

Supporting Information

Amorphous NiO Electrocatalyst Overcoated ZnO Nanorod Photoanode for Enhanced Photoelectrochemical Performance

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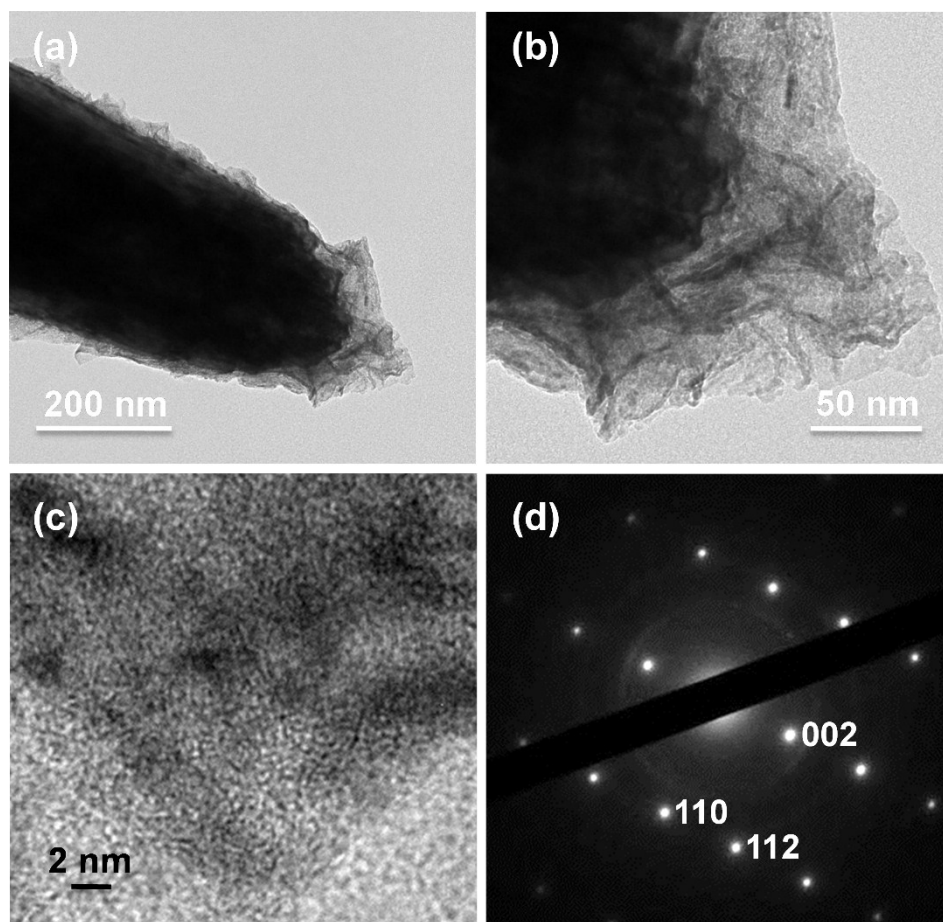


Fig. S1 (a) TEM image of a NiO/ZnO core-shell NR. (b) Magnified TEM image taken from the top of the core-shell NR in (a). (c) HRTEM image taken from the NiO shell. (d) Corresponding SAED pattern of the core-shell NR.

The detailed structure of the NiO/ZnO NRs was further investigated by TEM. The low-magnification TEM image in Fig. S1a directly exhibits the core-shell structure of the NiO/ZnO NRs. The wrinkled NiO nanosheets were tightly coated on the surface of ZnO NR. The magnified TEM image in Fig. S1b shows a lot of dark contrast stripes, which indicates the NiO nanosheets are highly folded. The width of the dark contrast stripes is ~2-3 nm, corresponding to the thickness of the nanosheet. The high-resolution TEM (HRTEM) image in Fig. S1c was taken from a part of the NiO nanosheet. It is revealed that the NiO shell has an amorphous structure. Fig. S1d is the corresponding selected-area electron diffraction (SAED) pattern of this core-shell nanorod in Fig. S1a. A set of bright spots decorated the broad and diffused halo diffraction ring. The bright spots can be indexed to hexagonal ZnO and confirm the single crystalline structure of the ZnO NR. The diffused halo ring is originated from the NiO nanosheets, indicating the amorphous feature of the NiO shell, which corresponds to the HRTEM and XRD results. The amorphous NiO shell can provide high electrocatalytic activity in oxygen evolution reaction from water. At the same time, the ZnO NR core with single crystalline structure can function as an effective electron transport pathway due to its high conductivity. Hence, the amorphous NiO nanosheet electrocatalyst shell on single crystalline ZnO NR semiconductor core form a promising composite photoanode configuration that may lead to a significant improvement of the PEC performance.

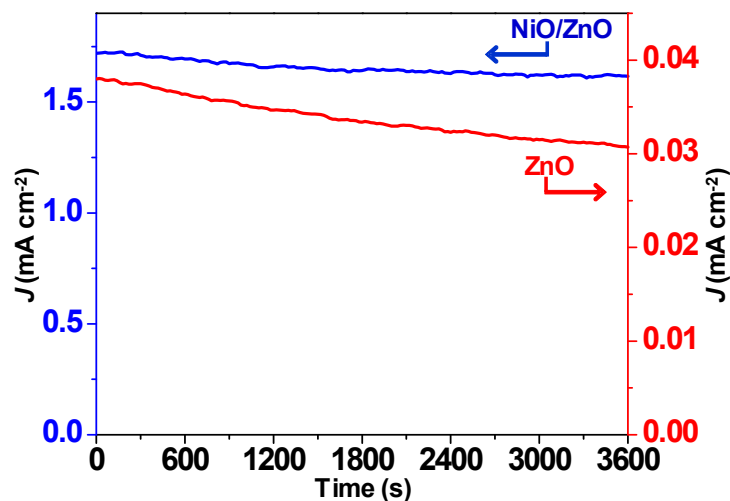


Fig. S2 Photocurrent stability performance over 3600 s of the NiO/ZnO and ZnO photoanodes at 1.2 V vs. RHE.

