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Transparent ALD-grown Ta_2O_5 protective layer for highly stable ZnO photoelectrode in solar water splitting

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Supporting Information

Preparation of ZnO seed layer

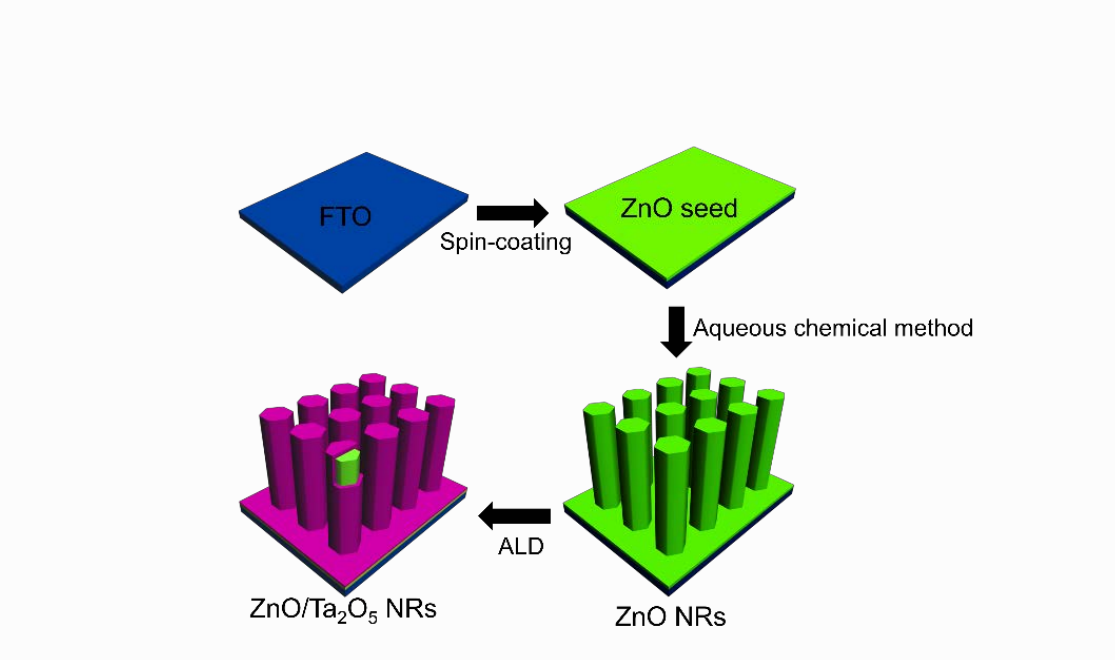
ZnO seed layer was produced on 1 cm × 2.5 cm FTO glasses (Nippon Sheet Glass, Japan) by a spin-coating method.[1] Firstly, the FTO glasses were ultrasonically cleaned in acetone, ethanol and distilled water bath for 15 min, sequentially. Then 10 mM $Zn(CH_3COO)_2 \cdot 2H_2O$ (98%, J&K Scientific Ltd.) was dissolved in ethanol. The prepared acetate solution was coated on the FTO glasses using a spin coater at 2500 rpm for 30 s and the coated glass substrates were dried in an oven at 130 °C for 5 min. This step was repeated five times and then the fully coated glass substrate was annealed at 350 °C for 0.5 h.

Preparation of ZnO nanorods

All reagents were analytical grade and used directly without any purification. 1.7849 g zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.0%, Tianjin Wei Chen Chemical Reagent Technology and Trade Co. Ltd.) and 0.8411 g hexamethylenetetramine (HMTA, 99.5%, Aladdin Industrial Inc.) were mixed in 120 ml deionized water ($[Zn^{2+}]$=[HMTA]=50 mM). The FTO substrates with seed layer were placed downward in the reaction solution and heated to T = 90 °C for 3 h. After the reaction, the samples were cleaned with de-ionized water, dried at 80 °C and annealed at 500 °C for 1 h.

