Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Local transformation of ZIF-8 powders and coatings into ZnO nanorods for photocatalytic application

Lik H. Wee,*[a] Nikki Janssens,[a] Sreeprasanth P. Sree,[a] Christian Wiktor,[b] Elena Gobechiya,[a] Roland A. Fischer,[b] Christine E. A. Kirschhock,[a] and Johan A. Martens[a]

[a]Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, B3001, Heverlee, Leuven, Belgium. Fax: +32 1632 1998; Tel: +32 1637 6748; E-mail: likhong.wee@biw.kuleuven.be
[b]Inorganic Chemistry II, Ruhr-University Bochum, Universitätsstrasse 150, 44801 Bochum, Germany.

Synthesis:
ZIF-8 was prepared from a synthesis mixture containing 11.75 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 25.92 g of 2-methylimidazole dissolved in 400 mL of DMF via vigorous stirring. The solution was poured into a 2 L SCHOTT bottle (DURAN®) and heated to 140 °C for 2h. The product was recovered and washed with ethanol through repeated centrifugation and redispersion in an ultrasonic bath. Solid was dried in an oven at 60 °C. Synthesis of ZnO@ZIF-8: 0.5 g of ZIF-8 powder was dispersed in 17.5 mL of 53.7 mM silver nitrate precursor Milli-Q ultrapure water:ethanol (v/v= 1:6) solution and agitated overnight. The solid was washed with absolute ethanol and dried at room temperature. ZIF-8 coatings on carbon paper were prepared according to the reported method by Hupp and co-workers, Adv, Mater. 2012, 24, 3970-3974. 15 (layers were coated).

Characterizations:
ZIF-8 and ZnO@ZIF-8 powders; ZIF-8 and ZnO@ZIF-8 coatings on carbon paper were characterized by a scanning electron microscope (SEM, Philips XL-30 FEG equipped with a tungsten filament); a powder X-ray diffractometer (XRD, STOE STADI MP diffractometer with a linear position sensitive detector (PSD) (6° 2θ window) in the region 2θ = 3 to 80°, with a step width of 0.5°, internal PSD resolution 0.01°, and a steptime of 150 s. The measurements were performed in Debye-Scherrer mode at room temperature using $CuK\alpha_1$ radiation with $\lambda = 1.54056$ Å selected by means of a Ge(111) monochromator. The ICDD database PDF-2 release 2008 has been used for the identification of the ZnO phase in the sample. XRD quantitative phase analysis using the Rietveld method [1] and FullProf software package [2] were employed to quantify the weight fraction of ZnO in ZnO@ZIF-8 sample. To verify the reliability of the result, a series of ZnO@ZIF-8 mixed samples containing 5, 15, 30, 50 and 70 wt% of ZnO were prepared and the weight fraction of ZnO in each mixture was determined by XRD quantitative phase analysis using the Rietveld method. The calibration curve, a linear fit of the data was calculated (see Fig. S2). As observed, the weight fraction of ZnO obtained from the Rietveld method is slightly lower (1-3 wt%) than in the prepared mixtures; a Nova Nano scanning electron microscope NanoSEM450 (FEI, Eindhoven), and a N_2 adsorption instrument (Micromeritics Tristar 3000); a solid state Cary Series UV-Vis NIR Varian spectrophotometer; Bright field TEM (BFTEM), high resolution TEM (HRTEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a FEI Tecnai F20 G^2 operated at 200 kV equipped with a Schottky field emission gun. A few drops of a dispersion of the material in methanol were put on a Cu TEM grid coated by a holey carbon film.

