Supporting Information

of

Facet-Dependent Photoreduction on Single ZnO Crystals

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Materials and reagents

Zinc acetate dihydrate (ZnO(CH\(_2\)COO)\(_2\)·2H\(_2\)O, ≥98.0%, Sigma-Aldrich), zinc nitrate hexahydrate (ZnO(NO\(_3\))\(_2\)·6H\(_2\)O, Reagent Grade, 98%, Sigma-Aldrich), sodium hydroxide (NaOH, >99%, VWR Chemicals), potassium hydroxide (KOH, >99%, Sigma-Aldrich), silver nitrate (AgNO\(_3\), ≥99.0%, Sigma-Aldrich) and acetic acid (CH\(_3\)COOH, ≥99.0%, Sigma-Aldrich) were used as received without further purification. In all experimental procedures, milli-Q water has been employed. Hydrothermal reactions were conducted in stainless steel Teflon-lined autoclaves in a Thermo Scientific Heratherm oven (OGS60). Suspensions were dispersed in a 60 W Branson 2200 Ultrasonic bath equipped with thermostatic heating.

Synthesis ZnO dumbbells\(^1\)

4.4 g of ZnO(CH\(_2\)COO)\(_2\)·2H\(_2\)O was dissolved in 20 mL of milli Q water under vigorous stirring. The pH of the clear zinc acetate solution was adjusted to pH 8 with a 4 M aqueous NaOH solution. The resulting reaction mixture was then transferred to a 30 mL stainless steel Teflon-lined autoclave and heated to 155 °C where the mixture was kept for 48 hours. After cooling down to room temperature, the solid product was filtered from the reaction liquid. The resulting crystals were thoroughly washed with milli Q water and dried overnight in an oven at 80 °C prior to use.

Synthesis ZnO microrods\(^2\)

14.9 g of ZnO(NO\(_3\))\(_2\)·6H\(_2\)O was dissolved in 50 mL of milli Q water at room temperature, resulting in a 0.5 M zinc nitrate aqueous solution. The pH of the solution was increased to pH 12 by adding dropwise a 1.5 M aqueous KOH solution, followed by vigorous stirring for 10 min. The white slurry mixture was transferred into a 30 mL stainless steel Teflon-lined autoclave and the hydrothermal reaction was conducted at 180 °C in an oven for 20 hours.
After the reaction was completed, the suspension was cooled down and the final product was collected by pressure filtration. The white powder was thoroughly washed with milli Q water and dried overnight in an oven at 120 °C for 12 hours.

**XRD spectra of the dumbbell and microrod samples**

![Graph S1. XRD spectrum of the synthesized dumbbell crystal sample.](image1)

![Graph S2. XRD spectrum of the synthesized microrod crystal sample.](image2)
iLEM specifications

Samples were analyzed by a FEI Quanta 250 FEG environmental scanning electron microscope with a customized chamber door (SECOM, Delmic BV). UV light generated by a Thorlabs LEDD1B, T-Cube LED Driver of 365 nm is directed into the SEM vacuum chamber by means of an optically transparent chamber window. A dichroic mirror and a 100x 1.4 NA CFI plan APO VC oil objective (Nikon) further direct the UV light onto the photocatalyst particles at the sample stage with an optical power density of 50.0 µW/cm². Such a configuration allows the study of silver photodeposition on ZnO photocatalysts using SEM in a correlated fashion. The possibility of conducting these experiments in one and the same setup implies that there is no need for shuttling the sample between dedicated setups which restricts sample contamination or alteration.

Scheme S1. The integrated light and electron microscope (iLEM) is applied to perform SEM imaging on the sample (a) before and (c) after deposition. (b) The iLEM is equipped with a customized chamber door (Delmic BV) featuring an optically transparent window that allows 365 nm UV light from outside the door to reach the high NA objective lens on the inside, guiding the light onto the field of view that is being imaged by SEM, without the needs to transfer the sample between dedicated systems.³
Glass cleaning and sample preparation for iLEM experiments

The glass coverslips were cleaned with Milli-Q ultrapure water (Millipore) followed by thermal treatment at 460°C overnight. In order to spread the ZnO crystals uniformly over the glass surface, the coverslip was placed in an UV-ozone photo reactor (PR-100) for several minutes to make the surface more hydrophilic. A suspension of 1 mg/mL of the ZnO crystals in ultrapure water was shaken thoroughly and dispersed in an ultrasonic water bath for 1 minute. Then, 15 µL of this suspension was dropcasted on top of the glass coverslip, resulting in a thin and uniform layer of ZnO crystals after drying in the dark.

