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Stable Bimetallic Au-Ag/TiO_2 Nanopaper for Aerobic Oxidation of Benzyl Alcohol

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Experimental Section

Synthesis of TiO_2 nanobelts. TiO_2 nanobelts were synthesized using a typical hydrothermal process in concentrated NaOH aqueous solution.[1,2] Commercial titanium dioxide (P25) was used as precursor. 0.1 g P25 mixed with 20 mL 10 M NaOH aqueous solution, followed by hydrothermal treatment at 200 °C in a 60 mL Teflon-lined autoclave for 72 h. The treated product was washed thoroughly with deionized water, followed by a filtration. Then the sodium titanate nanobelts were obtained. The nanobelts were immersed in 0.1 M HCl for 24 h, and were then washed thoroughly with deionized water to get the hydrogen titanate nanobelts. Finally, we got the TiO_2 nanobelts by annealing the hydrogen titanate nanobelts at 600 °C for 2 h.

Preparation of Au-Ag TiO_2-NBs structure. The Ag/TiO_2-NBs was prepared via photodeposition using a 500W Xe lamp. 0.05 g $AgNO_3$ and 0.1 g nanobelts were dispersed severally in 20 mL ethanol, and irradiated by the Xe lamp for 2 min under vigorous magnetic stirring. The resultant products were washed with ethanol and deionized water for several times, then were re-dispersed in deionized water for further usage.

For the preparation of Au/TiO_2-NBs, 0.1 g TiO_2-NBs and 1 mL 0.486 M $HAuCl_4$ (99.9%, Aldrich aqueous) were added into the mixture of 0.02 M sodium citrate and 0.1 M NaOH solution, and irradiated by Xe lamp for 2 min under vigorous magnetic stirring. The resultant product was thoroughly washed with deionized water and then dried.

The bimetallic Au-Ag/TiO_2-NBs nanostructure was obtained through a typical galvanic replacement reaction between photodeposited Ag/TiO_2-NBs and aqueous $HAuCl_4$ solution.[3] In a typical procedure, 5 mL of as-obtained dispersion of Ag/TiO_2-NBs sample was put into a 50 mL flask containing 20 mL deionized water. This diluted dispersion of Ag/TiO_2-NBs was then

refluxed for 10 min before a specific volume of $HAuCl_4$ solution (10 g/L) was added dropwise in dark. The mixture was refluxed until its color became stable. Vigorous magnetic stirring was maintained during entire process. The solution was cooled to room temperature, transferred into a tube and centrifuged at 10 000 rpm for 3 min. The resultant product was washed with ammonia water and hot deionized water for several times and the dried.

The preparation of Au-Ag/TiO_2 nanopaper. The nanopaper based on TiO_2-NBs loaded with metal particles was fabricated via a modified paper-making process.[1]

Characterization. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were carried out with a JOEL JEM 2100 microscope. HITACHI S-4800 field emission scanning electron microscope (FE-SEM) was used to characterize the morphologies. X-ray photoelectron spectroscopy (XPS) data were obtained on a Thermo ESCALAB 210 X-ray photoelectron spectrometer. The binding energy was determined utilizing C1s spectrum as reference at 285.0 eV. The UV absorption spectra were collected by use of a UV spectrophotometer (UV-2400PC, Shimadzu) with barium sulfate as a standard for the background correction. The metal loadings and the Au/Ag molar ratios of various Au-Ag/TiO_2-NBs samples were determined by inductively coupled plasma spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

Catalytic reaction tests. The gas-phase selective oxidation of benzyl alcohol was carried out with a continuous flow fixed-bed microreactor (8 mm i.d.). In the catalytic test, ten pieces of nanopaper catalysts (8 mm in diameter and total weight of 40 mg) were stacked vertically on a Teflon ring fixed to the inner wall of the quartz tubular reactor. The gas streams (44 mL/min, total space velocity of 1.32×10^5 h^{-1}) were supplied by mass flow controllers and benzyl alcohol (20

μL/min, WHSV of 63 h^{-1}) was fed continuously through a syringe pump. Liquid vaporization occurred in the preheater prior to the catalytic reaction bed. The catalytic reaction was carried out with inlet O_2/N_2 ratio of 21:79 and O_2/alcohol molar ratio of 0.6 at atmospheric pressure and at the temperature of 240°C. The condensable reaction products and the unreacted benzyl alcohol were cooled and collected using a cold trap (0 °C) and then analyzed with a Shimadzu Type GC-14C equipped with a flame ionization detector, using a SGE-30QC2/AC5 capillary column and N_2 as carrier gas. 1-Butanol was employed as an internal standard. GC-MS (Thermo Trace GC Ultra DSQ) was also employed to determine the reaction products.

