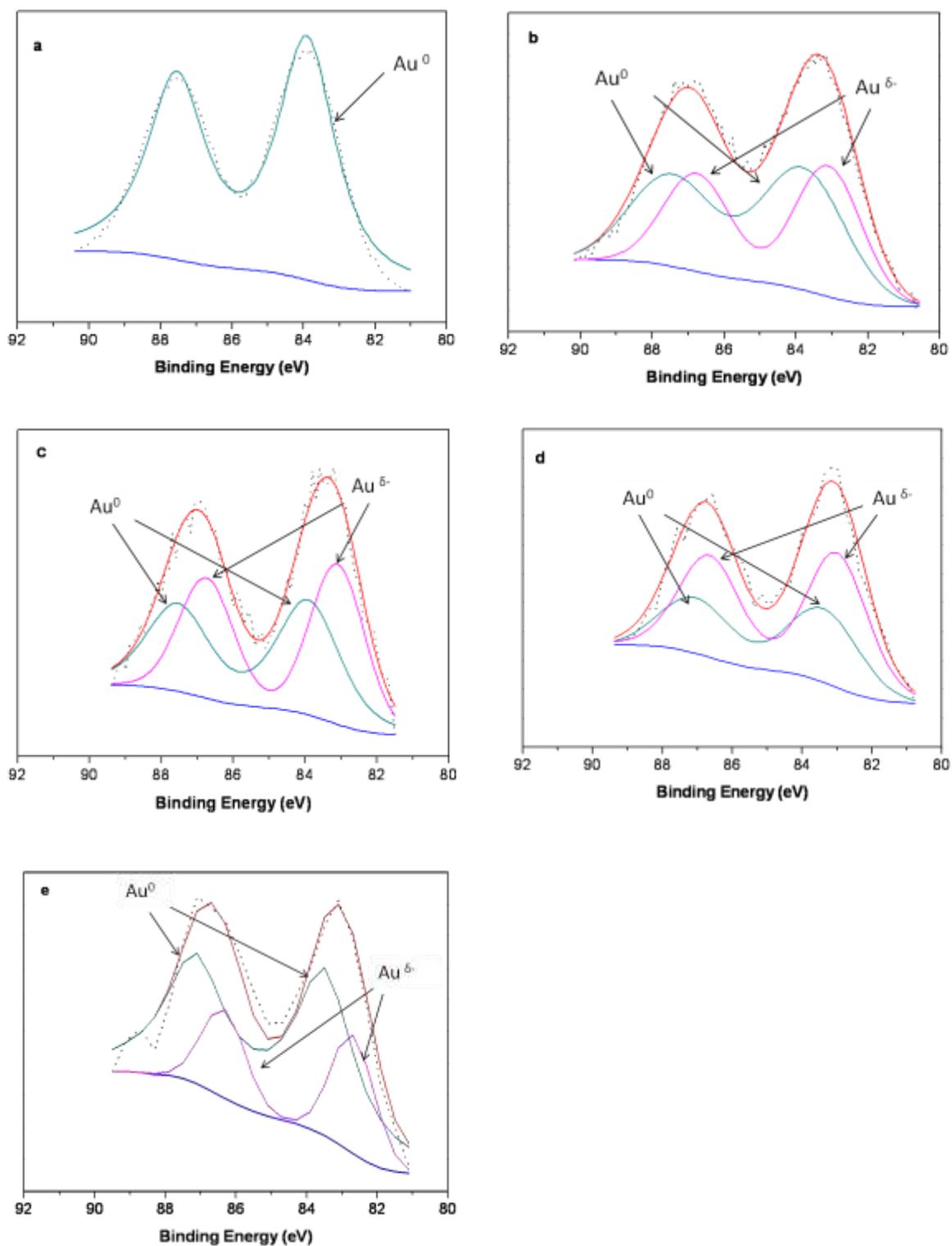


Figure S2. Au_{4f7/2} and Au_{4f5/2} XPS spectra in AuAg/TiO₂ with different Au/Ag molar ratios: (a)4/0; (b)3/1; (c)2/2; (d)1/3; (e)0.5/3.5.

