

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

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Nanowires have a high potential for use in a range of biomedical and nanotechnological applications, such as sensing, multiplexing, and imaging, and for gene delivery and vaccinations.^[1] Many single component nanowires with functional properties have been reported, e.g., optically active ZnO and CdTe,^[2] catalysts such as Au and Pt,^[3] and magnetic Ni, Fe₂O₃ and Fe₃O₄ phases.^[4] But a variety of metals, polymers, and metal oxide segments can also be incorporated sequentially into the wires, for instance via infiltration or templated electrodeposition techniques.^[5] Such a modular approach allows the fabrication of multifunctional nanowires that consist of different segments, each with their own specific function. Even functional properties not present in the individual segments may emerge when these are connected into a single nanowire. For instance, segmented Au|Pt nanowires have been reported that are able to move autonomously when placed in a hydrogen peroxide solution.^[3]

In the present communication, a novel type of segmented nanowire with emergent photocatalytic property is demonstrated. It can be used as such for photochemical conversion of suitable reactants, and/or be combined with other functional materials to realize multiple functions, including photocatalytic, in a single nanowire. While the emphasis of this study is to demonstrate the photocatalytic function of the metal-oxide|metal nanowire module, an example of a multifunctional nanowire will also be shown below.

Fujishima and Honda showed that water can be split under UV light by a rutile electrode coupled to a platinum electrode.^[6] Over 130 types of semiconductors have been identified in the mean time as photocatalysts.^[7] Among the

most intensively studied are titanium dioxide,^[8] zinc oxide,^[9] and iron oxide.^[10] When these materials are miniaturized into nanoparticles or nanowires, the surface-to-volume ratio is increased drastically, leading to improved photocatalytic efficiencies.^[7a,b,11] For the construction of our nanowire, we combined the photoactive n-type semiconducting ZnO phase with Ag via sequential electrodeposition in a polycarbonate track-etched (PCTE) membrane with straight-channel pores of 50–200 nm diameter and 6–30 μ m length.^[12] We used the conversion of methanol and water into hydrogen and carbon dioxide as a model reaction to show that a metal and a metal oxide nanowire component, connected via a Schottky barrier, allow the formation of hydrogen under the influence of UV light.

A scanning electron microscopy (SEM) image of a small bundle of three ZnO|Ag nanowires is shown in **Figure 1a**. The ZnO phase acts as photoanode, and Ag as cathode. In contrast to conventional photo-electrochemical cells, no external circuit connecting the electrodes is present. This aids in increasing efficiency by reducing Ohmic losses, and simplifies device architecture and ease of construction considerably in comparison with conventional photoelectrochemical cells. Figure 1b shows a schematic overview of the envisaged process. The combination of ZnO and Ag was selected because the electron affinity of ZnO is slightly higher (4.35 eV) than the work function of Ag (4.25 eV). This allows the formation of a Schottky barrier between these phases,^[13] across which excited electrons can flow freely from the conduction band of ZnO into Ag, without a chance of electron–hole recombination.^[14] Moreover, ZnO can be formed already at 60–90 °C in the active wurtzite phase, while most other photoactive oxides made via cathodic electrodeposition would require an intermediate high-temperature treatment in order to be formed.

The conversion of methanol–water mixtures into hydrogen and CO₂ is a relatively low-energy process. Methanol acts as a hole scavenger at the ZnO anode, and is oxidized into CO₂ following the net reaction $\text{CH}_3\text{OH} + \text{H}_2\text{O} + 6\text{h}^+ \rightarrow \text{CO}_2 + 6\text{H}^+$, where h^+ indicates an electron hole. At the silver cathode, protons are reduced to H₂ according to $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$. The net energy required for the overall reaction is 0.7 eV,^[8b] much smaller than the bandgap of ZnO (3.2 eV).

