Supporting Information

Controllable Reduced Black Titania with Enhanced Photoelectrochemical Water Splitting Performance

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Experimental

Preparation of black titania

P25 nanoparticles were uniformly mixed with Metal powders in different molar ratios prior to being sealed in a quartz tube and calcined at 500 ºC for 10 h. Specifically, the black titania obtained by Mg-reduction were labled Mg-x, where x denotes the molar ratio. The exact procedure was as follows: 2 g P25 TiO2 and Mg powder (0.3, 0.6, 0.9 g corresponding to the molar ratio of 0.5, 1, 1.5) were mixed and homogenized by grinding. Afterwards, the powder mixture was transferred into a quartz tube which was subsequently sealed and kept in an oven at 500 ºC for 10 h in a temperature ramp of 1 ºC min−1. After naturally cooling to room temperature, the product was immersed in deionized water to remove the salts and after ultrasound dispersion, most of the unreacted Mg sediments were discarded. Subsequently, the suspension was added with diluted hydrochloric acid solution and stirred mildly for 5 h to remove the Mg residue. Lastly, the black titania was separated by filtration and washed with de-ionized water for several times. After dried in an oven at 80 °C for 12 h, the black titania sample was prepared eventually.

Sample Characterization

Raman spectra were collected on a Thermal Dispersive Spectrometer using a laser with an excitation wavelength of 532 nm at laser power of 10 mW. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K α radiation (hν = 1253.6 eV). The EPR spectra were collected using a Bruker EMX-8 spectrometer at 9.44 GHz at 300 K. Solid-state ^{1}H magic-angle spinning

(MAS) NMR spectra were acquired on a Bruker Ascend-400 spectrometer (400.3 MHz) using standard Bruker pulse programs. XRD patterns were obtained with a Bruker D8 advance diffractometer operating with Cu Kα radiation. The morphologies of the samples were observed on a JEOL-JEM 2100F transmission electron microscope (TEM) (100 kV) and a Hitachi S-4800 field emission scanning electron microscope (FE-SEM) (5 kV). Diffuse reflectance spectra (DRS) and UV–visible absorption spectra were measured using a Hitachi U-4100 spectrometer with an integrating sphere accessory, using BaSO4 as the reference material.

Photoanodes preparation and electrochemical testing

PEC measurements were performed in a conventional three-electrode electrochemical workstation (CHI 600B, CHInstruments). The P25 titania and controllable reduced titania films were firstly prepared by spin-coating and used as working electrodes. The powders were dispersed in ethanol and milled for 6h to obtain a slurry. The precursor thin films of the samples were spin-coated on FTO substrates with subsequent annealing in argon atmosphere at 400 °C.The counter and reference electrodes are the Pt wire and Ag/AgCl respectively. A 1.0 M NaOH aqueous solution (pH = 13.6) was used as the supporting electrolyte to maintain the stability of the film. A 150W Xe lamp was used as the light source to simulate the sunlight irradiation. A set of linear sweeps and transient photocurrent responses were recorded in the dark and under illumination.

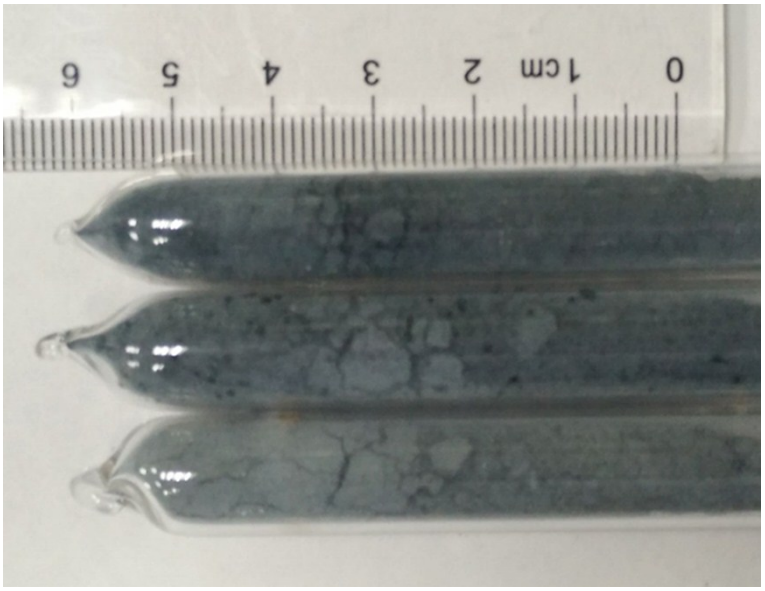

Fig. S1 Digital photograph of blue titania obtained by Zn reduction with different molar ratio at 800 ºC.

