Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting information

Size-related Native Defects Engineering in High-Intensity Ultrasonication of Nanoparticles for Photoelectrochemical Water Splitting

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Experimental details

Materials and Ultrasonic treatment:

All materials were used as received. ZnO nanoparticles with three kinds of sizes (<50 nm, 100 nm, 5 μm) were purchased from Sigma Aldrich, Germany. Sonication was provided by a Hielscher Ultrasonics generator (UIP1000hd, 20 kHz) with a titanium-alloy probe having a 0.7-inch solid tip which was immersed about 1.5 cm below the surface of the exposed colloidal aqueous solutions with a concentration of 0.4 mg/ml for each kind of ZnO nanoparticles. The ultrasonic treatment for each kind of ZnO nanoparticles was 10 min and with different irradiation intensities (63, 86, and 113 W cm^{-2}). During sonication, the reaction vessel was kept in an ice-water bath.

Characterization:

The optical extinction spectra of the ultrasonically treated ZnO nanoparticles with different sizes were obtained by using a quartz cell with 10-mm path length on a Varian CARY 50 UV/Vis spectrophotometer in the wavelength range from 270 to 1000 nm. Nanoparticle morphologies before and after ultrasonication were visualized by a Philips CM200 LaB6 instrument. A Nano Zeta Sizer (Malvern Instruments) was utilized to determine the diameter of the nanoparticles by DLS. The crystal structure of the nanoparticles was investigated with a D8 Bruker wide-angle X-ray diffractometer. The PL spectra were recorded in a Fluoromax-4 Spectrofluorometer (150 W Xenon lamp) with the excitation wavelength of 325 nm.

Photoelectrochemical measurement:

FTO was employed as transparent conductive substrates. Before spin coating all substrates were cleaned by sonication in acetone, ethanol, and water successively and finally dried with N_2 gas. ZnO raw nanoparticles (S3) and those treated by high intensity ultrasound with different intensities (63, 86, 113 W cm^{-2}) were spin-coated on FTO glass at a rotation speed of 500 rpm at room temperature. After the natural

drying of the ZnO nanoparticles, nafion solution (5 μL 0.5 wt%) was then coated on the working electrodes to fix the ZnO nanoparticles on the electrode surface. Photocurrent measurements were performed to estimate the solar photocurrent of the photoanodes in a three-electrode compartment (EG&G, 273A). 0.5 M K_2SO_4 aqueous solution with pH 7, a Pt wire, and an $Hg/HgSO_4$ electrode were employed as electrolyte solution, counter electrode, and reference electrode, respectively. The intensity of the incident light was 400 $mWcm^{-2}$ from a tungsten halogen lamp from Xenophot. All measurements were performed with illumination to both the ZnO/electrolyte interface and the back side through a 0.32 cm^2 mask that defines the electrode area exposed to the electrolyte and the light. The potential of the ZnO photoanodes was swept at a scan rate of 10 mV s^{-1} from cathodic to anodic potentials. The potential was converted to the reversible hydrogen electrode (RHE) potential. The differential electrochemical mass spectroscopy (DEMS) was designed to simultaneously measure released gases during an electrochemical measurement, and the films were illuminated using a tungsten halogen lamp from Xenophot (100 $mWcm^{-2}$).