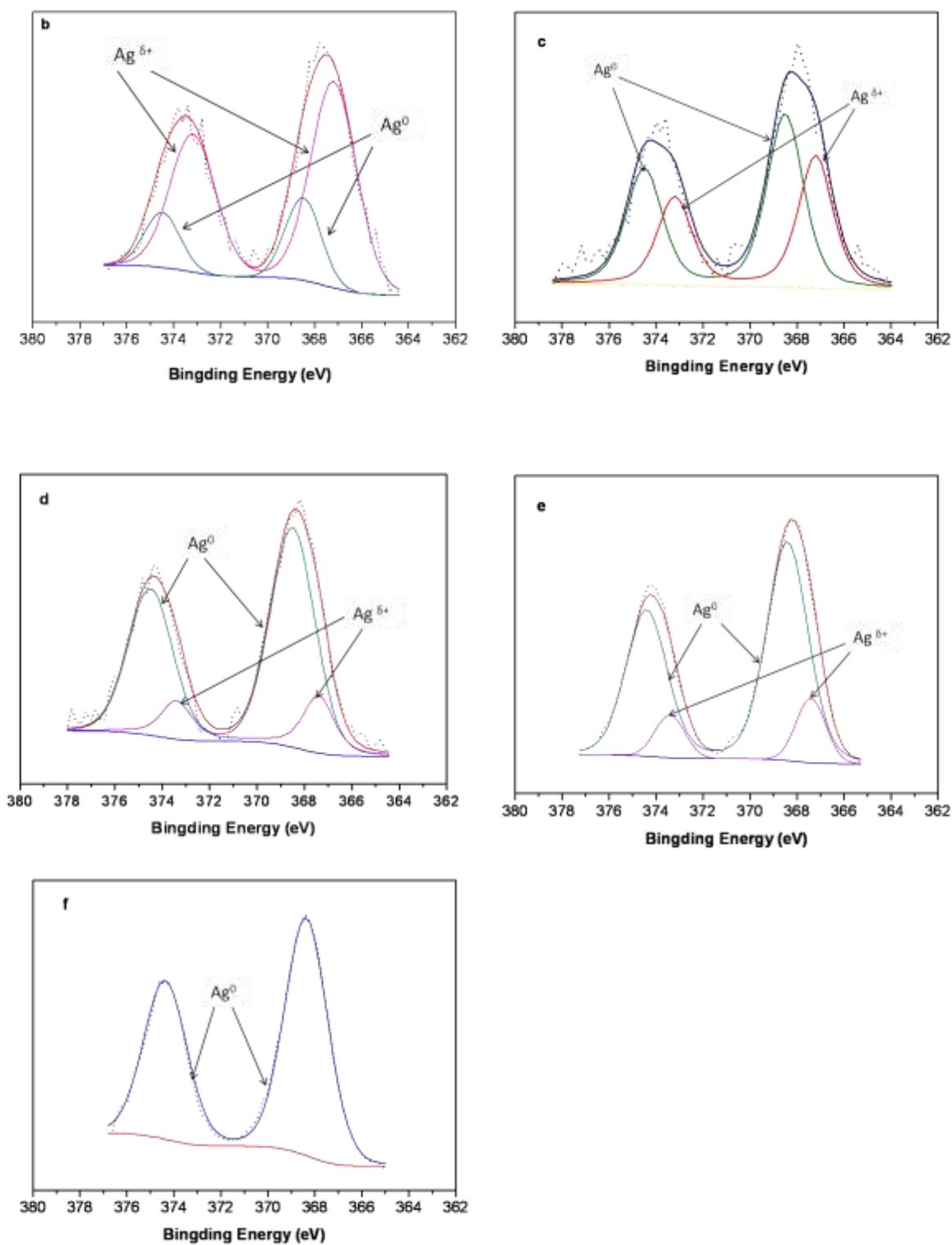


Figure S3. Ag3d 5/2 and 3d3/2 XPS spectra in AuAg/TiO₂ with different Au/Ag molar ratios: (b)3/1; (c)2/2; (d)1/3; (e)0.5/3.5;(f) 0/4.

Table S1. Surface composition and bulk composition of catalyst

Au/Ag (nominal)	Au/Ag (molar) ^a	Au ⁰ /Au ^{δ-} (molar) ^a	Ag ⁰ /Ag ^{δ+} (molar) ^a	Au/Ag (molar) ^b
4/0	∞	∞	-	∞
3/1	2.5	1.0	0.3	3.4
2/2	2.0	0.95	1.3	1.2
1/3	0.50	0.60	4.5	0.36
0/4	0	-	∞	0

a, Determined by ICP;

b, Determined by XPS.

