A Facile Approach to ZnO/CdS Nanoarrays and Their Photocatalytic and Photoelectrochemical Properties

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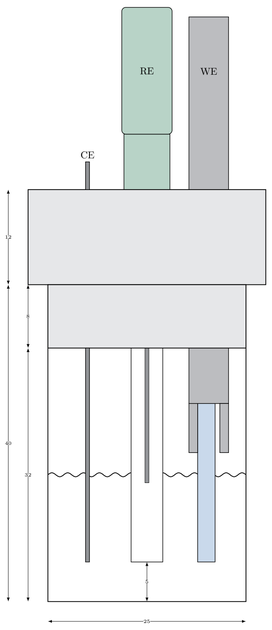
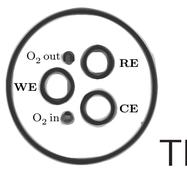
Electrochemical deposition of ZnO

The working electrode is kept at a potential negative to the reduction potential of O_2, which causes oxygen gas near the electrode to be reduced to hydroxide ions. The hydroxide ions react with the zinc ions and forms zinc hydroxide, zinc oxyhydroxide or zinc oxide (depending on temperature).

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \leftrightarrow 2\,OH^- \qquad (E^\circ = 0.40\,V)$$
$$Zn^{2+} + 2\,OH^- \rightarrow ZnO + H_2O$$



The oxygen is supplied by oxygen-bubbling into the headspace compartment (electrolyte solution is saturated prior to cell on).



The small schematic (above) shows the configuration of the cell as seen from above. The large schematic (left) shows the electrodeposition cell seen from the side (drawn to scale).

Cathodic deposition at −0.7 V vs. Ag/AgCl for 90 min with an initial pulse at −1.3 V vs. Ag/AgCl for 0.1 s, 0.5 s or 1.0 s.
Electrolyte: 0.1 mmol dm^{-3} $ZnCl_2$(aq) and 0.1 mol dm^{-3} KCl(aq).
A temperature of 80 °C was maintained using a thermostat-controlled waterbath.

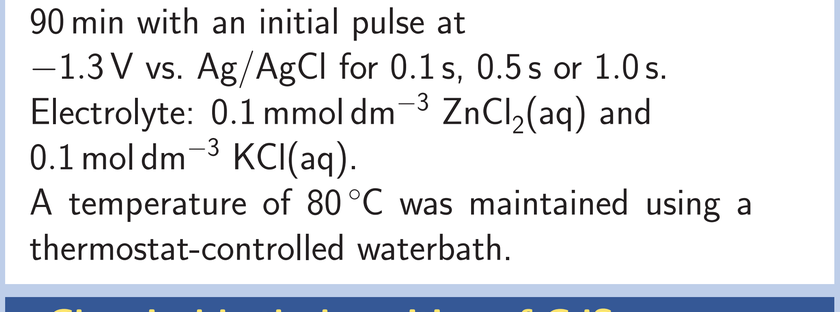
Chemical-bath deposition of CdS

An aqueous bath solution of 2 mmol dm^{-3} $CdSO_4$, 10 mmol dm^{-3} CH_4N_2S, and 1 mol dm^{-3} NH_3 was thermostatically maintained at 60 °C before immersing the substrate for a set amount of time (up to 2 h).

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
$$Cd^{2+} + 4\,NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$$
$$(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- \rightarrow S^{2-} + H_2O$$
$$Cd^{2+} + S^{2-} \rightarrow CdS\downarrow$$
$$Cd^{2+} + 2\,OH^- \rightarrow Cd(OH)_2\downarrow$$
$$Cd(OH)_2 + S^{2-} \rightarrow CdS\downarrow + 2\,OH^-$$

