Supplementary Information (SI)

S_N1 Mechanism Directed Synthesis of Oxide Nanoparticles

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Experimental details:

Materials

$SnCl_4 \cdot 5H_2O$, $SiCl_4$, $TiCl_4$, $FeCl_3$, $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, Zn(II) acetylacetonate ($Zn(acac)_2 \cdot xH_2O$), $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, benzyl alcohol, n-octanol, n-butanol, n-pentanol, n-hexanol, cyclohexanol, ethanol, acetone, dichloromethane, N-methyl-pyrrolidone (NMP), N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich, $AlCl_3 \cdot 6H_2O$, $SbCl_3$, $SnCl_2 \cdot 2H_2O$ and dodecylamine were purchased from Shanghai Chemical Reagent Company. All chemicals were used as received without further purification except specified.

Synthesis procedures

The synthesis of TiO_2 nanoparticles in benzyl alcohol: In a typical synthesis, 0.5ml $TiCl_4$ was rapidly added into 30ml glass bottle containing 5ml dichloromethane under stirring, and then the glass bottle was sealed until $TiCl_4$ was dissolved completely to form colorless transparent solution. Subsequently, 10ml benzyl alcohol was added slowly into glass bottle under stirring to obtain yellow transparent solution. Then as-prepared solution was transferred into 120^oC oven for 12h. White products were diluted by ethanol and collected by centrifugation.

The synthesis of TiO_2 nanoparticles in the mixed solution of benzyl alcohol and N-methyl-pyrrolidone (NMP): In a typical synthesis, 1ml $TiCl_4$ was rapidly added into 30ml glass bottle containing 10ml NMP under stirring, and then the glass bottle was sealed until $TiCl_4$ was dissolved completely and form homogeneous transparent solution. Subsequently, 10ml benzyl alcohol was added into glass bottle under stirring to obtain yellow transparent solution. Then as-prepared solution was transferred into 120^{o}C oven for 12h. White products were diluted by ethanol and collected by centrifugation.

Amine-assisted synthesis of TiO_2 nanoparticles: In a typical synthesis, 0.5ml $TiCl_4$ was rapidly added into 30ml glass bottle containing 5ml dichloromethane under stirring, and then the glass bottle was sealed by ground glass stopper until $TiCl_4$ was dissolved completely and form colorless transparent solution. Subsequently, 10ml benzyl alcohol was added slowly into glass bottle under stirring to obtain yellow transparent solution. Then 2.5ml dodecylamine was added under stirring to form transparent solution. As-prepared solution was transferred into 120^{o}C oven for 12h. White products were diluted by ethanol and collected by centrifugation.

The synthesis of SnO_2 nanoparticles: In a typical synthesis, 0.5g $SnCl_4{\cdot}5H_2O$ was dissolved by 10ml benzyl alcohol in 30ml glass bottle with ground glass stopper to form transparent solution. Then the solution was transferred into 120^{o}C oven for 12h. The solution was diluted by ethanol and white products were collected by centrifugation.

The synthesis of Fe_2O_3 nanoparticles: In a typical synthesis, 50mg $FeCl_3$ was dissolved by 10ml benzyl alcohol in 30ml glass bottle with ground glass stopper to form yellow transparent solution. Then the solution was transferred into 120^{o}C oven for 12h. The solution was diluted by ethanol and red products were collected by centrifugation.

The synthesis of Sb_2O_5 nanoparticles: In a typical synthesis, 50mg $SbCl_3$ was dissolved by 10ml benzyl alcohol in 30ml glass bottle with ground glass stopper to form colorless transparent solution. Then the solution was transferred into 150^{o}C oven

for 24h. The solution was diluted by ethanol and white products were collected by centrifugation.

The synthesis of ZnO nanoparticles: In a typical synthesis, 0.25g anhydrous $ZnCl_2$ was dissolved by 10ml benzyl alcohol in 30ml glass bottle to form colorless transparent solution. Then 0.5ml dodecylamine was added into the solution. Subsequently, the solution was transferred into 180^{o}C oven for 12h. The solution was diluted by ethanol and white products were collected by centrifugation.