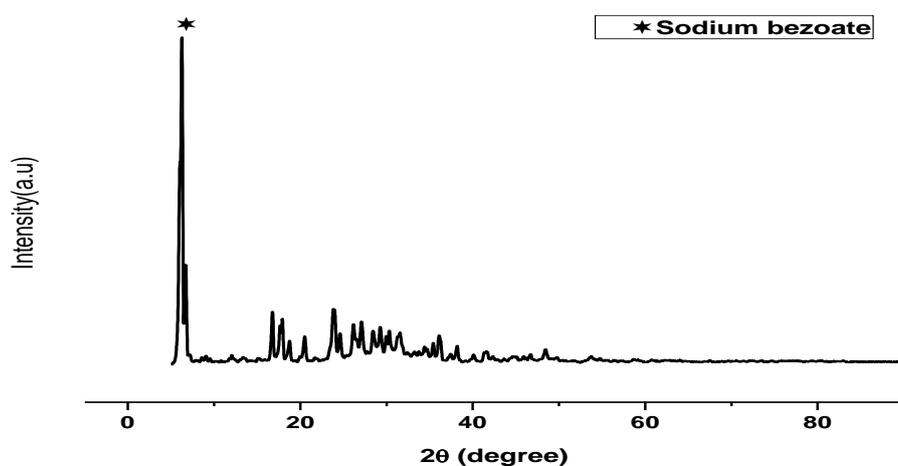


Figure S4 XRD pattern of the product sodium benzoate

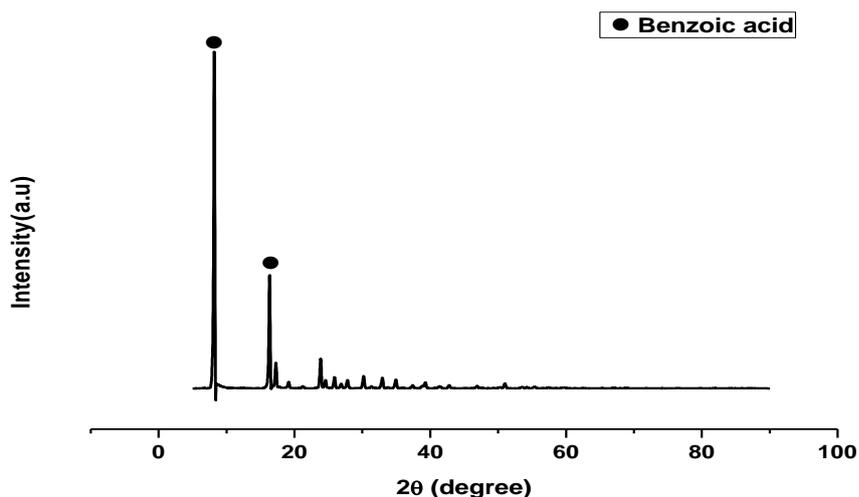


Figure S5 XRD pattern of the product benzoic acid

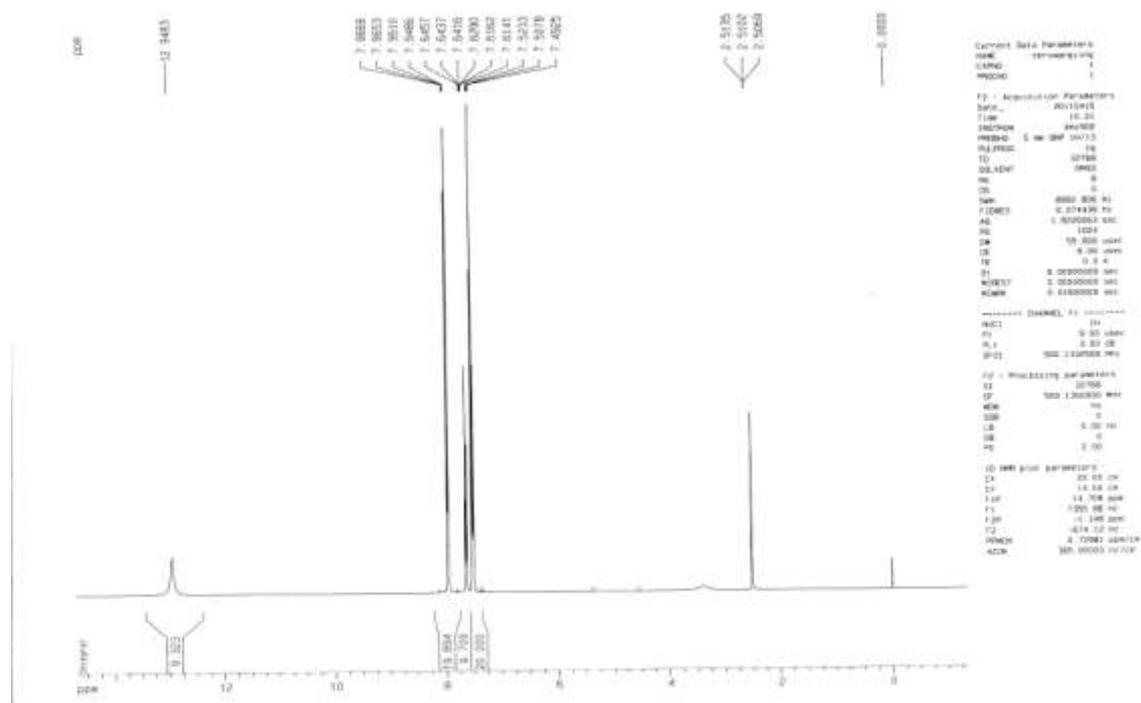


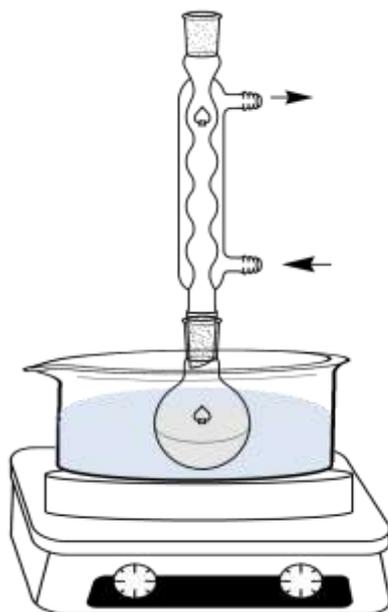
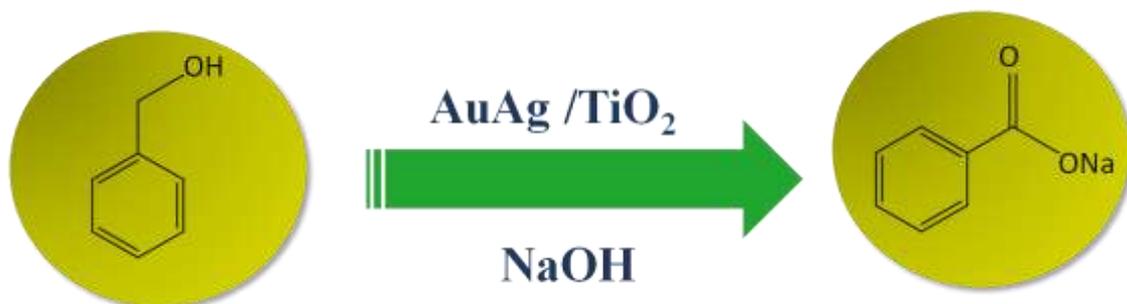
Figure S6 The ¹H NMR spectrum of benzoic acid

Table S2 ¹H NMR results

Sample	δ <chem>c1ccccc1</chem>	δ <chem>—COOH</chem>
benzoic acid	7.9668~7.4925 ppm	12.9483 ppm

Table S3 FT-IR bands of benzoic acid

wave number (cm ⁻¹)	functional groups
3103, 3087	=C-H stretching vibration
1588, 1571, 1519, 1494	stretching vibration of benzene ring
925, 831, 745, 708, 631	C-H bend vibration
3000~2500 (multiple peak)	O-H
935	O-H
1400	C=O
1250	C-O-H



Scheme S1 Diagram of the reaction equipment.