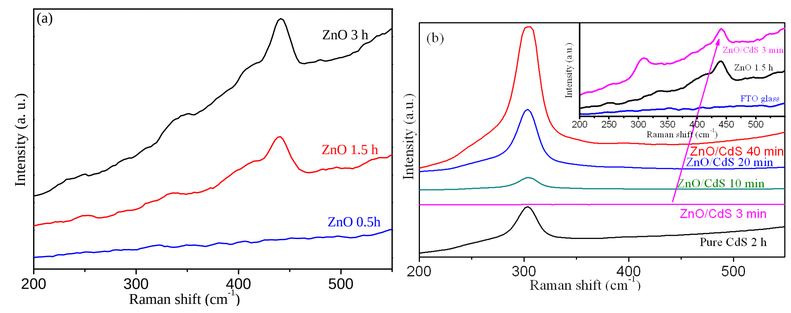
The substrate was suspended vertically and the solution was continuously stirred during deposition.

X-ray diffraction



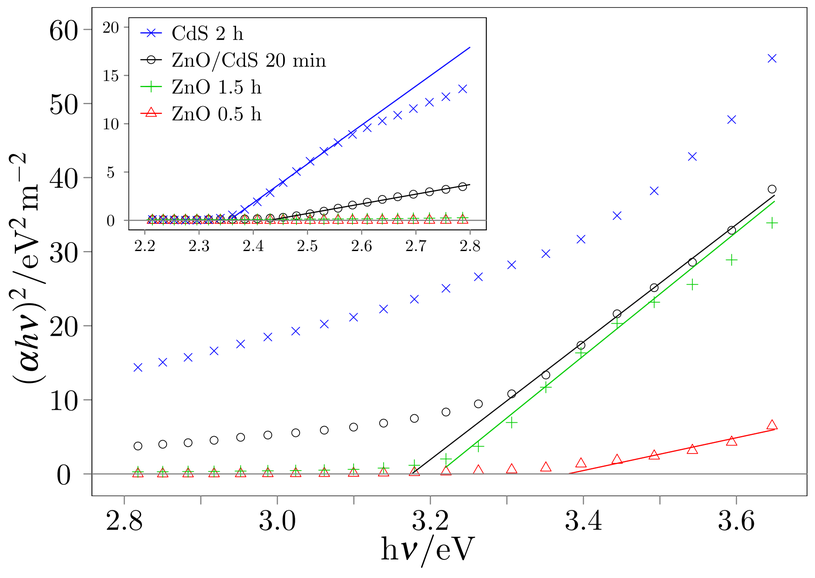
All ZnO samples have a hexagonal wurtzite structure. Preferential growth along the [0001] direction (normal to the (002) plane). As more ZnO deposits, the pH of the solution acidifies, and eventually the deposited rods suffer etching. Stopping the deposition after 90 min resulted in a maximum amount of deposited crystals.

Raman spectroscopy



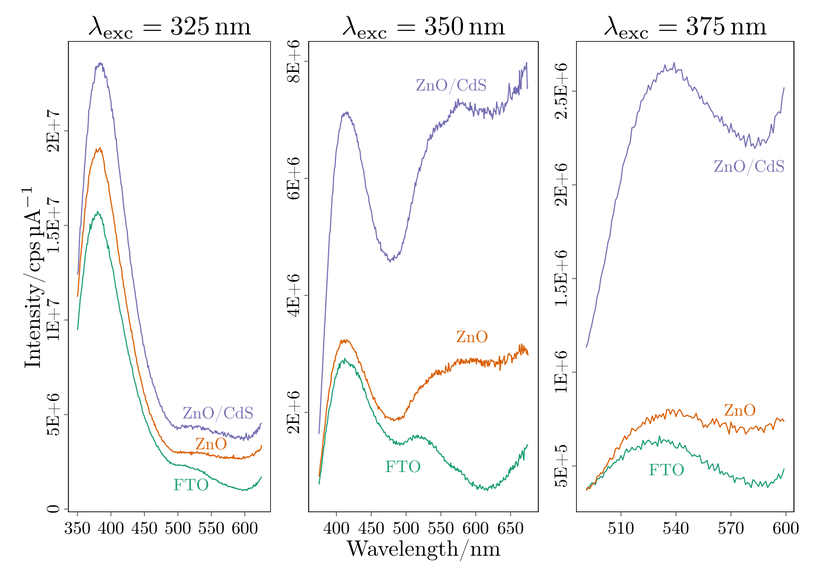
The 1LO peak of CdS at ≈ 309 cm^{-1} indicates the presence of the hexagonal CdS phase. It is probably stabilized by the hexagonal ZnO substrate. Both the ZnO and CdS peaks grow with longer deposition times.