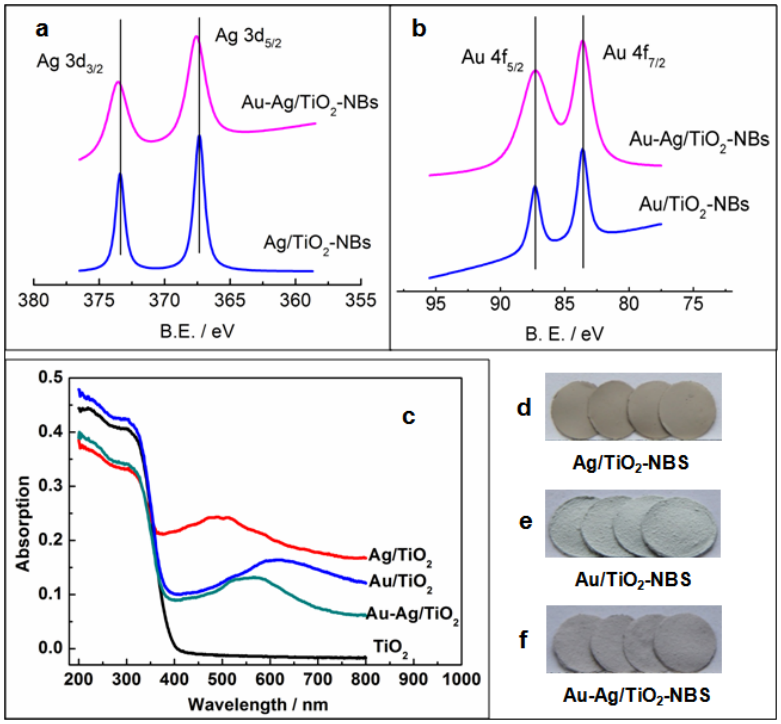

Fig. S1 Ag 3d XPS spectra (a) in Ag/TiO_2-NBs and Au-Ag/TiO_2-NBs; (b) Au 4f XPS spectra in Au/TiO_2-NBs and Au-Ag/TiO_2-NBs. (c) UV-vis diffuse reflectance spectra of TiO_2-NBs, Ag/TiO_2-NBs, Au/TiO_2-NBs, Au-Ag/TiO_2-NBs; (d), (e) and (f) are digital pictures of corresponding nanopapers.

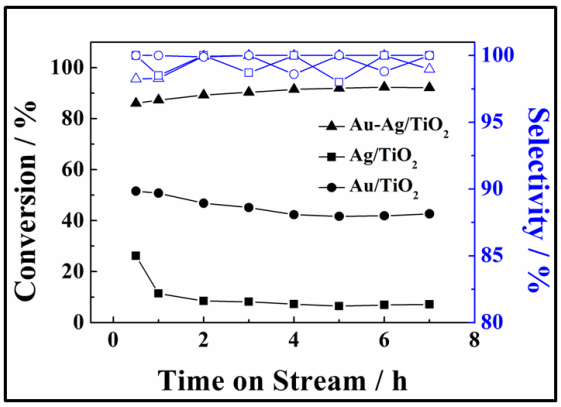

Fig. S2 The comparison of benzyl alcohol oxidation over nanopaper catalysts composed of Au/TiO_2-NBs, Ag/TiO_2-NBs and Au-Ag/TiO_2-NBs.

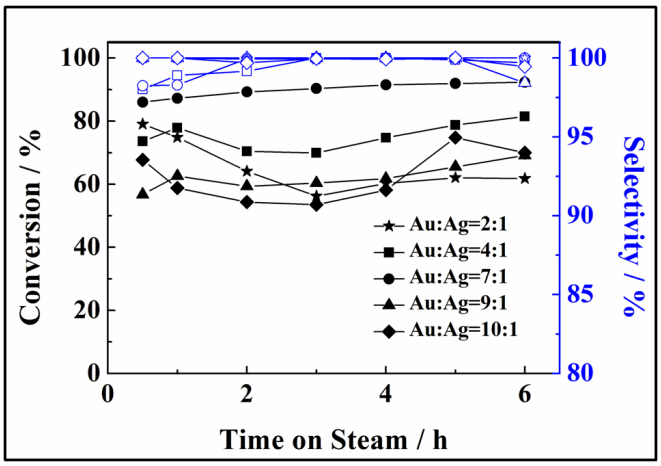

Fig. S3 The benzyl alcohol oxidation over Au-Ag/TiO_2 nanoper catalysts with different Au/Ag molar ratios. A metal loading of 2.44 wt.% (Au) and 0.205 wt.% (Ag) for the Au-Ag/TiO_2-NBs sample with Au/Ag molar ratios of 7:1 was determined by ICP analysis.