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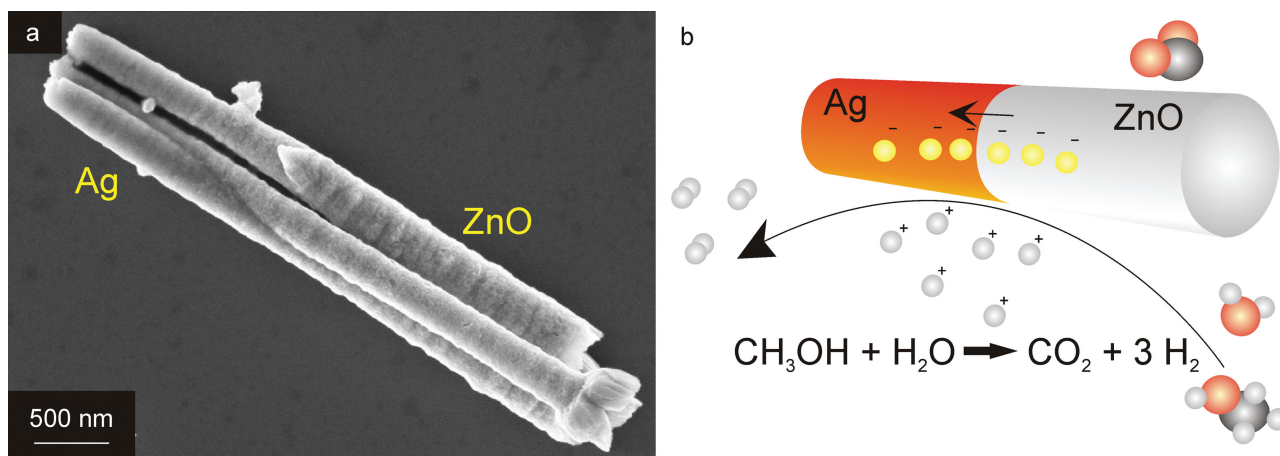


Figure 1. a) SEM image of axially segmented ZnO|Ag nanowires of 200 nm diameter and 6 μm length; b) working principle of photoactive segmented Ag|ZnO nanowire. UV radiation is absorbed by the ZnO segment, creating an electron–hole pair. The electrons flow into the Ag phase and are consumed in an electrochemical reduction process. The hole in the ZnO segment is consumed in an oxidative half-reaction.

In order to verify that a Schottky barrier had formed between the silver and wurtzite phases, the I – V curves of an ensemble of segmented Ag|ZnO wires was determined by sputtering a small gold electrode on top of a PCTE membrane containing as-grown nanowires, and characterized by two-point measurements. This method ensures good ohmic contacts between electrodes and nanowires, but the number of wires included in the measurement is not known exactly. Moreover, the PCTE matrix is still present, which might influence the experimental data. So while the presence or absence of a Schottky barrier in the wire may be determined from this measurement, the absolute conductivity can not be estimated.

The I – V characteristics of single-component Ag and ZnO wires were therefore also determined (**Figure 2**). To this end, a PCTE matrix containing as-grown wires was dissolved in dichloromethane, followed by breaking off the nanowires from the bottom electrode via ultrasonic treatment. The wires in solution were then positioned between gold microelectrodes using a dielectrophoretic alignment technique.^[15] This method ensures that the measured current passes through a single wire, but establishing good ohmic contacts between microelectrodes and nanowire is challenging. However, the overall shape of the I – V curve measured from the nanowire ensemble in Figure 2c was exactly the same as for the single nanowire,^[15] and the difference in conductivity may be attributed to the uncertainty in the number of wires that contributed to the conductivity of the ensemble.

An example of an aligned Ag|ZnO nanowire is shown in Figure 2a. The I – V characteristics of Ag, ZnO, and segmented Ag|ZnO nanowire ensembles are shown in Figure 2b–d. The current responses of Ag and ZnO nanowires showed ohmic and semiconducting behavior, respectively. Their response was symmetrical and did not show rectifying behavior, suggesting ohmic contacts with the gold electrodes. The shape of the Ag|ZnO curve is also representative of a semiconductor, implying ohmic contacts to the Au

electrode and the Ag segment of the nanowire. However, the I – V curve was symmetrical around $V = +200$ mV. This indicates a small energy barrier between silver and zinc oxide, in agreement with theoretical expectation. Since it requires more energy to inject electrons into ZnO via the silver segment, the symmetry point is expected to move to positive values under a forward bias, indicating the presence of a space charge layer. These measurements show that Ag|ZnO segmented nanowires behave like Schottky barriers, as theory predicts.

The photocatalytic activity of the nanowires was tested in a 4:1 v/v methanol/water solution. A Pd-based sensor placed in the atmosphere directly above the solution was used to detect gaseous hydrogen (**Figure 3**). It is noted that this experiment cannot detect hydrogen dissolved in the methanol/water phase. As can be seen in Figure 3a, the Pd-based sensor is also slightly cross-sensitive to methanol, so therefore a reference sample without nanowires was also measured. After UV exposure, the signal for the sample with segmented Ag|ZnO nanowires increased much faster than the signal from the reference sample.