Photocatalytic reactions:
The photocatalytic tests were carried out in a Luzchem photoreactor with rotating sample carousel and equipped with 14 UV-A light tubes (Hitachi, FL8BL-B, 8 Watt; Sylvania, T5 lamp, 28 watt, cool white), 8 of which were positioned at the top and 3 sideways of the reactor compartment. Air-saturated aqueous solutions (5 mL) of methylene blue (50 ppm) to which 10 mg of ZnO@ZIF-8 photocatalyst, 1.1 mg of Degussa P25 TiO_2 (Evonic) or pure ZnO nanopowder (Sigma-Aldrich) was added in closed Pyrex test tubes (10 mL volume), each provided with a magnetic stirring bar. To exclude any possible influence of the temperature on the degradation of the organic compound, the temperature in the reactor was set at 35 °C by

using a thermostat. Prior to UV light illumination, the suspension was strongly magnetically stirred for 3 h in the dark for adsorption/desorption equilibrium.The UV irradiation time was 3 h. After reaction the catalyst was separated from the aqueous solution by centrifugation. The percentage of methylene blue degradation was determined by a UV-Vis spectrophotometer (Infinite 200 PRO, Tecan).

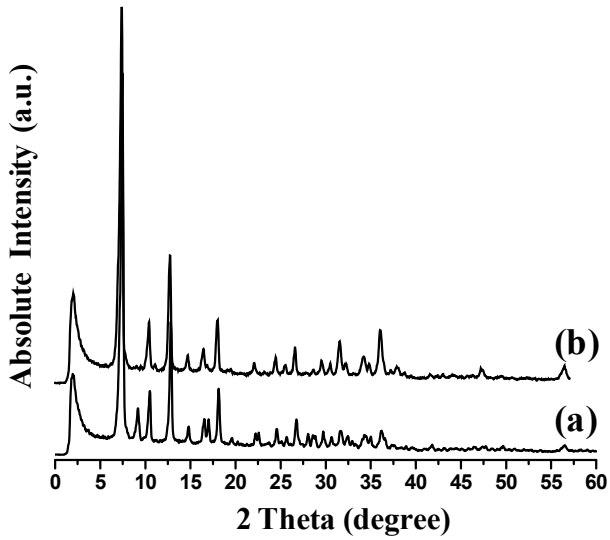

Figure S1. XRD patterns of (a) as-synthesized ZnO@ZIF-8 and (b) UV photoreacted ZnO@ZIF-8 catalyst. Data collected on STOE STADI P high-throughput setup in a transmission mode with an image plate position sensitive detector (IP PSD).

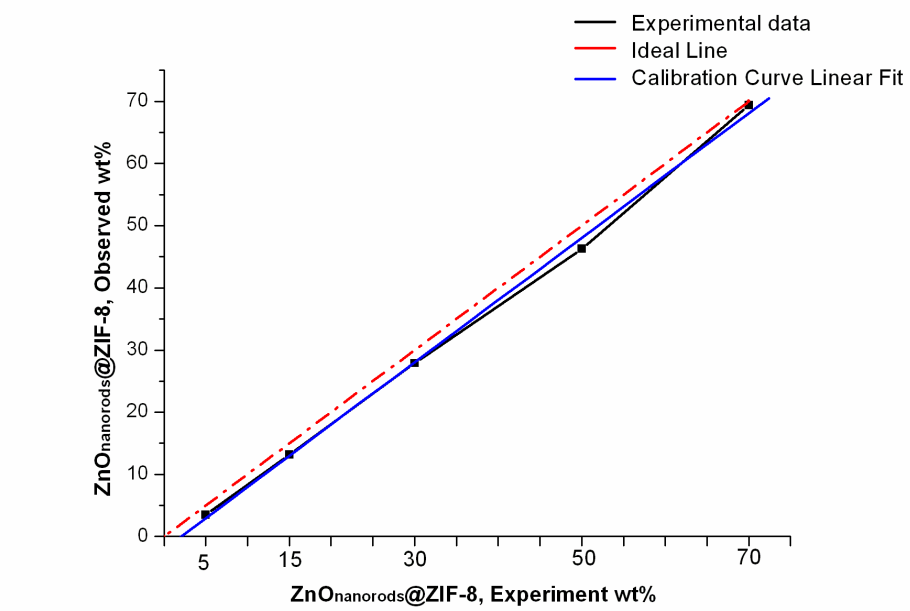

Figure S2. Calibration curve for the XRD quantitative phase analysis using Rietveld method.

[1] D. L. Bish and S. A. Howard, *J. Appl. Cryst.,* 1988, **21**, 86-91.
[2] J. Rodríguez-Carvajal, *Physica B: Condensed Matter,* 1993, **192**, 55–69