Electronic Supplementary Material (ESI) for Faraday Discussions.

Spatial distribution of active sites on ferroelectric $PbTiO_3$ photocatalyst for photocatalytic hydrogen production

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1. Sample preparation.

$PbTiO_3$ photocatalyst was synthesized by a traditional solid-state-reaction process. Commercial PbO_2 and TiO_2 powders (2.0 mmol) were mixed together and grinded in the mortar for 30 min, and then transferred to corundum crucible and put in a muffle furnace for calcination at 1273 K for 6 h. The photo-reduction deposition of the Pt (Au) was achieved with H_2PtCl_6 ($HAuCl_4$) as the precursor. In a typical procedure, 200 mg $PbTiO_3$ sample was suspended in 150 mL deionized water. Then H_2PtCl_6 solution and 5 ml CH3OH were added and the suspension was then irradiated by a 300 W Xe lamp (Ushio-CERMAXLX300) under a constant stirring. After reaction for 2 h, the suspension was centrifuged five times in deionized water and anhydrous ethanol, respectively, and dried at 70 ℃ for 12 h in a vacuum oven. The photo-oxidation deposition of the MnO_x was achieved with $MnSO_4$ as the precursor, and $NaIO_3$ was employed as the electron acceptor. In a typical procedure, 200 mg $PbTiO_3$ sample was suspended in 150 mL deionized water containing 0.20g $NaIO_3$. Then $MnSO_4$ solution was added and the suspension was irradiated by a 300 W Xe lamp (Ushio-CERMAXLX300) under a constant stirring. After photo-deposition for 2 h, the suspension was centrifuged five times in deionized water and anhydrous ethanol, respectively, and dried at 70 ℃ for 12 h in a vacuum oven.

2. Evaluation of photocatalytic hydrogen production.

Photocatalytic H_2 production reaction were carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp (Ushio-CERMAXLX300). Normally, 100 mg photocatalyst was dispersed in 150 mL CH3OH-H2O (20% CH3OH) solution in a Pyrex reaction cell. Before irradiation, the reaction system was thoroughly degassed by evacuation in order to drive off the air inside. The amount of evolved H_2 was determined by an on-line gas chromatograph (Agilent, GC-

7890, TCD, Ar carrier). The amount of Pt or/and MnO_x cocatalysts were 0.1 wt% for the evaluation of photocatalytic performance.

3. Characterizations

The as-prepared samples were characterized by X-ray power diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. The sample power was scanned using Cu-Kα radiation with an operating voltage of 40 kV and current of 200 mA. The scan rate of 5°/min was applied to record the patterns in the range of 20-80°at a step size of 0.02°. UV-visible (UV-vis) diffuse reflectance spectra were recorded on a UV-vis spectrophotometer (JASCO V-650) equipped with an integrating sphere. The morphologies of photocatalysts were examined by scanning electron microscopy (SEM) taken with a Quanta 200 FEG scanning electron microscope with an operating voltage of 20.0 kV.

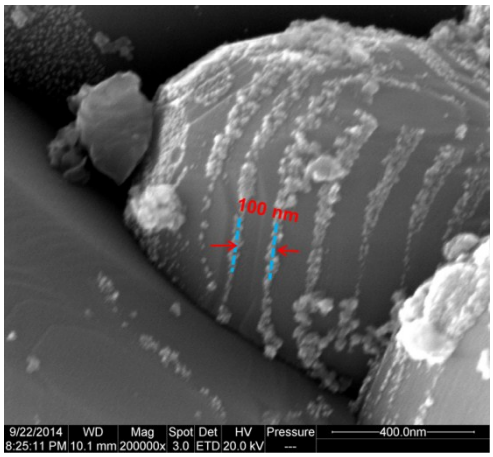

Figure S1. SEM image of photo-reduction deposition of Au nanoparticles on as-prepared $PbTiO_3$ photocatalyst.

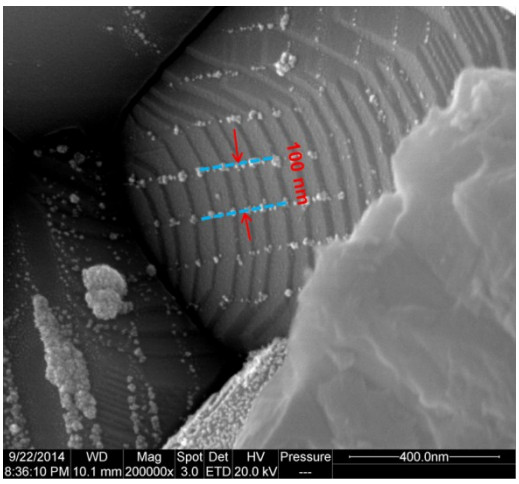

Figure S2. SEM image of photo-reduction deposition of Pt nanoparticles on $PbTiO_3$ crystals with step-like structure on the surface.