Atomic layer deposition of Ta_2O_5 thin film

Ta_2O_5 thin film was deposited onto ZnO NRs at 200 °C in a home-made ALD system using $Ta(NMe_2)_5$ (99.99%, Sigma-Aldrich Co. LLC.) and H_2O as precursors. The precursors were held at 65 °C and 25 °C respectively. One ALD cycle consists of $Ta(NMe_2)_5$ dose for 2 s, N_2 purge for 15 s, water dose for 0.2 s and N_2 purge for 10 s.



Scheme 1. Schematic of the synthesis process of ZnO/Ta_2O_5 NRs.

Structural and optical characterization

X-ray diffraction patterns were recorded with a Bruker D8 Focus operating at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation (λ = 1.54056 Å) and operating in a 2θ range of 20 – 80 at a scan rate of 6 per minute. The morphologies were characterized by field emission scanning electron microscope (FE-SEM, S-4800) and transmission electron microscopy (TEM, JEM-2100F, 200 kV). XPS analysis of the samples was carried out on a Physical Electronics PHI 1600 ESCA system with an Al Kα X-ray source (E = 1486.6 eV). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. The optical properties of Ta_2O_5 thin films were characterized by an M-2000 DI spectroscopic ellipsometer (J.A. Woollam Co., Inc.). UV-visible reflectance spectra and transmittance spectra of nanorod samples were obtained on a SHIMADZU UV-2550 spectrophotometer.

PEC measurements

PEC measurements were performed in 0.1 M KOH (pH 13) using a custom quartz 3-electrode cell with Pt foil as the counter electrode, Ag/AgCl as the refrence electrode and ZnO or ZnO/Ta_2O_5 sample as the working electrode. In order to simulate sunlight, a 300 W xenon lamp (PLS-SXE300C, Beijing Perfectlight) equipped with an AM 1.5 filter was used as the light source, and the power intensity of the light was calibrated to 100 mW/cm^2. All potentials were converted to reversible hydrogen electrode (RHE) scale by: $V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059pH$.

The voltage measured at reference electrode in RHE scale could be used as the potential between the working electrode and the counter electrode ($V_W - V_C$) to calculate the photo-conversion efficiency (η), since reaction at the counter electrode (Pt electrode) is the reduction of H^+ to H_2.

For a 1 cm^2 sample, 1.3 coulombs of electric charges is needed to fully oxidize a dense ZnO film of 1 μm thickness, which is far less than the electric charges that passed through the electrode over the entire stability test (16 coulombs for ZnO/Ta_2O_5 electrode and 8.7 coulombs for ZnO electrode under AM 1.5G). Therefore, the stable photocurrent of ZnO/Ta_2O_5 (trace ii, Fig. 3) over a 5 h period should be long enough to exclude the existence of electrode corrosion, considering that the ZnO NR sample in this study contains less ZnO compared with a dense 1 cm^2 by 1 μm ZnO film because of the relatively loosely packed ZnO NRs of ~1 μm in length.

The thickness of planar Ta_2O_5 on Si monitor substrate is obtained from spectroscopic ellipsometry (M-2000 DI, J.A. Woollam Co., Inc.) at 60° and 70° incident angle, by fitting the amplitude ratio (Ψ) and phase shift (Δ) of polarized light with the Cauchy dispersion model at 0.72 – 4.2 eV (below the band gap of Ta_2O_5). The Si monitor substrate was placed 10 mm next to the ZnO NR sample.

Structure of the optical model:

Layer 2	Ta_2O_5 (Cauchy model)
Layer 1	Native oxide (1.69 nm, measured before deposition)
Substrate	Si

Fitting results: Ta_2O_5 thickness = 1.83 nm (30 ALD cycles) with MSE =1.142

The quality of the fitting was assessed by the mean-squared error (MSE) function:

$$\mathrm{MSE} = \frac{1}{2N-M} \times \sum_{i=1}^{N} [(\frac{\psi_i^{\mathrm{mod}} - \psi_i^{\mathrm{exp}}}{\sigma_{\psi,i}^{\mathrm{exp}}})^2 + (\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}})^2]$$

where N represents the number of (Ψ, Δ) experimental pairs, M is the number of variable parameters in the model, and σ are the standard deviations on the experimental data points.

