Synthesis of Metal Oxide Nanosheets through a Novel Approach for Energy Applications

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Experimental Section

Synthesis of Fe_2O_3 , Co_3O_4 , and ZnO nanosheets. All these transition metal oxide nanosheets were prepared via a similar two-step procedure including the pre-calciantion and final calcination procedures. As a typical example of the preparation of ZnO nanosheets, mixture of 5 g glucose and 1 g urea was added into 5 mL 0.1 mol/L of Zn(NO₃)₂·6H₂O solution in a 250 mL breaker to form a clear solution. After that, the breaker was put into an oven at temperature of 140 °C for 6 h to pre-calcine glucose and vapor the urea. A porous block was obtained after the pre-calcination process, which was then annealed at 500 °C for 10 h in a tube furnace in air. White samples were subsequently collected after the sample was allowed to cool down to room temperature.

 $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ solution with concentration of 0.1 mol/L was used for the synthesis of Fe_2O_3 and Co_3O_4 nanosheets respectively through similar procedures to the synthesis of ZnO nanosheets.

Synthesis of WO₃ nanosheets. WO₃ nanosheets were synthesized via a similar procedure to the synthesis of ZnO except that $(NH_4)_6W_7O_{24}\cdot 6H_2O$ that dissolved in hydrogen peroxide solution (5 mL, 0.1 mol/L) was used.

Synthesis of TiO₂ nanosheets. Tetrabutyl titanate was firstly dissolved into absolute ethyl alcohol with concentration of 0.1 mol/L. Then a mixture of 5 g glucose and 1 g urea was added into 10 mL of the fresh prepared Tetrabutyl titanate solution followed with vigorous stirring. After that, the mixture was put into an oven with temperature of 140 °C for 6 h. A porous block was obtained after the pre-calcination process, which was annealed at 500 °C for 10 h in a tube furnace in air. TiO₂ nanosheets were subsequently collected after the sample was allowed to cool to room temperature.

Characterization. The crystal structure of the samples was characterized with a powder X-ray diffractometer (XRD, Rigaku D/max-2000) using Cu-K α radiation ($\lambda = 0.15406$ nm, 45 kV, 50 mA). Field-emission scanning electron microscope (FESEM, FEI, Quanta 200F) and

transmission electron microscope (TEM, FEI Tecnai G²) working at 300 kV was employed to observe the morphology of the samples. XPS measurements were carried out on a K-Alpha XPS spectrometer (PHI 5700 ESCA System), using Al K α X-ray radiation (1486.6 eV) for excitation. Carbon C1s line with position at 284.6 eV was used as a reference to correct the charging effect. Infrared (IR) spectra were recorde with a FTIR spectrometer (Shi-madzu) in the form of KBr pellets. The surface area and pore structure of the materials was analyzed by the Brunauer–Emmett–Teller (BET) method with a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020.

Photocatalytic reactions: The photocatalytic properties of the TiO₂ and ZnO were evaluated by monitoring the degradation of RhB (100 mL, 10 mg·L⁻¹) at room temperature. Typically the reaction system containing RhB (100 mL, 10 mg·L⁻¹) and the as-synthesized TiO₂ or ZnO nanosheets (10 mg) were firstly put into an ultrasonic bath to disperse photocatalyst and then magnetically stirred in the dark for 50 min to reach the adsorption equilibrium. A 300W Xe lamp (Trusttech PLS-SXE 300, Beijing) was used as light source. At specific time intervals, about 4 mL of the reaction solution was withdrawn by a syringe. The solution was centrifuged to remove the catalyst sample before being analyzed by UV–vis absorption spectroscopy (Hitachi UH-5300, Japan). As comparison, P25 or nanosized ZnO were also used to take the place of TiO₂ or ZnO nanosheets. Blank experiments were carried out follow the same procedure but without addition of any catalyst.

