## Porous Cerium Dioxide Hollow Spheres and their Photocatalyic Performance

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**Photocurrent response experiment.** The prepared samples (0.03g) were dissolved into the acetone for 1h ultrasonic, and then added a grain of iodine for 30 min ultrasonic. The samples were electroplated on the surface of the ITO glass with an area of 6 cm<sup>2</sup>. The Plating voltage is 15 V, and the time of duration is 10 min. Photoelectrochemical measurements were performed with a homemade photoelectrochemical system. A 500 W Xe lamp equipped with a cutoff filter ( $\lambda > 325$  nm) was used as the irradiation source. Photocurrent was measured on an ALS 604D electrochemical workstation. Photocurrent response measurements were conducted in 1.0 M Na<sub>2</sub>SO<sub>4</sub> solution in a three-electrode system. Indium tin oxide (ITO) electrode with ceria was employed as the working electrode. A coiled Pt wire was used as the counter-electrode and a saturated Ag/AgCl as the reference electrode. The interval of light-on and light-off is 4 s.

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Image (A)  $\sim$  (D) shown the different stages of the reaction process. At the first stage, the little crystals formed, and then they aggregated into large solid spheres. Attributed to the driving force of the Ostwald ripening process, the cavity formed internally. Prolonged reaction time of system, the hollow structure obtained with an obvious interface.



Fig S1 Formation mechanism investigation of  $CeO_2$ -PH from TEM images for the different reaction time at 180 °C (A) 0.5h (B) 3h (C) 24h (D) 48h

Sample A and B were synthesized in the mixed solution of water, ethanol and glycol; sample C and D were synthesized in the mixed solution of water and ethanol. The activity of both samples was not good, while the content of Ce<sup>3+</sup> in A was higher than in B due to glycol addition. However, sample D has a special structure— Mesocrystals.<sup>[1]</sup> It is a potential research point in my future plans.



Fig S2 Prepared samples in the same condition without PVP, (A) and (B) with EG, (C) and (D) without EG.

[1]. H. Colfen and M. Antonietti, *Angewandte Chemie*, 2005, 44, 5576-5591.