The synthesis of Mn_3O_4 nanoparticles: In a typical synthesis, 0.25g $MnCl_2$ (from $MnCl_2 \cdot 4H_2O$, dehydrated at 220^{o}C for 5h before use) was dissolved by 10ml benzyl alcohol in 30ml glass bottle with ground glass stopper to form transparent solution. Then 2ml dodecylamine was added under stirring to form transparent solution. Subsequently, the solution was transferred into 160^{o}C oven for 12h. The solution was diluted by ethanol and brownish black products were collected by centrifugation.

The synthesis of Co_3O_4 nanoparticles: In a typical synthesis, 0.25g $CoCl_2$ (from $CoCl_2 \cdot 6H_2O$, dehydrated at 220^{o}C for 8h before use) was dissolved by the mixed solution of 5ml benzyl alcohol and 5ml dodecylamine in 30ml glass bottle with ground glass stopper to form transparent solution. Subsequently, the solution was transferred into 160^{o}C oven for 12h. The solution was diluted by ethanol and black products were collected by centrifugation.

The synthesis of Sb-doped SnO_2 nanoparticles: In a typical synthesis, 0.475g $SnCl_2 \cdot 2H_2O$ was dissolved into 10ml benzyl alcohol, and then 0.025g $SbCl_3$ was added under stirring to form transparent solution. Subsequently, the solution was transferred into 150^{o}C oven for 6h. The solution was diluted by ethanol and white products were collected by centrifugation.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Philips X'pert diffractometer with Cu Kα radiation (λ=1.54178Å). The morphology and structure of the samples were investigated by scanning electron microscopy (JEOL JSM-820), field emission scanning electron microscopy (FE-SEM, JEOL JSM-6335F) and transmission

electron microscopy (Philips FEG CM20) with an accelerating voltage of 200kV. High-resolution transmission electron microscope (HRTEM) was performed on a JEOL-2010 transmission electron microscope. The compositions of liquid products in benzyl alcohol solution were detected by gas chromatography-mass spectrometry (GC-MS) (HP 5973 Mass Selective Detector and HP 6890 series GC system) and electrospray ionization mass spectrometry (ESI-MS) (PE SCIEX API 150EX). Energy-dispersive X-ray spectrometry was carried out by using INCA system. Photoluminescence (PL) spectra were measured by spectrofluorometer (Fluormax-4).

Measurement of photocatalytic performance

The photocatalytic performance of as-prepared ZnO sample was evaluated by the degradation of methylene blue (MB) in an aqueous solution under UV light irradiation. A 35W UV lamp (λ = 365 nm, ML-3500S/F, Spectroline) was used as UV light source. As-prepared ZnO products were centrifuged and washed three times with ethanol, and dried for 24h at 60^{o}C, and then directly used as catalyst without any further heat treatment. 30 mg ZnO powders was added into 60 ml aqueous solution of MB (4.0×10^{-5} M) and sonicated for 2 mins to achieve homogeneous dispersion of ZnO in the solution. Then The mixed suspensions were magnetically stirred for 0.5 h in the dark to reach an adsorption–desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to UV irradiation. At given time intervals of 10 min, 2 ml of the mixed suspensions were extracted and centrifuged to remove the photocatalyst. The degradation process was monitored by measuring the absorption of MB in the filtrate using a UV-vis absorption spectrophotometer (Agilent 8453, UV-AG-2). The photocatalytic performance of P25 and the degradation process of MB in the absence of photocatalyst were measured by the same way mentioned above.

