Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Enhancing photocatalytic efficiency of TiO_2 nanopowder for H_2 production by using non-noble transition metal co-catalysts

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1. General

$Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, K_2PtCl_6, $NaBH_4$, triethanolamine (TEOA), HBF_4 and anatase TiO_2 nanopowder (particle size <25nm, 99.7% trace metals basis, surface area 200-220 $m^2.g^{-1}$) were purchased from Sigma Aldrich Co. and used as received without any purification.

TEM was carried out using a JEOL 2100F microscope with a field emission gun and the acceleration voltage for microscopes was 200 kV. Thin film X-ray diffraction (XRD) studies were carried out on a Shimadzu LabX-XRD-6000 X-ray diffraction instrument using Cu K_α radiation. TiO_2 films were prepared by spin-coating a dispersion of TiO_2 in ethanol on glass slides. Diffuse reflectance UV-vis spectra of TiO_2 films were performed employing Lambda 750S UV-Vis spectrometer (Perkin Elmer) and using $BaSO_4$ reference. X-ray photoelectron spectroscopy (XPS) characterization were measured in an ultrahigh vacuum (UHV) VG ESCALAB 220i-XL system equipped with a monochromatic Al Kα (1486.6 eV) source and a concentric hemispherical energy analyzer. The background pressure in the analysis chamber was in the 10^{-10} Torr range. The analyzer was calibrated with pure gold, silver and copper (polycrystalline) standard samples by setting the Au $4f_{7/2}$, Ag $3d_{5/2}$ and Cu $2p_{3/2}$ peaks at binding energies of 83.98 ± 0.02 eV, 368.26 ± 0.02 eV and 932.67 ± 0.02 eV. The survey and high energy resolution scans were recorded with pass energy of 150 eV and 10 eV, respectively.

2. Preparation of TiO_2/M x%

In a typical preparation procedure, TiO_2 nanopowder (1.26 mmol, 100 mg) was dispersed into 50 mL deionized water by sonication for 1h. This suspension was then stirred under nitrogen flux for 30 min. for saturation before adding of predetermined volume of 0.03M $Co(NO_3)_2$, 0.03M $Ni(NO_3)_2$, or 0.03M K_2PtCl_6 solution. Reduction of the cations to

metals was achieved by adding 50 equivalents of freshly prepared 0.156M $NaBH_4$ solution under a nitrogen atmosphere. The suspension was continuously stirred at RT for 2h. The resulting modified TiO_2 nanopowder was then collected from suspension by centrifugation, washed 5 times with DI water and then 3 times with ethanol before drying under vacuum at RT for 1h.

3. Preparation of Co, Ni, and Pt electrodes and evaluation electro-catalytic activities of these electrodes for hydrogen evolution reaction (HER)

Co, Ni electrodes were prepared following electrodeposition process reported by Soto et al[1] with modification. Deposition bath contains 10mM of $Co(NO_3)_2$ or $Ni(NO_3)_2$ in 0.5M NH_4Cl electrolyte solution (pH5.4). A conventional three electrode configuration was employed with Pt mesh counter electrode, Ag/AgCl (CHI Instrument) reference electrode, and carbon glassy working electrode ($0.071cm^2$, CHI Instrument). Carbon electrode was first polished with aluminum powder (0.05 μm) and washed several times via ultra-sonication in deionized water. Electrodeposition of Co, Ni metal films on carbon electrode was performed by chrono-amperometric deposition at -1.0V *vs.* Ag/AgCl. After passing 0.1 C through carbon electrode, a bright metal film was obtained on carbon electrode.

Platinum black film was obtained on carbon electrode after passing 0.1C for electrodeposition using 1mM K_2PtCl_6 solution in 0.5M NH_4Cl at -0.65V. These conditions were chosen to minimize catalytic reduction of proton into H_2 during platinum deposition.

Electrocatalytic activities for HER of freshly prepared Co, Ni, Pt electrodes were tested using de-aerated pH7 0.1M potassium phosphate buffer electrolyte solution. Three electrode configuration described this above was employed. Linear sweep voltammetry, sweep rate of $2mV.s^{-1}$, was performed on these electrodes with cathodic scan direction.