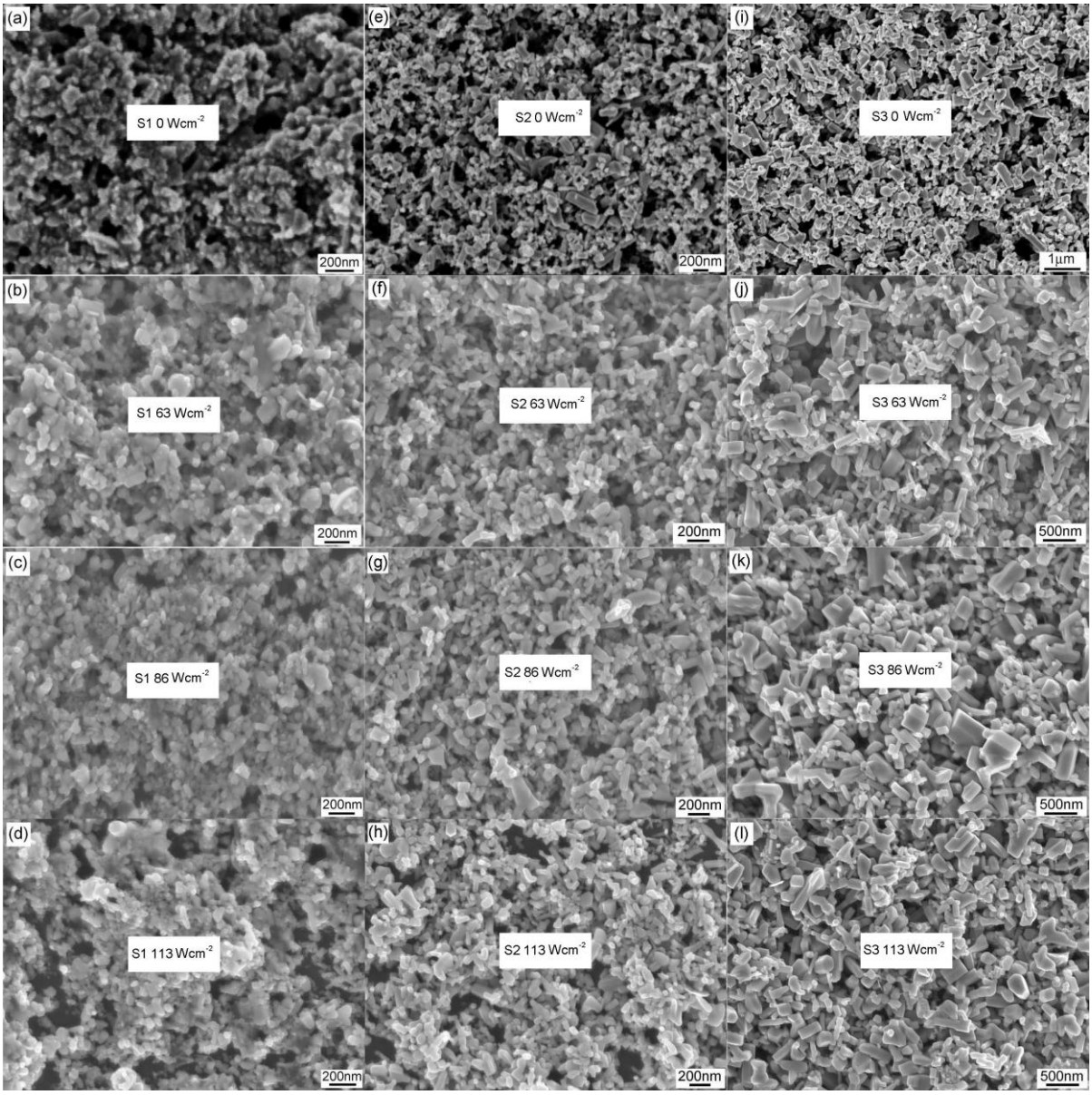

Figure S1 FESEM images of ZnO nanoparticles before and after high intensity ultrasonication with different intensities.