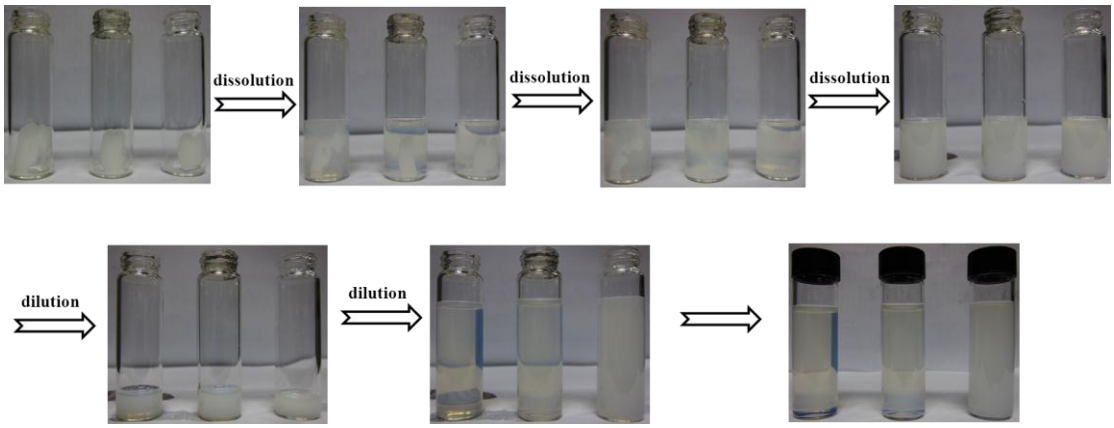

Fig. S1 The dissolution process of TiO_2 synthesized in the mixed solvent n-pentanol/benzyl alcohol and the dispersion in different solvents: DMF (left); Water (middle); Ethanol (right).

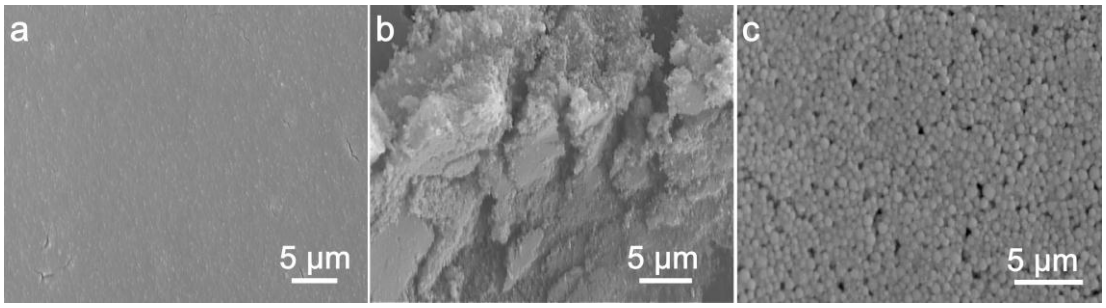

Fig. S2 SEM images of TiO_2 partcles synthesized in different alcoholic solvents at 140^{o}C by using $TiCl_4$ as the precusor, a) benzyl alcohol; b) cyclohexanol; c) n-octanol.

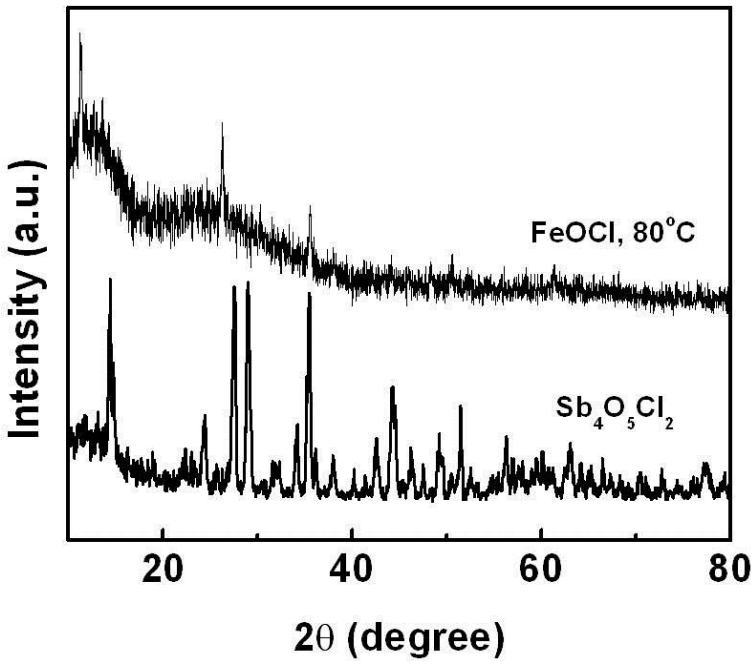

Fig. S3 XRD patterns of FeOCl prepared by the reaction of $FeCl_3$ and benzyl alcohol at 80°C, and $Sb_4O_5Cl_2$ synthesized through the reaction between $SbCl_3$ and benzyl alcohol in high $SbCl_3$ concentration, such as 0.2M.