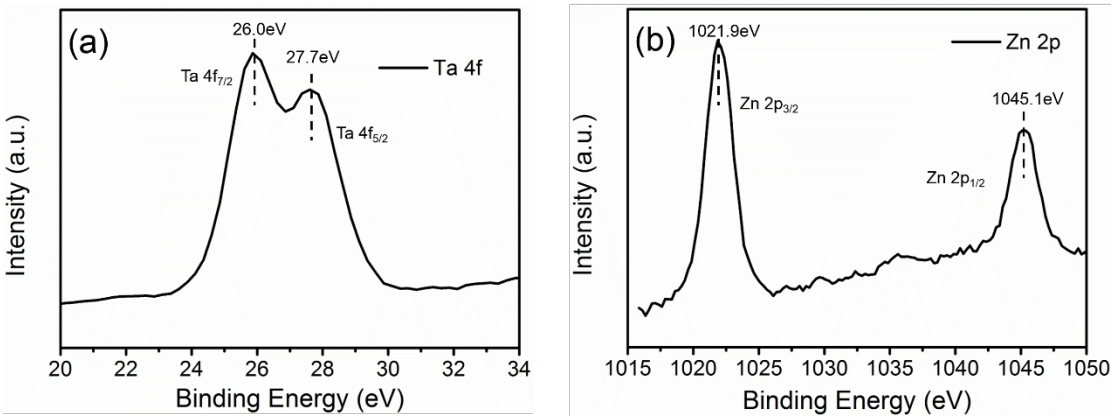


Fig. S1 (a) Ta 4f XP spectra of ZnO/Ta_2O_5 NRs. (b) Zn 2p XP spectra of ZnO/Ta_2O_5 NRs.

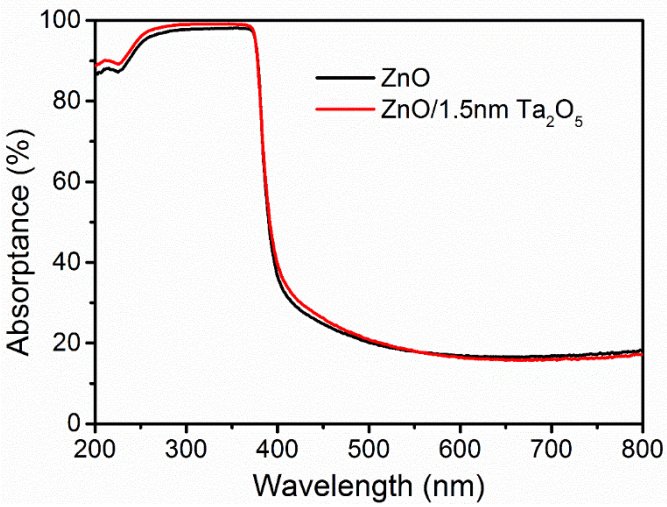


Fig. S2. UV-visible absorptance spectra of ZnO NRs and ZnO/Ta_2O_5 NRs, where absorptance (A) is defined as A = 100 – transmittance – reflectance (%)

