Supporting information for p-type Cr-doped TiO_2 photo-electrode for photo-reduction

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Experimental

Cr-doped TiO_2 photo-electrode and local Cr-doped TiO_2 photo-electrode were fabricated using pulsed laser deposition (PLD) method. Cr-doped TiO_2 pellet (atomic ratio Cr: Ti=6: 100) and pure TiO_2 pellet were utilized as the targets. Sn doped Indium-oxide-coated glass sheet (ITO) were selected as the substrates. The pellets and ITO were set in the PLD machine (ST-PLD; Pascal co., Japan), and the distance between the pellet and the ITO was set to be 5 cm. After that, the film-preparation chamber of the PLD machine was evacuated to 0.001 Pa, and then pure O_2 was introduced into the chamber until the pressure became 4 Pa. After ITO substrate was heated to 550 °C, the target was irradiated by the laser pulse (60 mJ per pulse; 355 nm in wavelength) emitted from a Nd:YAG laser. After the deposition, the substrate temperature (550 °C) was still kept for 1 h in the presence of O_2 (9.6×10^4 Pa) for the post-heat treatment of the samples.

Cr-doped TiO_2 thin films were fabricated by irradiating Cr-doped TiO_2 target for 1 h. Local Cr-doped TiO_2 thin films were fabricated by irradiating Cr-doped TiO_2 target for 40 min firstly and then irradiating TiO_2 target for 20 min.

After the pulsed laser deposition process, Pt was loaded by using photo-deposition method. The local Cr-doped TiO_2 thin films were immerged in 0.5 wt% H_2PtCl_6 aqueous solution under the light irradiation condition for 1 h. After the photo-deposition, the samples were heated at 400 °C for 1 h.

Chemical compositions of the prepared photo-electrodes were evaluated with a transmission electron microscope (2100F, JEOL Co., Japan), field-emission scanning electron microscope (JSM-6701F, JEOL Co., Japan) and XPS. Photocurrent densities were measured with an electrochemical station (ALS/CH model 650A) using three-electrode mode. Platinum and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. In the photoelectrochemical measurement, the photo-electrodes were illuminated with the light from the side of the electrolyte/film interface in aqueous Na_2SO_4 solution (0.1 M) through a quartz window. AM 1.5 Solar simulator (PEC-L01, Pecell Co., Japan) was utilized as the light sources.

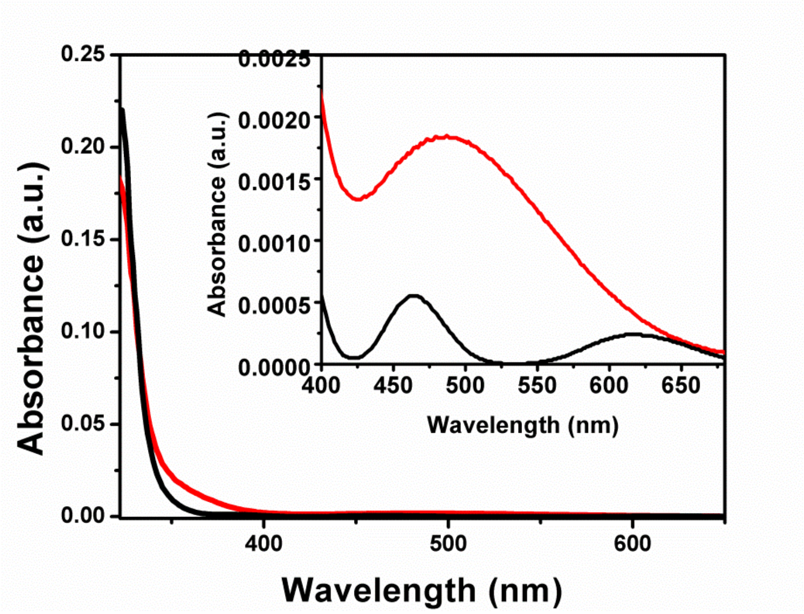

Fig.S1 UV-vis spectra of uniformly Cr doped TiO_2 thin film and TiO_2 thin film.

Fig. 1 shows the UV-vis spectra of the as-prepared TiO_2 and uniformly Cr-doped TiO_2 photo-electrodes by PLD method. The absorbance of uniformly Cr-doped TiO_2 photo-electrode exhibits an obvious shift towards longer wavelength, comparing with that of the TiO_2 photo-electrode. The inset of **Fig. 1** shows that uniformly Cr-doped TiO_2 can absorb the visible light with the wavelength shorter than about 650 nm. Here, the oscillation of the TiO_2 photo-electrode absorbance curve in the region from 400 nm to 680 nm should be due to the interference effect caused by the TiO_2 layer, not by the light absorbance of TiO_2.