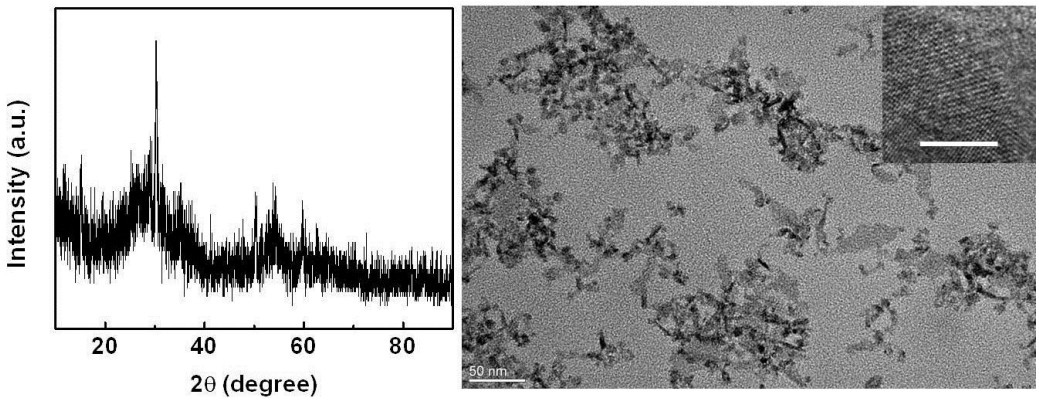

Fig. S4 XRD patterns of Sb_2O_5 prepared by the reaction of $SbCl_3$ and benzyl alcohol at 180°C for 24h, and corresponding TEM and HRTEM images of Sb_2O_5 nanoparticles, insert: scale bar is 5nm.

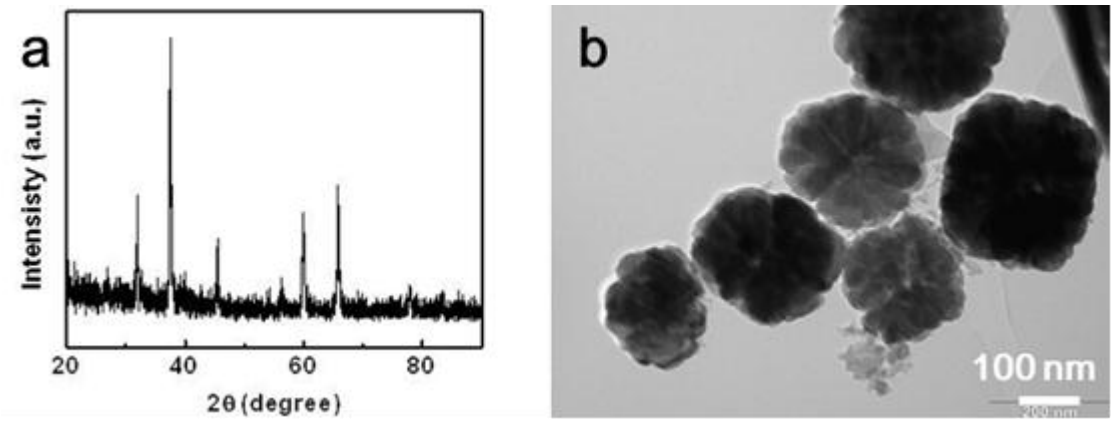

Fig. S5 XRD pattern and TEM image of Co_3O_4 particles prepared by the reaction of $CoCl_2$ and benzyl alcohol under the assistance of dodecylamine at 160°C for 12h.