Electrochemical measurements. The electrochemical characterization was carried out on 2025 type coin cells in which lithium metal foils were used as counter electrode. The working electrodes were prepared by a slurry coating procedure, in which the as-synthesized Co_3O_4 , acetylene black and polyvinylidene fluoride (PVDF) were mixed with a weight ratio of 8 : 1 : 1 and dissolved in N-methylpyrrolidinone (NMP). After stirring for 6 h, the slurry was coated uniformly on a copper foil current collector. Finally, the electrodes were dried in a vacuum at 120 °C for 12 h. After that, the coated electrodes were pressed at 6 MPa pressure to avoid

ecclasis. The test cells were assembled in an argon-filled glove box. The cells were assembled with the as-prepared working electrode, lithium foil as the counter electrode, and Celgard 2400 film as the separator. 1 M LiPF₆ in a mixture of ethylene carbonate and diethylcarbonate (w/w=1:1) was used as the electrolyte. The galvanostatic charge and discharge performance was measured between 0.01 and 3.0 V at current densities of 100, 200, 500, 1000 mA g⁻¹ with a NEWARE BTS-610 (Neware Co., Ltd, China) battery tester. Cyclic voltammetry (CV) electrochemical impedance spectroscopy (EIS) were performed on a CHI660C (Shanghai Chenhua instrument company, China) electrochemical workstation.



Fig. S1 Thermal analysis of glucose and urea in air. (a) DSC curve of glucose (violite), (b) TG curve of glucose (blue) and (c) TG curve of urea (red).



Fig. S2 Photograph of sample that containing glucose along after being heated at 140 °C for 6h.



Fig. S3 Photographs of the samples that containing urea and glucose (left), urea, glucose and $Zn(NO_3)_2 \cdot 6H_2O$ (right).



Fig. S4 XRD pattern of carbon foam from the mixture of glucose, $Zn(NO_3)_2 \cdot 6H_2O$ and urea when being pre-calcined at 140 °C for 6 h.



Fig. S5 High-magnification SEM image of ZnO nanosheet.



Fig. S6 Nitrogen adsorption-desorption isotherms



Fig. S7 SEM image of ZnO samples by change the calcination temperature. (a) Precalcination temperature to 160 °C (6 h), calcination temperature 500 °C (10 h); (b) Precalcination temperature to 140 °C (6 h), calcination temperature 600 °C (10 h).



Fig. S8 SEM image of ZnO sample which was synthesized by calcined the mixture of the mixture of glucose, $Zn(NO_3)_2$ ·6H₂O and urea directly at 500 °C for 6h.



Fig. S9 FT-IR spectrum of ZnO nanosheets.

Two bands are observed in the FT-IR spectrum of ZnO nanosheets. Broad band 3446 cm⁻¹ and a sharp band at 1633 cm⁻¹ correspond to the stretching and bending vibrations of–OH group in water molecules. Bands that attributed to organic compounds are not observed in the FT-IR spectrum, indicating that the organic parts are completely thermal decomposed.



Fig. S10 XPS spectra of as-synthesized ZnO nanosheets. (a) N 1s; (b) survey; (c) Zn 2p; (d) O 1s.

No peaks attributed to N 1s peak Peaks attributed to N in N 1s XPS spectrum has also not been observed, indicating that no residual of N-containing compounds or N-doping process happens in the as-synthesized ZnO nanosheets. In the XPS survey of ZnO nanosheets, peaks attributed to Zn, O and C are observed, in which C originates from the organic compound in the vacuum system in XPS analysis.^[1] In addition, Zn 2p1/2 and 2p3/2 peaks at 1044.1 and 1021.0 eV are observed in Zn 2p spectra, corresponding to the spin–orbit split in ZnO.^[2] O 1s XPS spectra can be deconvoluted into two peaks at 531.2 and 529.8 eV. The peak at 529.8 eV represents the O 1s level in the ZnO, which is surrounded by Zn atoms. On the other hand, the peak at 531.2 eV is attributed to the formation of zinc hydroxide with chemisorbed oxygen species.^[3]



Fig. S11 SEM images, XRD patterns and nitrogen adsorption-desorption isotherms of assynthesized TiO_2 (a, b, c), Fe_2O_3 (d, e, f), Co_3O_4 (g, h, i) and WO_3 (j, k, l).



Fig. S12 UV-vis spectral changes of RhB aqueous solution over (a) nano-ZnO, (b) ZnO nanosheets, (c) P25 and (d) TiO₂ nanosheets.



Fig. S13 CV curves of Co_3O_4 at a scan rate of 0.5 mV s⁻¹ from 0.01 to 3.0 V.



Fig. S14 Nyquist plots of the Co_3O_4 nanosheets.

References

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