Band gap via UV/Vis spectroscopy

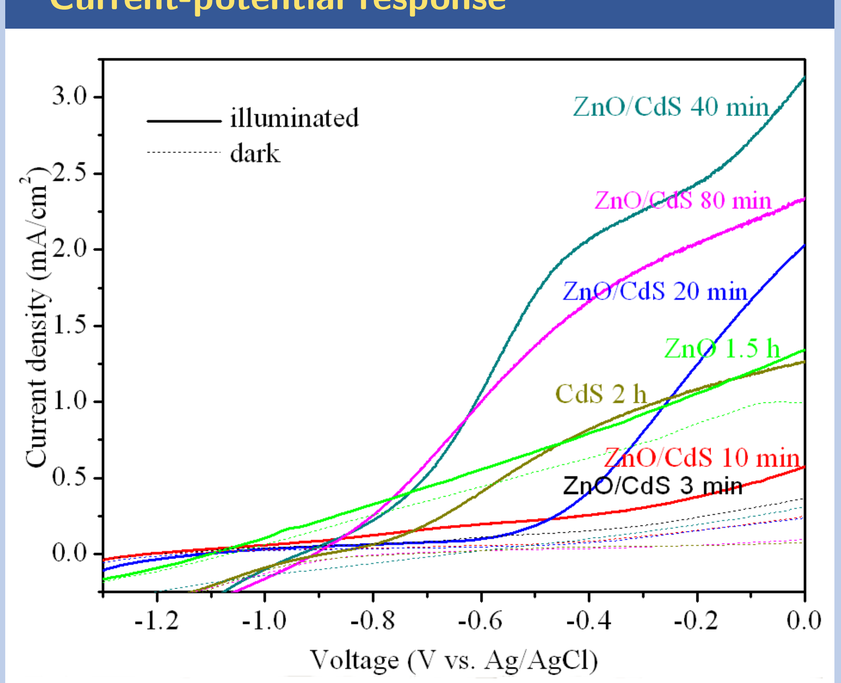


Band gap determination using Tauc plot assuming allowed direct transition. $E_g(ZnO) \approx 3.3$ eV, and $E_g(CdS) \approx 2.4$ eV. The band gap of CdS decreased with increasing deposition time, indicating crystallite growth.