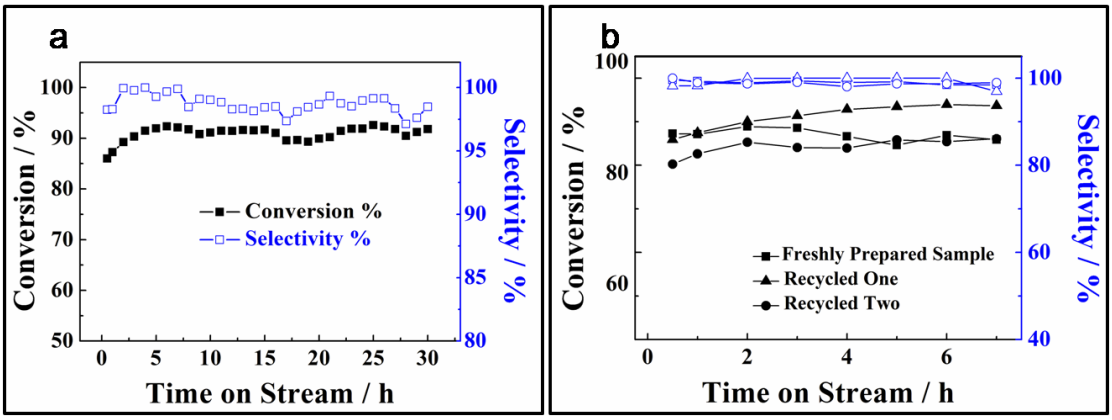

Fig. S4 The stability test of Au-Ag/TiO_2-NBs catalyst at 240°C. The catalysts tested in recycled one (b) is the ones underwent the 30 h stable reaction (a) and followed by being stored for a week, then they were stored for another week and reused in recycled two (b).

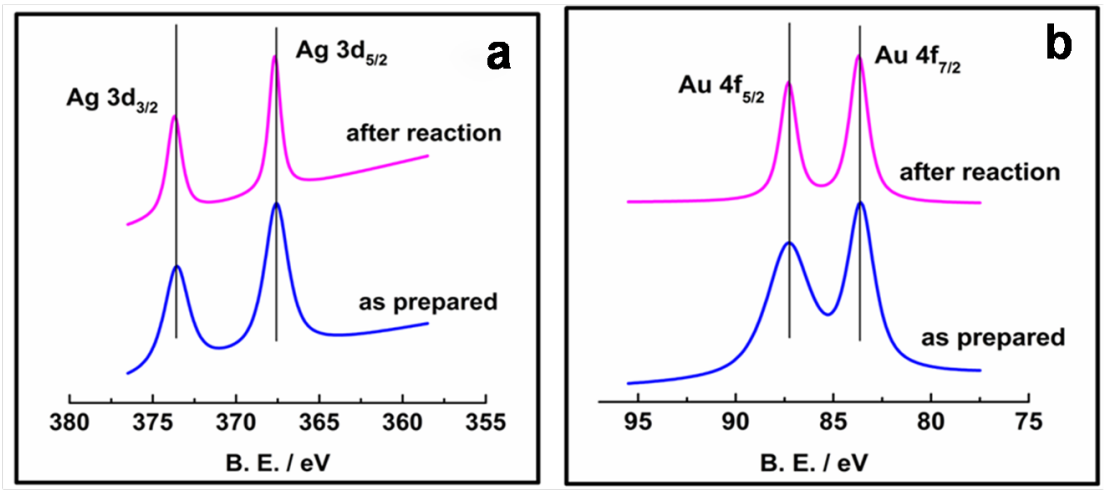

Fig. S5 The XPS spectra of Ag (g) and Au in the Au-Ag/TiO_2-NBs nanopaper catalysts before and after reaction.