The increase in potential indicates that gaseous hydrogen was forming and evolving from the solution. This was supported by the visual observation of the formation of small gas bubbles in the test tube. By comparing the potential response of the sensor in a 4 vol% H_2 in N_2 gas stream, it was estimated that approximately 0.2 vol% H_2 had formed in the gas volume by the Ag|ZnO nanowires after 17 min. It is noted that the presence of methanol vapor may slightly poison the Ni-Pd sensor surface and causes a slight decrease of output potential. However, the effect should be small compared to the change that we measured experimentally in this experiment, and it was observed that the signal returned to its original value in air after the experiment.

When the same experiment was repeated in the absence of nanowires, no gas bubble evolution was observed. In this case the sensor showed a very small increase of potential with time directly after UV exposure. Other reference experiments

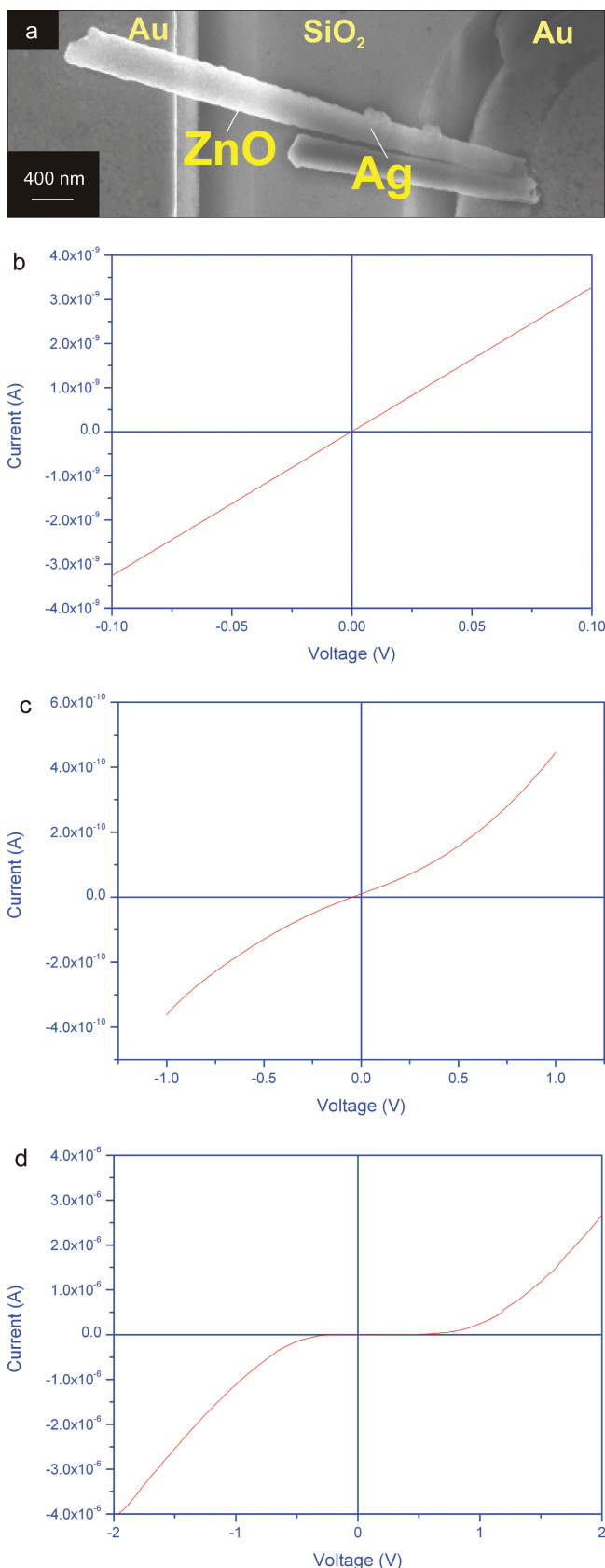


Figure 2. a) Segmented Ag|ZnO nanowire placed between gold microelectrodes via dielectrophoretic alignment; b–d) *I*–*V* curves of b) Ag nanowires, c) ZnO nanowires, and d) Ag|ZnO nanowires.

with single-phase ZnO or Ag nanowires, not shown here, gave no indication for the formation of hydrogen.