Photoluminescence spectroscopy



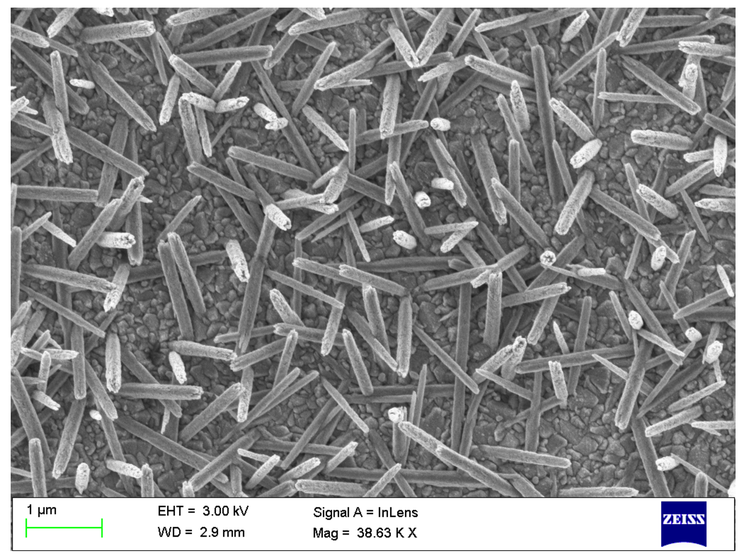
Current-potential response

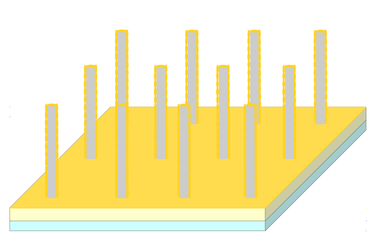


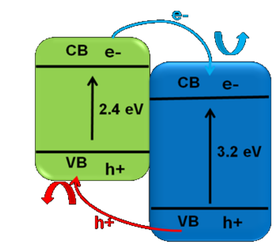
Summary

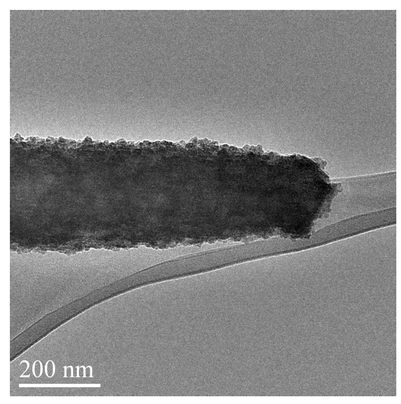
- Synthesis directly onto substrate by combining electrochemical deposition and chemical-bath deposition
- Good crystallinity, no need for calcination
- Well-matched band edges ensure good charge separation across the sc-sc interface, as shown by PL spectroscopy
- CdS/ZnO shows improved photoactivity compared to bare ZnO nanorods

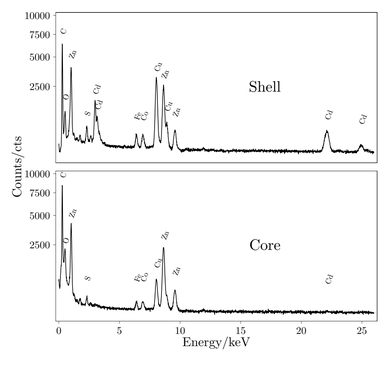
Morphology and composition



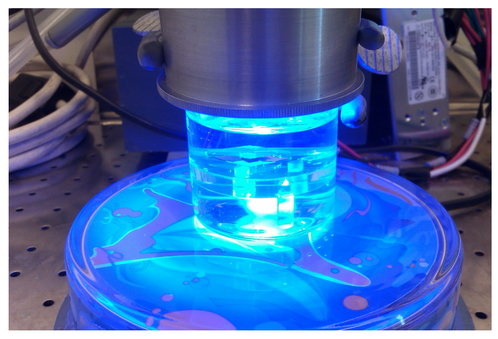




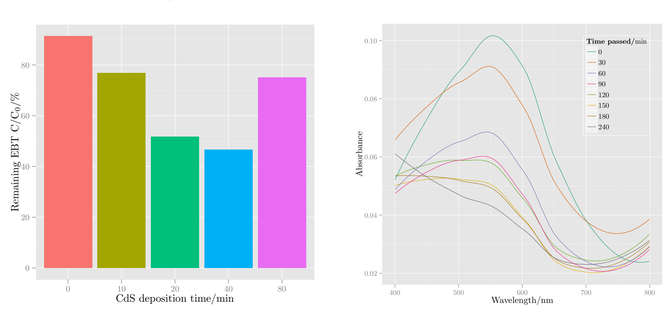




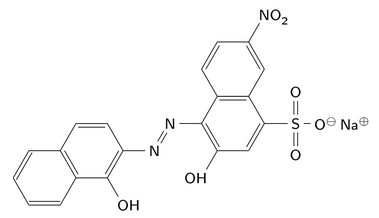
Photodegradation of Eriochrome Black T



A blue LED (450 nm) with an intensity of 0.4 W cm^{-2} (at the sample level) was used for photodegradation tests.



Left: Remaining EBT concentration after irradiation for 90 min. Right: Absorption spectra at different times for the ZnO/CdS 40 min sample.



Structural formula of Eriochrome black T dye.

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