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One-pot, low-temperature synthesis of self-doped NaTaO₃ nanoclusters for visible-light-driven photocatalysis

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Experimental Section:

Self-doped NaTaO₃ nanclusters were prepared by one-pot solvothermal synthetic method. First, 1.60 g of NaOH and 0.48 g of TaCl₅ were dissolved in 5ml of 30% H_2O_2 under stirring, and then the resulting solution was transferred into a 60 mL teflon-lined stainless-steel autoclave, which subsequently was filled with ethanol to 75% of the total volume. Then, the autoclave was sealed and put into a preheated oven to perform solvothermal treatment under autogenous pressure for 24 h at 110 °C. Then the autoclave was cooled down to room temperature naturally. The resultant precipitates were collected by centrifugation and washed with deionized water and ethanol thoroughly for several times. Finally, self-doped NaTaO₃ nanclusters were obtained after the sample was centrifuged and dried at 60 °C for 8 h in air. For comparison, pristine NaTaO₃ was also prepared by conventional preparation method in this study,^[1] in which NaOH and Ta₂O₅ were used as the staring materials and deionized water as the reaction solvent.

References

[1] D. R. Liu, Y. S. Jiang, G. M. Gao, Chemosphere, 2011, 83, 1546.

Characterization:

The structural properties of all samples were analyzed by a Shimadzu XRD-6000 X-ray diffractometer using Cu-K α ($\lambda = 1.54178$ Å) irradiation with a scan rate of 5° per minute. XRD data for Rietveld refinement were analyzed using GSAS software. The morphologies of all samples were examined using a field-emission scanning electron microscope (FESEM, JEOL JSM-7500F) with an energy-dispersive X-ray (EDS) spectrometer. Transmission electron microscope (TEM) images were taken on a JEOL JEM-2010 TEM instrument. The EPR data were taken with a X-band EPR spectrometer (JEOL JES FA-200) operating at 9.055 GHz. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (Perkin-Elmer) to characterize the surface composition. UV-vis diffuse reflectance spectra were achieved using Shimadzu UV-vis spectrophotometer (UV-3600).

Photocatalytic Experiments:

The water splitting experiments were carried out in a pyrex reaction cell connected to a closed gas circulation and evacuation system (CEL-SPH2N, Jinyuan). 100 mg of self-doped NaTaO₃ nanoclusters were dispersed in 100 mL of aqueous solution containing 0.1 M Na₂S and 0.02 M Na₂SO₃ as the sacrificial agent. The suspension was stirring in an outer irradiation Pyrex glass cell for 15 minutes and then evacuated to vacuum before irradiation. A 300 W xenon lamp was focused on the side window of the cell with a 420 nm cut-off filter. High purity nitrogen gas was used as the carrier gas. The amount of hydrogen was measured by a gas chromatography (N2000, Zhejiang University) with TCD detector and a capillary column.

The photocatalytic activity of self-doped NaTaO₃ nanoclusters were also evaluated by photodegradation of Safranine O. In a typical measurement, 0.1 g of catalyst was dispersed into a beaker, which was filled with 100 mL of 30 mg L⁻¹ Safranine O. Prior to light irradiation, the suspension was magnetically stirred in dark condition for 30 min to establish adsorption equilibrium. The suspension was then irradiated by a 300 W xenon lamp with a 420 nm cut-off filter. The solution was sampled every 10 minutes and centrifuged to filter out the catalyst before UV-vis measurement to determine the concentration of Safranine O. In addition, the blank test was carried out without adding any catalyst and the contrast experiments were tested by using P25 and pristine NaTaO₃ as photocatalysts with the same experimental procedures.

Detection of ·OH radicals:

Hydroxyl radicals produced on the surface of self-doped NaTaO₃ nanoclusers were detected by the photoluminescence (PL) technique using terephthalic acid (TA) as a probe molecule. Experimental procedure is similar to the measurement of photocatalytic activity except that Safranine O aqueous solution was replaced by the 5×10^{-4} M TA aqueous solution with a concentration of 2×10^{-3} M NaOH solution. The suspension was irradiated by a 300 W xenon lamp (with a 420 nm filter). At every 10 min, 2 mL of the suspension was collected and centrifugated. PL spectra of generated 2-hydroxyterephthalic acid were measured by a Hitachi F-7000 fluorescence spectrophotometer (Hitachi, Japan).



Fig. S1 XRD patterns of samples obtained with different temperatures (a) and with different molar ratios of OH^{-} to Ta^{5+} (b).



Fig. S2 N₂ adsorption-desorption isotherms of self-doped NaTaO₃ nanoclusters.



Fig. S3. SEM images of samples obtained at 140 $^{\circ}$ C (a) and 160 $^{\circ}$ C (b) for 24 h.



Fig. S4. SEM image of pristine NaTaO₃



Fig. S5 XRD patterns of samples obtained using deionized water as solvent under different reaction temperatures for 24 h.



Fig. S6. XRD patterns of self-doped samples obtained with different dosage of H₂O₂.



Fig. S7. H₂ evolution of self-doped NaTaO₃ after long times irradiation under visible light (black curve) and UV light (red curve)