The photocurrent stability measurements of the NiO/ZnO and ZnO photoanodes were performed under a potential of 1.2 V vs. RHE, as shown in Fig. S2. The photocurrent density of the bare ZnO photoanode dropped 19% after 3600 s. In contrast, the NiO/ZnO photoanode exhibited an improved stability, which only dropped 6% after 3600 s. The superior stability of the NiO/ZnO photoanode is ascribed to the outer NiO electrocatalyst layer, which can quickly consume holes, and hence largely decrease the photocorrosion and electrocorrosion of ZnO.¹

The measured potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale through the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + \frac{\theta}{n} E_{\text{Ag/AgCl}}^{\circ}$$

where E_{RHE} is the converted electrode potential vs. RHE. $E_{\text{Ag/AgCl}}$ is the experimentally measured potential vs. Ag/AgCl reference electrode, and $E_{\text{Ag/AgCl}}^{\circ} = 0.1976$ V at 25 °C. The solar-to-hydrogen conversion efficiencies (η) were calculated from the photocurrent curves by using the following equation:²

$$\eta (\%) = J_{\text{ph}}(1.23 - E_{\text{app}})/P_{\text{light}}$$

where J_{ph} is the photocurrent density, P_{light} is the illumination power density (100 mW cm^{-2}), and E_{app} is the absolute value of the applied potential between the working and counter electrodes. E_{app} is obtained as $E_{\text{app}} = E_{\text{mea}} - E_{\text{aoc}}$, where E_{mea} is the electrode potential (vs. RHE) corresponding to the measured J_{ph} , and E_{aoc} is the open circuit potential.

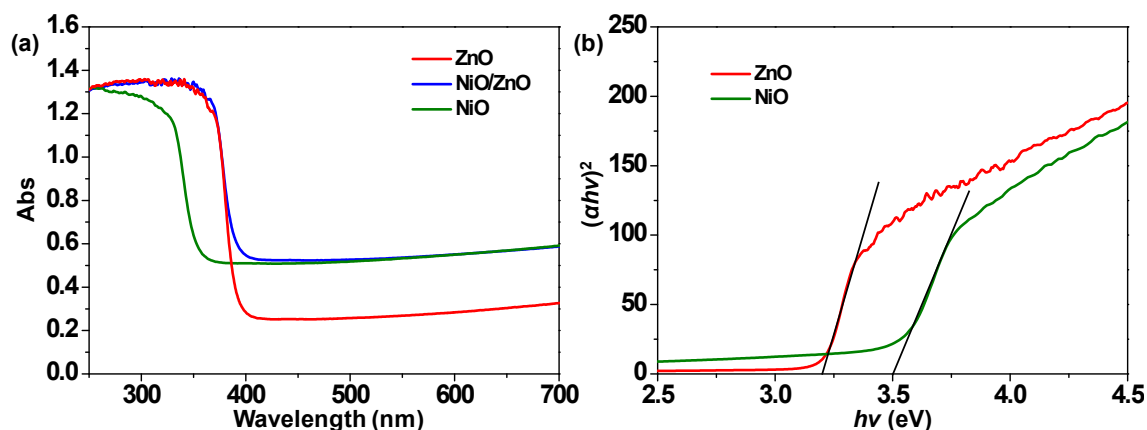


Fig. S3 (a) DRS spectra of bare ZnO, NiO/ZnO, and bare NiO. (b) $(\alpha hv)^2$ vs hv curves for bare ZnO and NiO.

The DRS spectra of bare ZnO, NiO/ZnO, and bare NiO were shown in Fig. S3a. In comparison to the bare ZnO, the NiO/ZnO exhibited a higher absorption in the wavelength range between 400 and 700 nm. Both the NiO/ZnO and ZnO have a similar absorption edge at ~ 380 nm, which is consistent with the ZnO band gap (E_g). Nevertheless, in the spectra of NiO/ZnO, the absorption edge corresponding to the E_g of NiO was not observed. It is because NiO has a larger E_g than ZnO and its absorption edge can be covered by that of ZnO. Thus, the DRS spectra of bare NiO was further investigated. As shown in Fig. S3a, the absorption edge of NiO was located at a lower wavelength (~ 350 nm) compared to ZnO. The E_g values of bare NiO and ZnO can be calculated from the equation of $(\alpha hv)^2 = A (hv - E_g)$. Here α is the absorption coefficient, A is a constant for the material, and hv is the photon energy. As shown in Fig. S3b, by extrapolating the value of hv to $\alpha = 0$, the E_g values of NiO and ZnO were obtained to be 3.5 and 3.2 eV, respectively.

Table S1 Summary of PEC performance parameters of ZnO NR and NiO/ZnO core-shell NR

photoanodes. $E_{\text{H}_2\text{O}/\text{O}_2}^\ominus$ is the thermodynamic potential (1.23 V vs. RHE) for oxygen evolution.

Photoanode	$J@ E_{\text{H}_2\text{O}/\text{O}_2}^\ominus$ (mA cm ⁻²)	Onset potential (V)	η (%)
ZnO	0.04	0.98	0.06
NiO/ZnO	1.87	0.72	1.81

References

- 1 S. Xie, W. Wei, S. Huang, M. Li, P. Fang, X. Lu and Y. Tong, *J. Power Sources* 2015, **297**, 9-15.
- 2 S. U. M. Khan, M. Al-Shahry and W. B. Ingler, *Science*, 2002, **297**, 2243-2245.