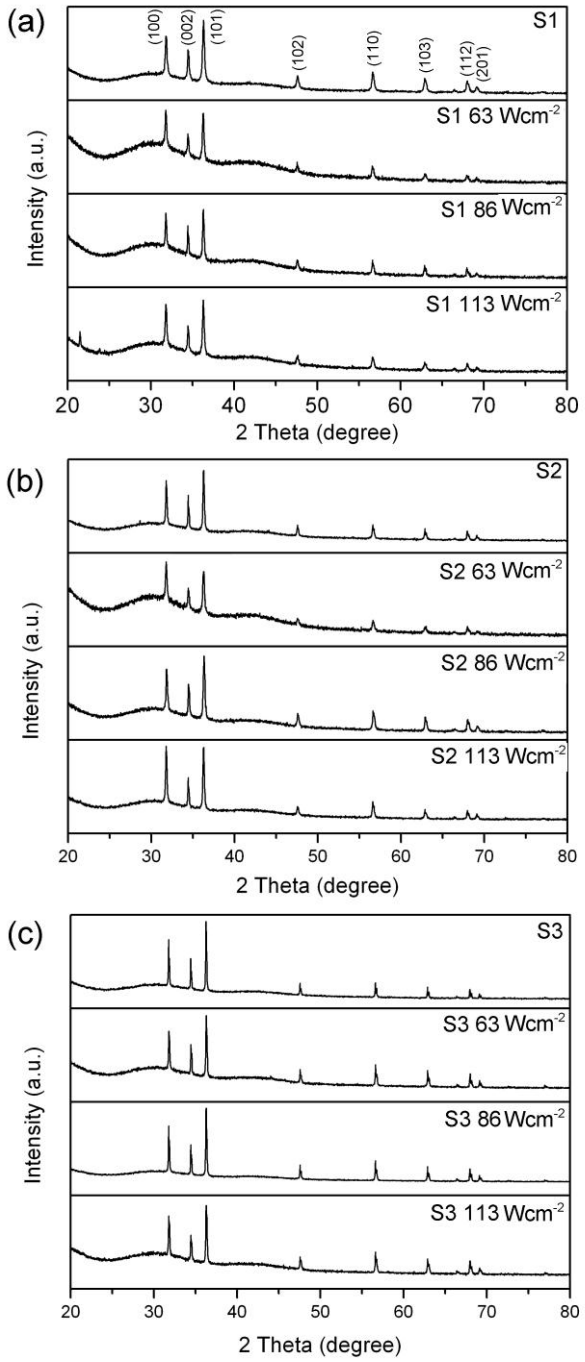

Figure S2 XRD results of of ZnO nanoparticles before and after high intensity ultrasonication with different intensities. The broad continuum in the range of 2theta=20-45 degrees comes from the supporting substrate in the XRD measurement.

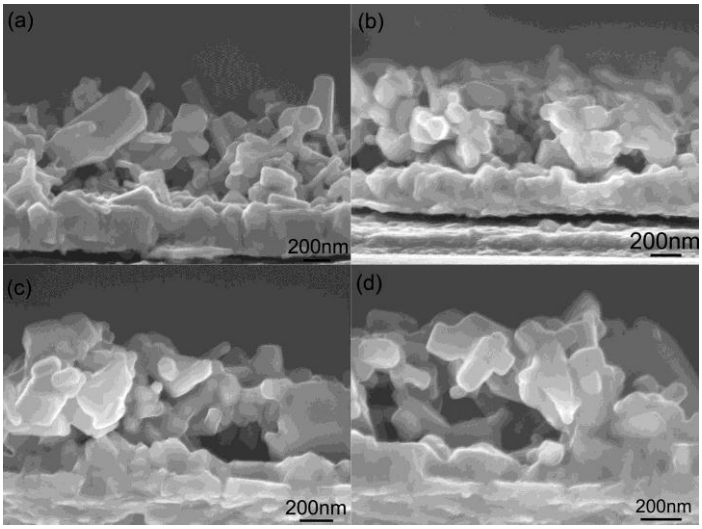

Figure S3 Cross sectional FESEM image of ZnO films covered PEC working electrode, in which the ZnO films were obtained by spin coating of ZnO nanoparticles treated with sonication of different densities: a) 86, b) 0, c) 63, and d) 113 W cm^{-2}.

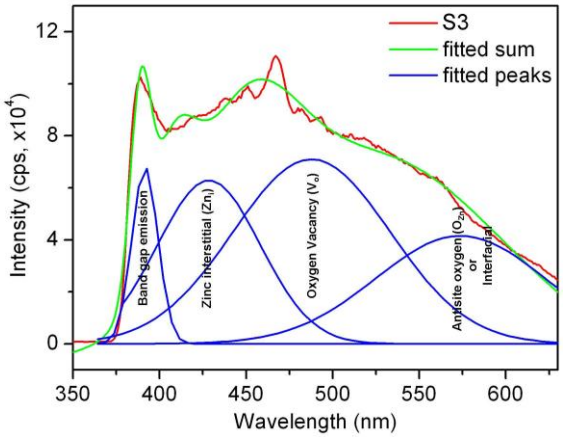

Figure S4. PL spectra of S3 and the corresponding Gaussian fitting.

Table T1. Crystal size calculation from the FWHM of the strongest diffraction peak (101) on the basis of the Debye Scherrer equation.

	0 W cm^{-2}	63 W cm^{-2}	86 W cm^{-2}	113 W cm^{-2}
S1	33.5 nm	38.1 nm	39.9 nm	38.1 nm
S2	49.3 nm	41.9 nm	43.0 nm	44.1 nm
S3	105.4 nm	99.1 nm	105.4 nm	99.1 nm

Table T2. Average sizes of three kinds of ZnO nanoparticles before and after sonication with different intensities (63, 86, 113 W cm^{-2}), which was obtained from Dynamic Light Scattering analysis.

	0 W cm^{-2}	63 W cm^{-2}	86 W cm^{-2}	113 W cm^{-2}
S1	204 nm	135 nm	134.9 nm	133.4 nm
S2	258 nm	167.8 nm	159.2 nm	154.1 nm
S3	517.3 nm	312.8 nm	308.3 nm	288.5 nm