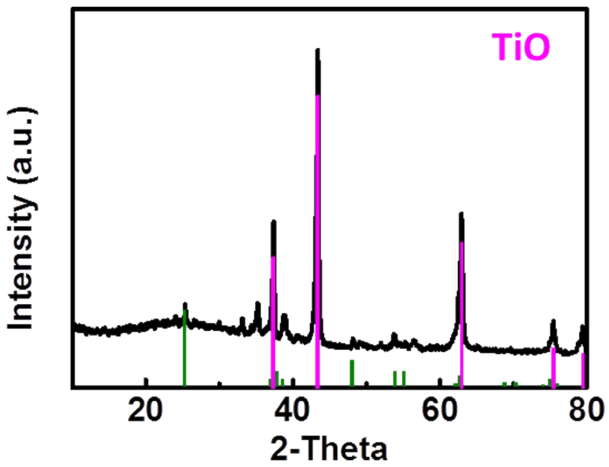

Fig. S2 XRD patterns obtained black titania of Mg-2.0 reacted at 500 ºC.

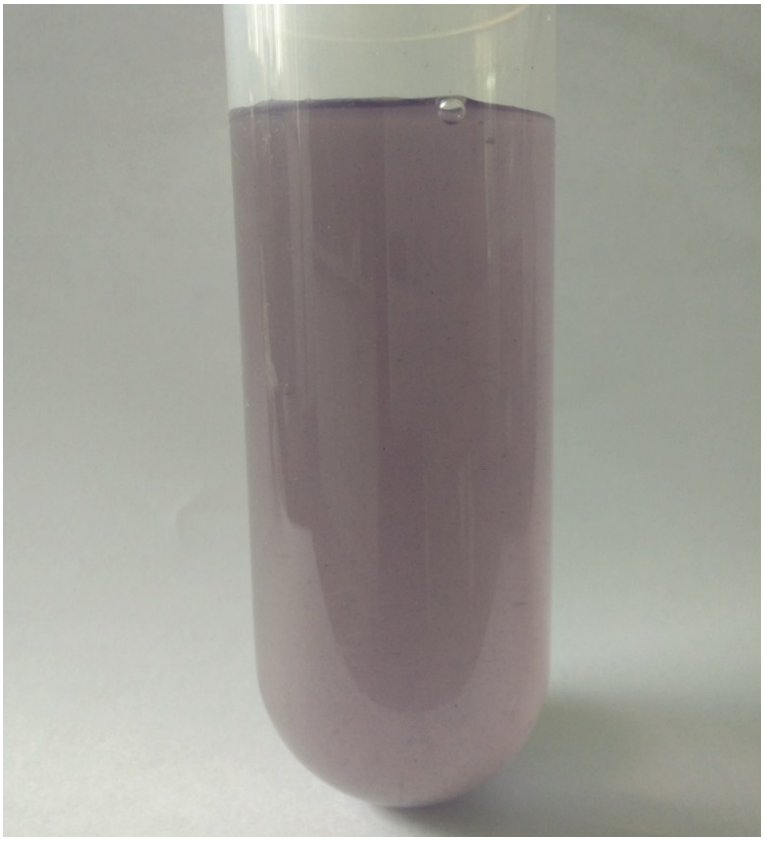

Fig. S3 The purple solution consisting of Ti^{3+} obtained by Mg-2.0 reacted at 550 ºC with the use of dilute HCl.

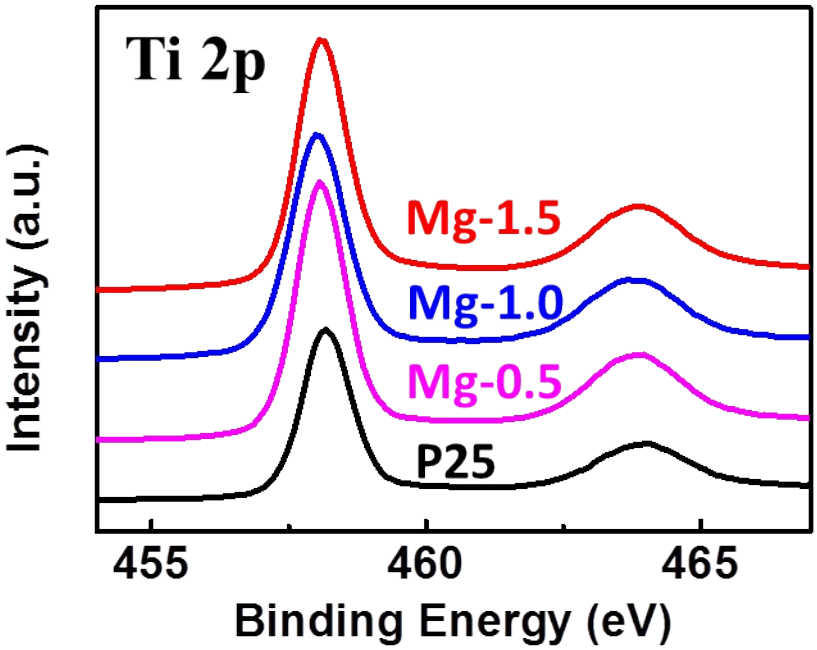

Fig. S4 XPS spectra of the controllable reduced titania and pristine P25 nanoparticles.