Supporting Information

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Hydrogen Generation from Photocatalytic Silver | Zinc Oxide Nanowires: Towards Multifunctional Multisegmented Nanowire Devices

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Experimental Details

Nanowire Templates: Commercially available Nuclepore® (Whatman Inc.) polycarbonate track-etched (PCTE) membranes with a thickness of 6 μm, a pore diameter of 200 nm and a pore density of ~3x10^8 pores/cm^2 were used as template for the formation of nanowires with lengths up to 6 μm.
To obtain templates for the synthesis of multifunctional multisegmented nanowires of more than 6 μm length, polycarbonate foils with a thickness of 30 μm were irradiated at the GSI in Darmstadt with swift heavy ions with fluences in the range 10^4–10^9 ions/cm^2. In order to obtain cylindrical pores the ion tracks were etched using a solution of 5 M NaOH containing 10% methanol at 50 °C. In this way we prepared membranes containing pores with diameters ranging from 130 nm to 500 nm. Further details can be found elsewhere.[S1,S2]

Nanowire Synthesis: Prior to electrodeposition, a gold layer with a thickness of 50 nm was sputtered on one side of the membrane. The gold coated side was then attached to a glass slide with double-sided tape and used as working electrode in a 3-electrode setup using a Bank Elektronik POS 73 potentiostat and an Autolab PGSTAT 128N potentiostat from Metrohm. As counter electrode a small piece of platinum mesh was used. The reference potential was set by a 3M KCl Ag/AgCl reference electrode (REF 321, Radio Analytical) or a Ag/AgCl reference electrode (Metrohm). Silver segments were deposited from an electrolyte solution containing 0.20 M AgNO₃ (99+%%, Acros) and 0.10 M H₃BO₃ (99.99%, Sigma-Aldrich). The pH was adjusted to 1.5 with nitric acid. Silver deposition was done potentiostatically at room temperature at +0.10 V versus reference. Zinc oxide segments were deposited at -1.00 V at 70°C from an aqueous electrolyte solution containing 0.10 M Zn(NO₃)₂·6H₂O (98%, Sigma-
Platinum segments were deposited at -0.3 V from an aqueous solution containing 0.01 M H₂PtCl₆·6H₂O (Sigma-Aldrich). Gold segments were deposited using a saw-tooth potential ranging from +0.97 V to 0 V and back to +0.97 V at a scan rate of 0.01 V/s from an aqueous solution containing 0.005 M HAuCl₄·3H₂O (Sigma-Aldrich). Nickel segments were deposited at -1.00 V from an aqueous electrolyte solution containing 0.23 M NiSO₄·6H₂O (>99.0%, Sigma-Aldrich) and 0.15 M H₃BO₃ (99.99%, Sigma-Aldrich). After deposition, the PCTE membranes were dissolved in dichloromethane (Merck).

Characterization: The isolated nanowires were characterized using a Zeiss HR-LEO 1550 FEF Scanning Electron Microscope (SEM), before and after the photocatalytic experiments. EDX mapping was done using a NORAN EDS spectrometer equipped in the SEM. The $I-V$ characteristics were determined using a Karl Suss PM8 low leakage Manual Probe Station and a Keithley 4200 power source.

Photocatalytic experiments: Approximately 0.1 g of segmented nanowires were suspended in 50 mL of a 4:1 vol/vol methanol/water mixture in a sealed quartz tube with a total volume of 72 mL. A Pd-based Kebaili KHS-100 hydrogen sensor, based on a palladium/nickel alloy which is highly selective for hydrogen, was placed in the plug and properly sealed. The hydrogen sensor was connected to a standard Wheatstone bridge. The voltage response was logged every second with a Peaktech multimeter connected to a computer. A UV-source of 60 W was used, at a distance of 10-15 cm from the sample. The experiments were performed in ambient atmosphere.

References