4. Hydrogen Photoevolution Experiments

A 40mL schlenk flask (glass stopcock, Ref. Z515981 purchased from Sigma Aldrich) was loaded with 18 mg of TiO_2 nanopowders photocatalyst and 20 mL of pH7 triethanolamine buffer solution (TEOA, 1M). This suspension was sonicated for 30 min. and then saturated by a nitrogen flux for 1h. Irradiation was performed by using Halogen lamp (Dolan-Jenner Fiber-Lite Illuminator MI-150, 150W). The light source was kept 15cm from schlenk flask. The intensity at the reaction vessel was 150 $mW.cm^{-2}$. Two small fans were employed to keep reaction temperature of ca. 30°C during photocatalytic essay experiments. Gas from head cap of the schlenk was manually sampled every hour and analyzed by GC. Hydrogen produced was calculated following the calibration curves performed on the GC using the 5%H_2/Ar and 1%H_2/Ar mixtures.

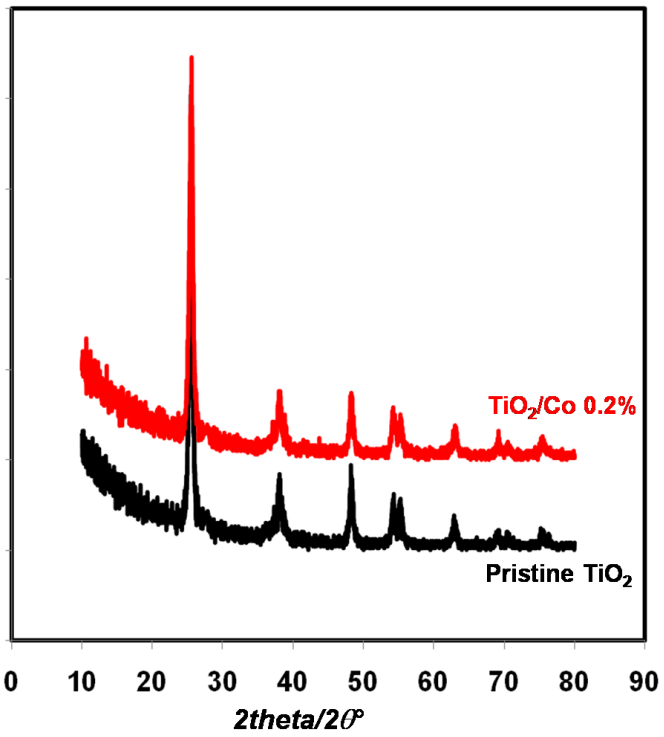

Figure S1: *XRD of pristine TiO_2 and TiO_2/Co 0.2%*

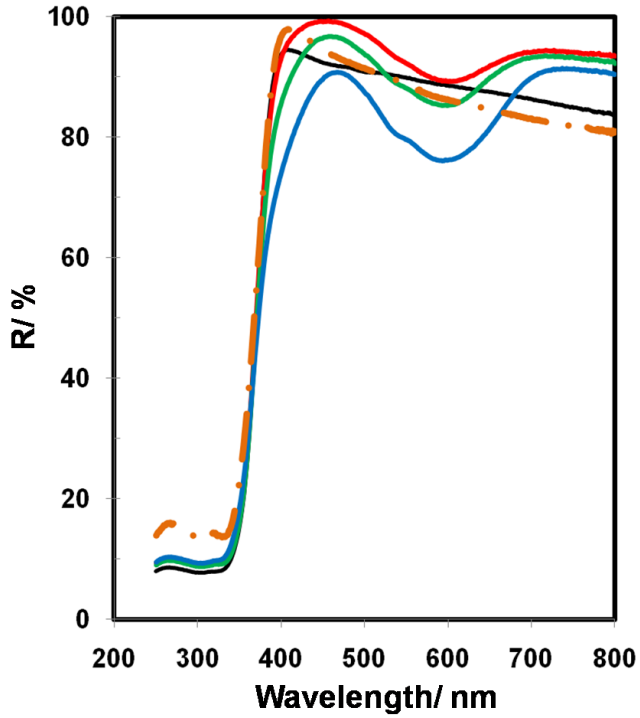

Figure S2: *Diffuse reflectance UV-vis spectra of TiO_2 films: Pristine TiO_2 (black), TiO_2/Ni 0.5% (dash-point, orange), TiO_2/Co 0.1% (red), TiO_2/Co 0.5% (green) and TiO_2/Co 1.0% (blue) films*