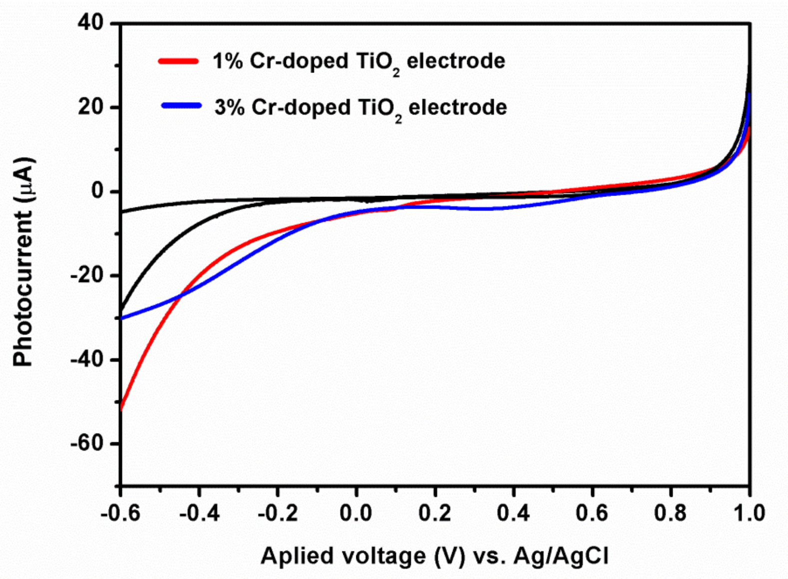

Fig. S2 The photocurrent vs. potential curve of 1% and 3% Cr-doped TiO_2 electrode.

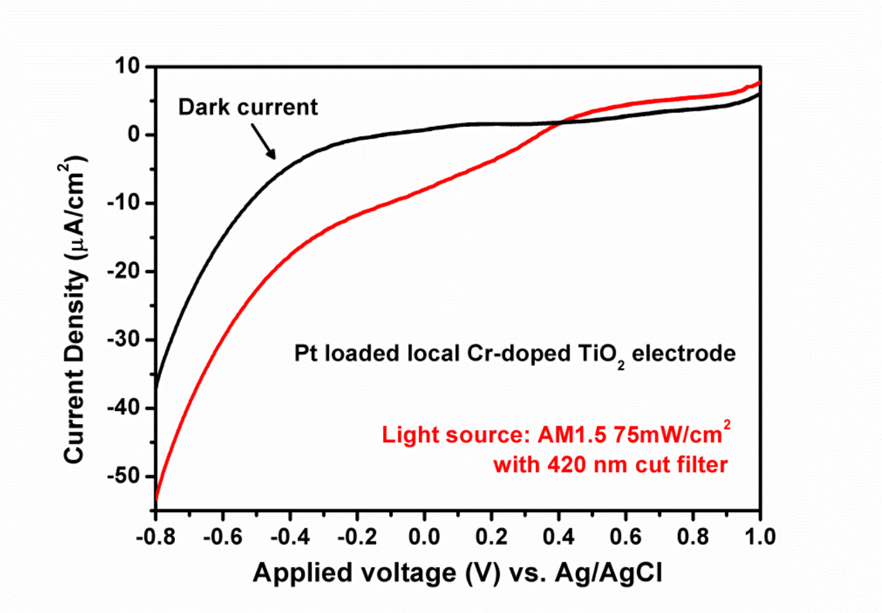

Fig.S3 I-V curves of inner Cr-doped TiO_2 thin film with Pt-loading under visible light.

Inner Cr-doped TiO_2 photo-electrode with Pt-loading exhibited obvious visible light response. As showed in **Fig. 2**, a negative photocurrent density could be observed under AM1.5 solar simulation with 420 nm cutoff filter.

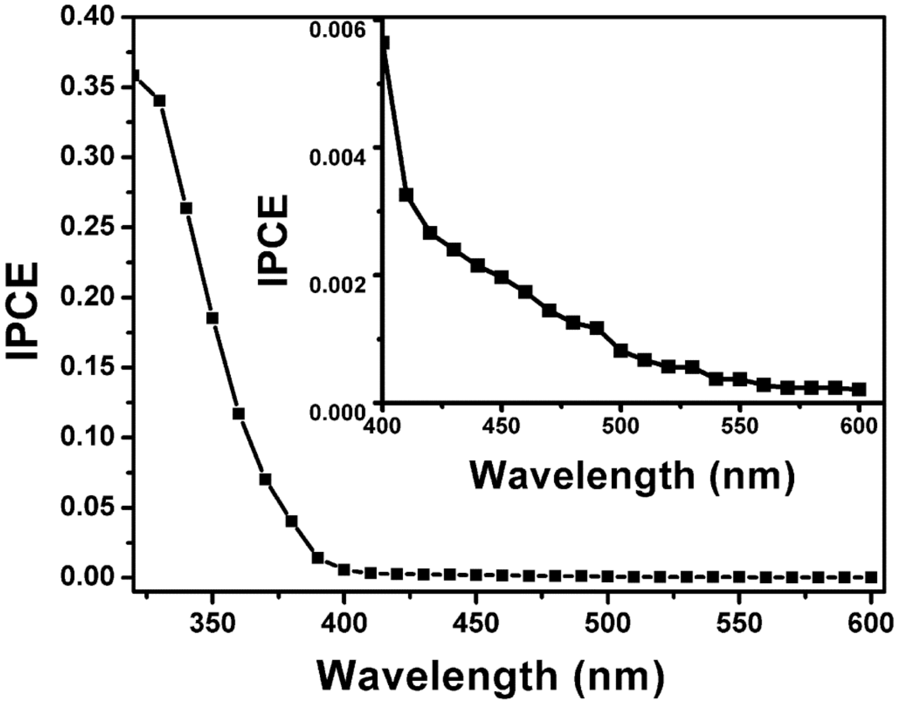

Fig.S4 IPCE of inner Cr-doped TiO_2 thin film with Pt-loading at -0.2 V vs. Ag/AgCl/