In the UV experiments involving nanowires, the formation of gas bubbles typically ended after ~48 h of irradiation. The reason for the loss of activity can be ascribed to photocorrosion of ZnO, following the reaction $\text{ZnO} + 2\text{h}^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2}\text{O}_2$.^[16] Figure 3b shows an SEM image of a Ag|ZnO segmented nanowire after experiments. The surface of the ZnO segment is corroded and appears much rougher than the as-synthesized wires of Figure 1b. To verify that the corrosion was in fact the result of photocorrosion and not of electrolytic corrosion, segmented nanowires were suspended in the methanol/water mixture and left in darkness for 48 h, but no indication of corrosion was found in that case. Methods for the inhibition of ZnO photocorrosion, including grafting of ZnO nanorods on TiO₂ nanotubes, and hybridization of ZnO nanoparticles with a monolayer of polyaniline or C₆₀ have been reported in the literature.^[16c,17]

It is envisaged that the Ag|ZnO couple could be applied as a photoactive module in multisegmented nanowires that can carry out more than one function at a time. The SEM image in **Figure 4** shows a 20 μm long nanowire with a diameter of 450 nm, containing six segments: Pt|Au|Pt|Ni|Ag|ZnO, that are responsible for three functions: i) The Pt|Au segments are electrochemically active in aqueous solutions containing a ‘fuel’ such as hydrogen peroxide, and they can propel the nanowire to move autonomously as a nanomotor;^[3,18] ii) The Ni segment is ferromagnetic, so that an external force can be applied to the nanowire in solution via an external magnet;^[18d] and iii) The Ag|ZnO segments are photoactive as demonstrated above. The six-segment nanowire in Figure 4 was made by sequential electrodeposition of the respective phases in nanopores. This modular approach is very versatile and could also be utilized to construct other multifunctional nanowires.

In summary, we demonstrated that Ag|ZnO nanowire diodes of 200–450 nm diameter and a length of about 6 μm are photocatalytically active in the conversion of methanol to hydrogen under UV illumination. These nanowires could find application in multifunctional nanowires and nanowire devices.

Experimental Section

Nanowire Synthesis: Segmented Ag|ZnO nanowires were made by templated electrodeposition in polycarbonate track-etched (PCTE) membranes with a thickness of 6–30 μm , pore diameter of 130–500 nm, and pore density of $\sim 3 \times 10^8$ pores/cm². A three-electrode setup was used, in which a Au-coated PCTE membrane acted as working electrode.

Silver segments were deposited from an electrolyte solution containing 0.20 M AgNO₃ (99+%, Acros) and 0.10 M H₃BO₃ (99.99%, Sigma-Aldrich) at room temperature at +0.10 V versus Ag/AgCl reference. Zinc oxide segments were deposited at –1.00 V at 70 °C from a 0.10 M Zn(NO₃)₂ solution. Platinum was deposited at –0.3 V from a 0.01 M H₂PtCl₆ solution. Gold segments

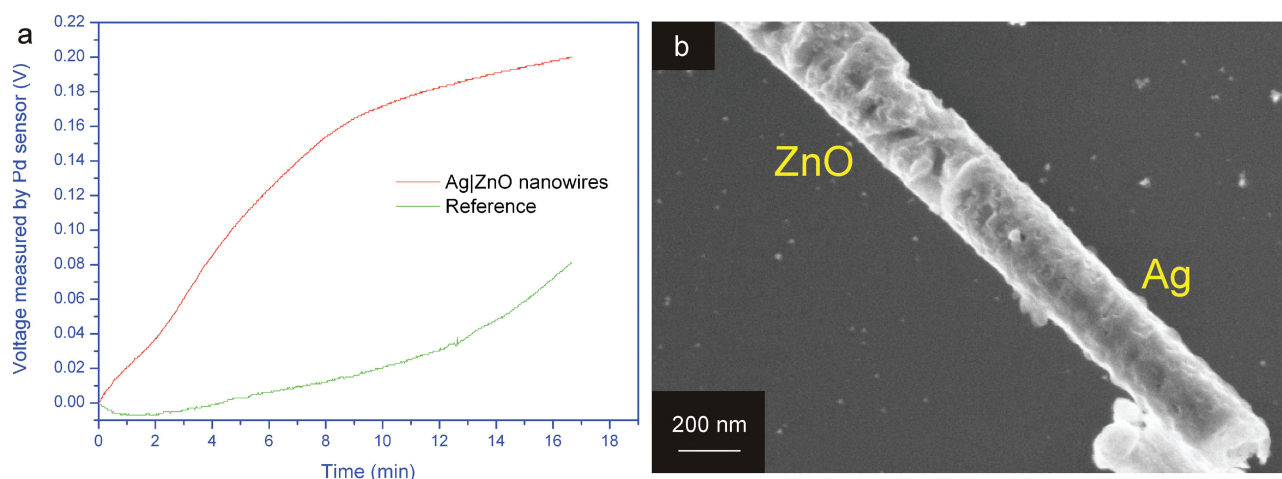


Figure 3. a) Hydrogen sensor response during UV irradiation of a methanol/water solution containing Ag|ZnO segmented nanowires (red line). Reference experiment without nanowires is indicated by a green line; b) SEM image of Ag|ZnO nanowire after 48 h of UV exposure.