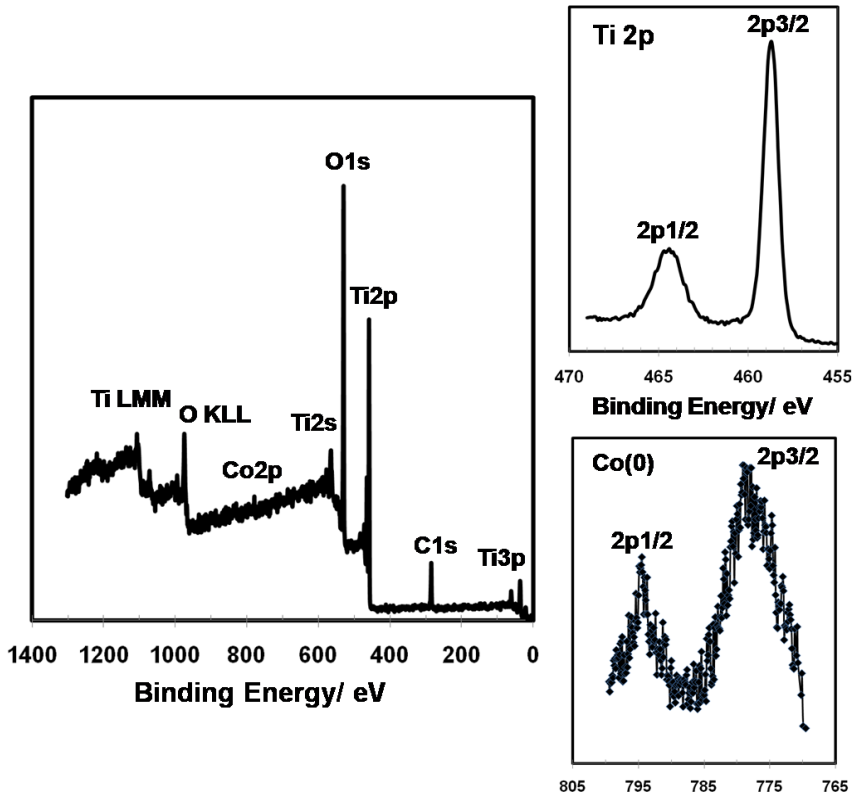

Figure S3: *XPS analysis for TiO_2/Co 0.2% sample*

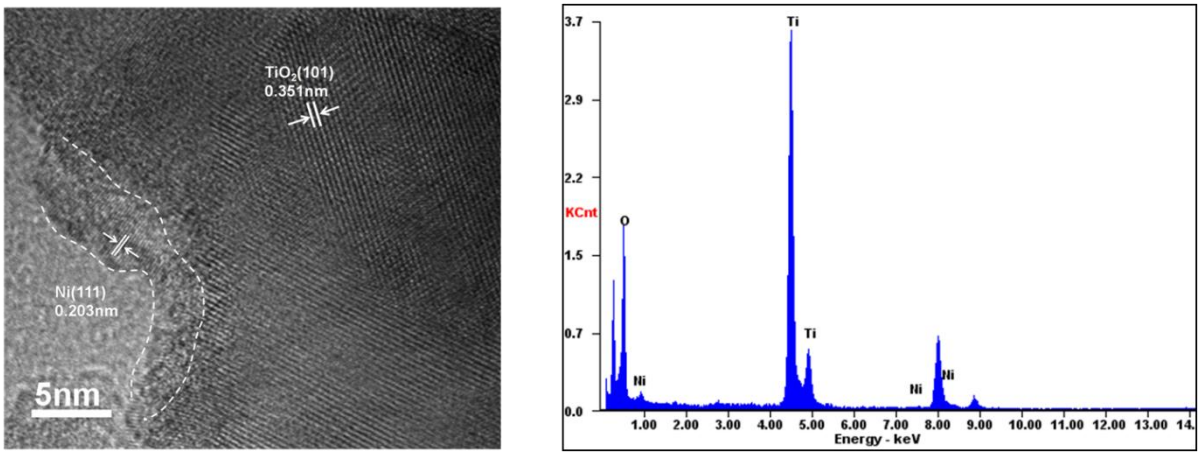

Figure S4: *TEM and EDS of TiO_2/Ni 0.1%*

References:

1. A. B. Soto, E.M. Arce, M. Palomar-Pardave, I. Gonzalez, *Electrochimica Acta*, 41, **1996**, 2647-2655