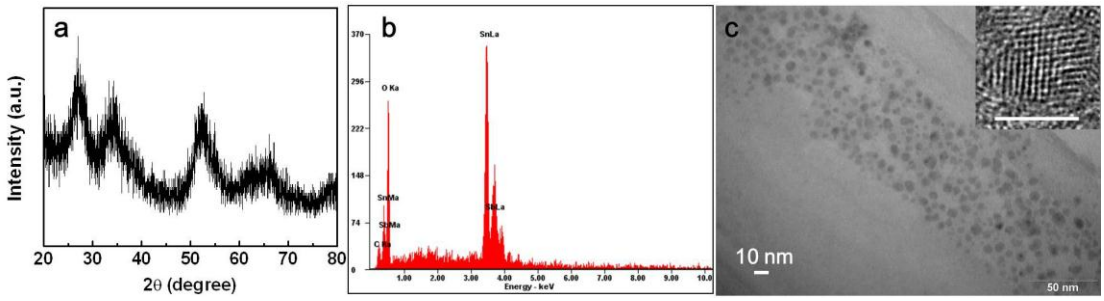

Fig. S6 XRD patterns, EDX results and corresponding TEM and HRTEM images of $Sb_{0.05}Sn_{0.95}O_2$, insert: scale bar is 5nm.

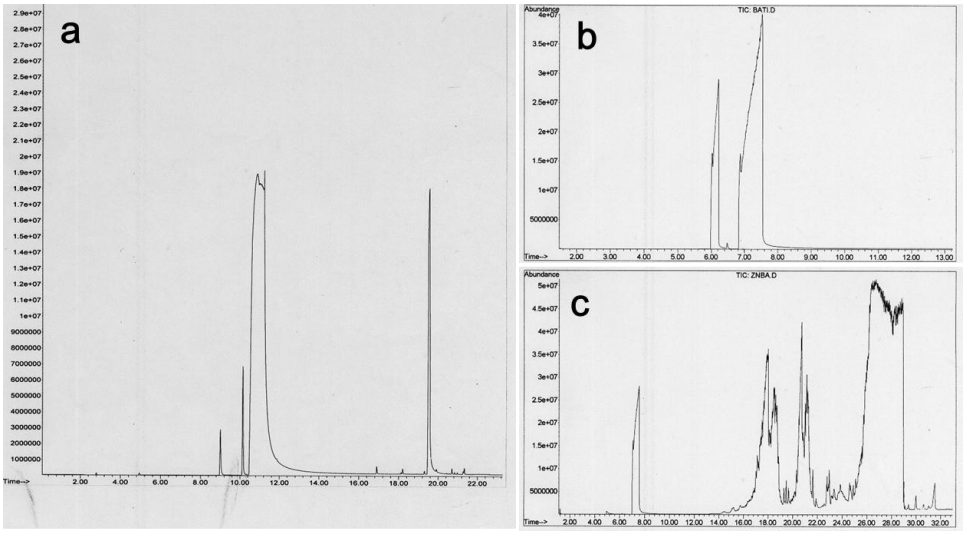

Fig. S7. GC-Mass spectra that indicate the compositions of liquid products in the reactions of benzyl alcohol and metal chlorides, a) FeCl3/benzyl alchol, the peaks from left to right corresponded to benzaldehyde, benzyl chloride, benzyl alcohol, benzyl ether respectively; b) TiCl4/benzyl alcohol, the peaks from left to right corrsponded to benzyl chlorides and benzyl alcohol; c) $ZnCl_2$/benzyl alcohol/dodecylamine, the peaks corresponded to benzyl alcohol and various benzyl amines.