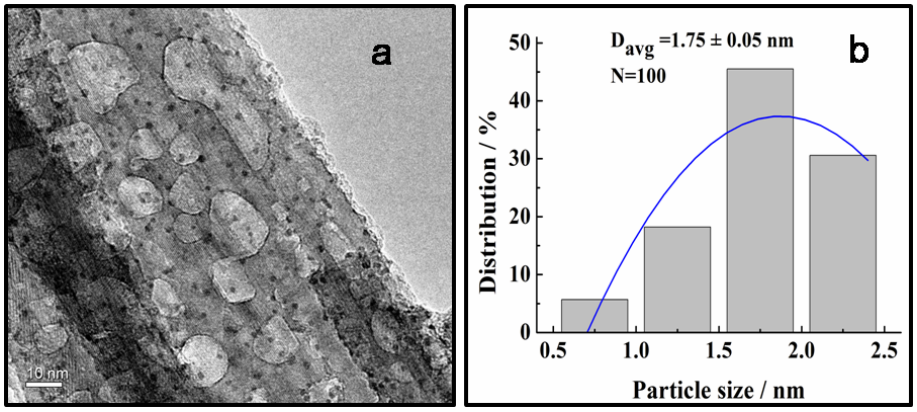

Fig. S6 TEM image (a) and corresponding particle size distribution (b) of Au-Ag/TiO2-NBs calcined at a high temperature of 500 °C for 2 h in N_2.

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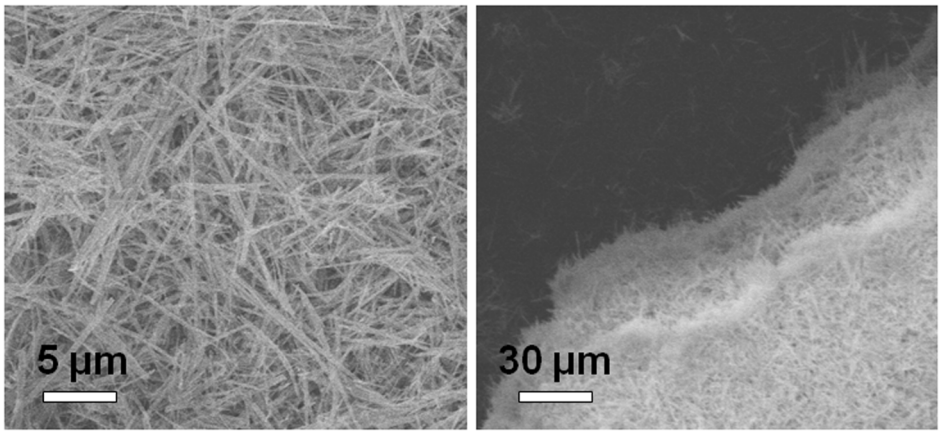

Fig. S7 Typical SEM images of Au-Ag/TiO_2-NBs nanopaper catalyst after aerobic oxidation reaction of benzyl alcohol.

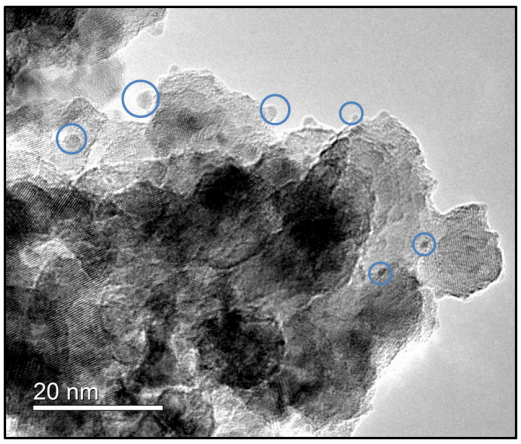

Fig. S8 Representative TEM image of Ag/P25 prepared with the same photodeposited conditions as that of Ag/TiO_2-NBs. The obtained Ag particles sizes are widely distributed from 1 to 5 nm.

Notes and references

1 Y. M. Wang, G. J. Du, H. Liu, D. Liu, S. B. Qin, N. Wang, C. G. Hu, X. T. Tao, J. Jiao, J. Y. Wang, Z. L. Wang, *Adv. Funct. Mater.,* 2008, **18**, 1131.

2 W. J. Zhou, H. Liu, J. Y. Wang, D. Liu, G. J. Du, J. J. Cui, *ACS Appl. Mater. Interfaces,* 2010, **2**, 2385.

3 Y. G. Sun, Y. N. Xia, *Nano Lett.,* 2003, **3**, 1569.