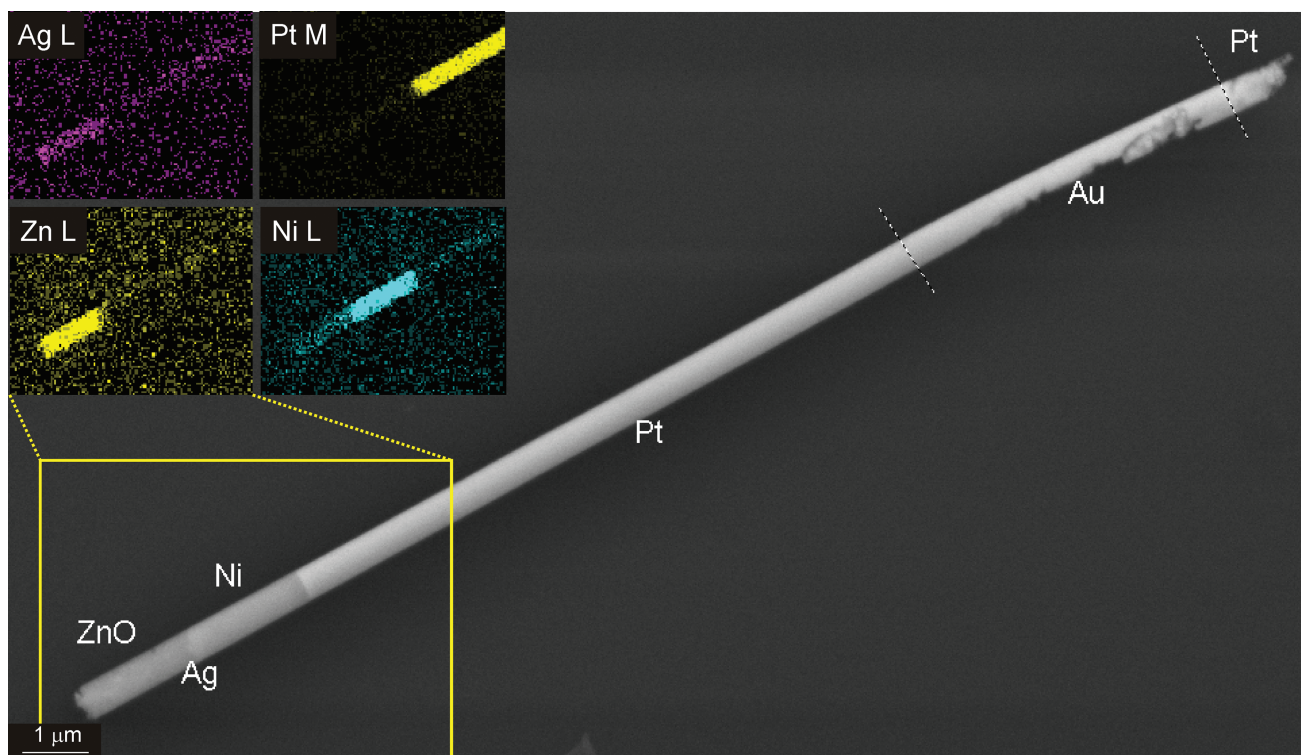


Figure 4. Multifunctional nanowire composed of six segments Pt|Au|Pt|Ni|Ag|ZnO. The inset gives energy dispersive X-ray (EDX) spectroscopy maps indicating the distribution of the metallic elements, Ag, Zn, Pt, and Ni, in the part of the nanowire at the bottom left corner of the figure.

were deposited using a saw-tooth potential ranging from +0.97 to 0 V and back to +0.97 V at a scan rate of 0.01 V/s from a 0.005 M HAuCl₄ solution. Nickel segments were deposited at −1.00 V from a solution containing 0.23 M NiSO₄ and 0.15 M H₃BO₃. Further details can be found in the Supporting Information.

Photocatalytic Experiments: A 0.1 g sample of nanowires were suspended in 50 mL of a 4:1 v/v methanol/water mixture in a sealed quartz tube with a total volume of 72 mL. A Pd-based hydrogen sensor was used to detect hydrogen. A UV-source of 60 W was used, at a distance of 10–15 cm from the sample. These experiments were performed in ambient atmosphere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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