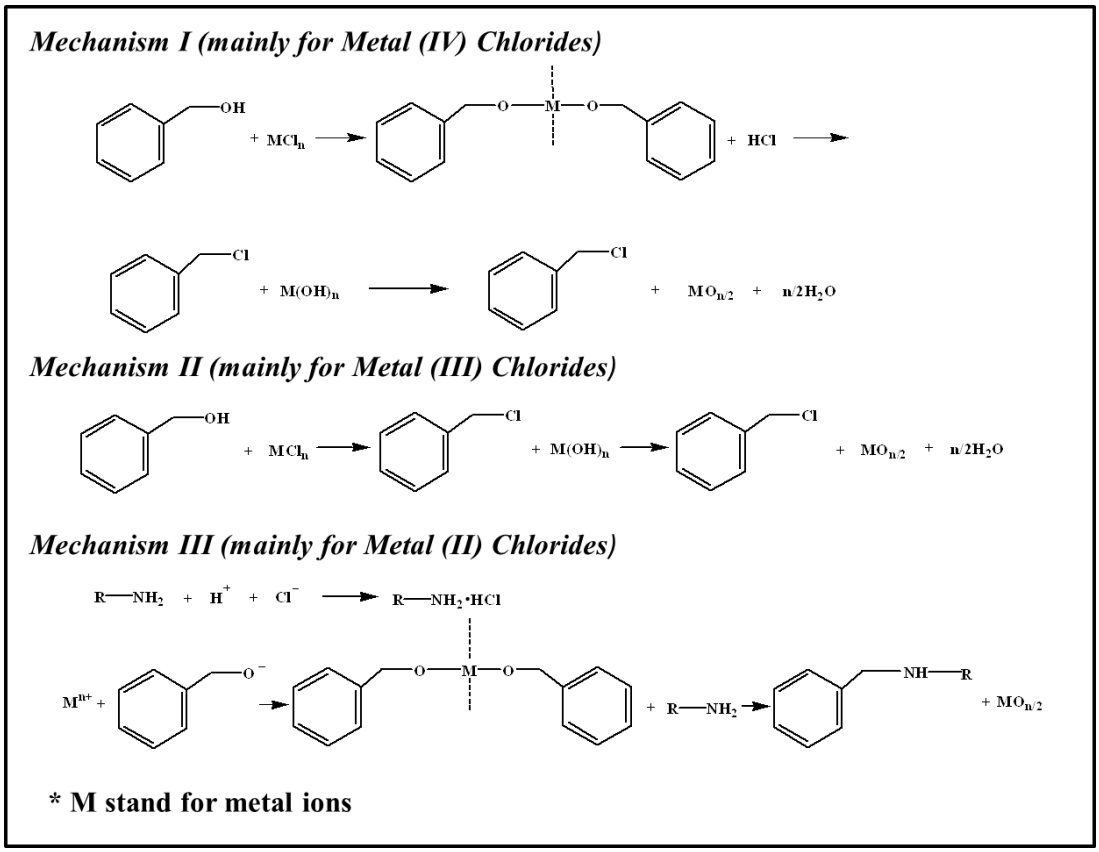

Fig. S8 three proposed reaction types between benzyl alcohol and metal chlorides with different valence for the synthesis of oxides nanoparticles.

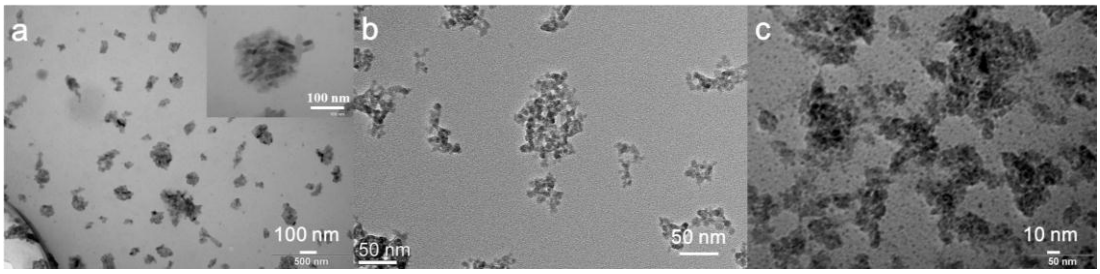

Fig. S9. TEM images of the aggregates of different oxides synthsized in benzyl alcohol, a) ZnO nanoparticles synthesized by the reaction of $Zn(acac)_2$ and benzyl alcohol; b) Sb_2O_5 nanoparticles; c) TiO_2 nanoparticles.