Photodeposition of silver nanoparticles on the ZnO crystal surface

After obtaining initial SEM micrographs on the ZnO crystal of interest, the sample chamber was vented to atmospheric pressure and a droplet of 1 mM aqueous silver nitrate was added on the top of the envisioned ZnO crystal on the glass coverslip. The ZnO photocatalyst was subsequently illuminated for 20 seconds with 365 nm UV light from an LED source outside the vacuum chamber coupled in via an optically transparent window in the chamber door. Afterwards, the liquid was carefully removed before pumping down the EM chamber and recording new SEM images.

Glass cleaning and sample preparation for single-particle photoluminescence experiments

The glass coverslips were purchased from Matsunami Glass and cleaned by sonication in a 20% detergent solution (As One, Cleanace) for 6 hours, followed by five times sonication in warm water for 30 minutes. Finally, the coverslips were rinsed with Milli-Q ultrapure water (Millipore). 15 µL of the well-dispersed 0.5 mg/mL aqueous suspensions of the ZnO crystals
was drop-casted on the cleaned coverslip. The coverslip was dried in the dark to immobilize the particles on the surface.

**Single-particle photoluminescence measurements by confocal microscopy**

Single-particle photoluminescence images and decay profiles of the ZnO samples were recorded using an objective-scanning confocal microscope system (PicoQuant, MicroTime 200) coupled with an Olympus IX71 inverted fluorescence microscope. The samples were excited through an oil-immersion objective lens (Olympus, UPlanSApo, 1.40 NA, 100x) using a circular-polarized 405 nm pulsed laser (0.45 μW, PicoQuant, FWHM = 54 ps, 20 MHz) controlled by a PDL-800B driver (PicoQuant). The emission from the sample was collected by the same objective and detected by a single-photon avalanche photodiode (Micro Photon Devices, PDM 50CT) through a dichroic beam splitter (Chroma, 405rdc), long pass filter (Chroma, HQ430CP) and a 75 μm pinhole for spatial filtering to reject out-of-focus signals. All the experimental data were obtained at room temperature.

**Photoluminescence decay profile analysis**

Since the decay profiles correspond to a biexponential decay, the amplitude weighted average lifetime ($\tau_{amp}$) is determined as the average charge carrier lifetime along the length of the crystals. The analysis is performed using SymPhoTime (PicoQuant, Germany) and is based on the following formula:

$$\tau_{amp} = \frac{(A_1 \cdot \tau_1) + (A_2 \cdot \tau_2)}{A_1 + A_2}$$

$\tau$ corresponds to the decay components and $A$ to the respective amplitudes.
**Figure S1.** SEM images of typical dumbbell-shaped ZnO microcrystals as prepared.

**Figure S2.** Acidic dissolution experiments. SEM images of (a) ZnO dumbbell crystals and (b) ZnO microrods before (left panel) and after (right panel) treatment with a 0.01 M aqueous solution of acetic acid, pH 4. The droplet of acetic acid was left for 5 minutes on the glass coverslip and then rinsed with milli-Q ultrapure water, readily leading to the degradation of the oxygen terminated (000̅1) facet.⁴
Figure S3. (a) SEM images of ZnO dumbbell crystals after silver photodeposition during 20 seconds of illumination with UV light. (b) Distribution plot of the angle between 50 pyramidal facets and corresponding polar (0001) planes to determine the average value.

Figure S4. SEM images of ZnO microcrystals obtained before (a) and after (b) silver photodeposition during 20 seconds of illumination with UV light. A rod-like ZnO crystal is observed in this batch of dumbbell-shaped crystals (see right side of micrographs). On this ZnO microrod, a more homogeneous silver nanoparticle photodeposition (inset a.1) is observed on the seemingly defect free crystal side faces (inset b.1).
**Figure S5.** SEM images of typical rod-like ZnO crystals as prepared.
Figure S6. Data of the photoluminescent lifetime experiments that are represented in Figure 3 in the main article. Data includes, from top left to bottom right, the transmission image, the PL lifetime image with the probed positions (Both included in the manuscript as well), the PL...
lifetime image with the emission maxima for the probed positions, the measured lifetime decay data, the table with the fitted parameters and the obtained PL emission spectra with the wavelengths of the corresponding emission maxima

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