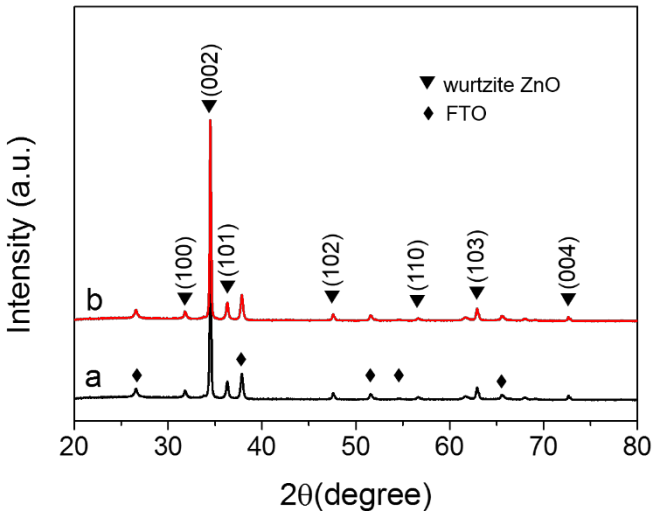


Fig. S3 X-ray diffraction (XRD) patterns of (a) ZnO NRs, (b) ZnO/Ta_2O_5 NRs

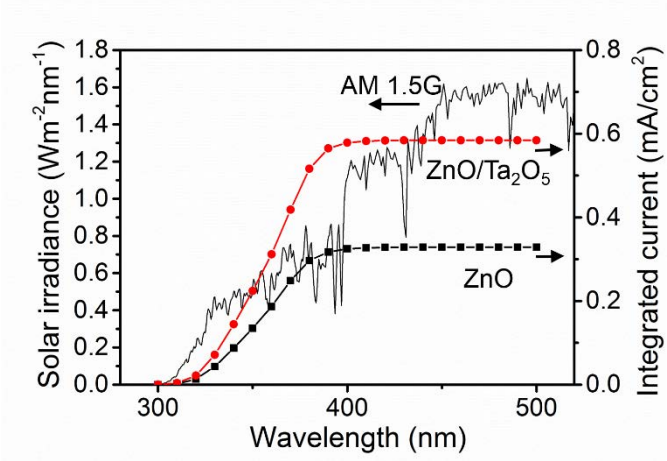


Fig. S4 Solar irradiance of AM 1.5G (ASTM G173-03) and calculated photocurrent by integrating IPCE over the photon flux of AM 1.5G.

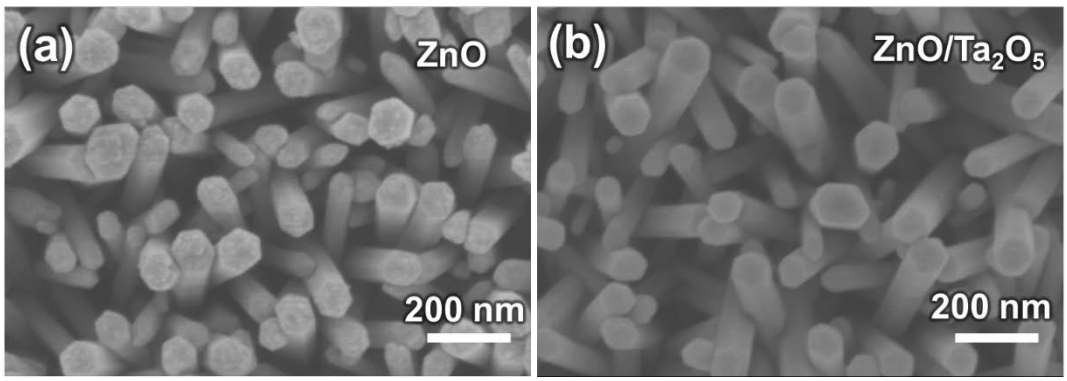


Fig. S5 SEM images of samples after 5 h stability test under simulated AM 1.5G illumination: (a) ZnO NRs (coarser surface due to the corrosion of ZnO). (b) ZnO/Ta_2O_5 NRs (no corrosion)

In order to investigate the optical properties of Ta_2O_5, spectroscopic ellipsometry measurement of a thick ALD Ta_2O_5 film (200 cycles deposited with the identical condition as the 1.5 nm film used in PEC and stability measurements) on Si substrate was conducted from 193 – 1690 nm at 60° and 70° incident angle. The Tauc-Lorentz dispersion model was used to fit the results over the entire measured wavelength region.

Structure of the optical model:

Layer 2	Ta_2O_5 (Tauc-Lorentz dispersion model)
Layer 1	Native oxide (1.69 nm, measured before deposition)
Substrate	Si

Fitting results:

Ta_2O_5 thickness = 11.3 nm, MSE: 2.614

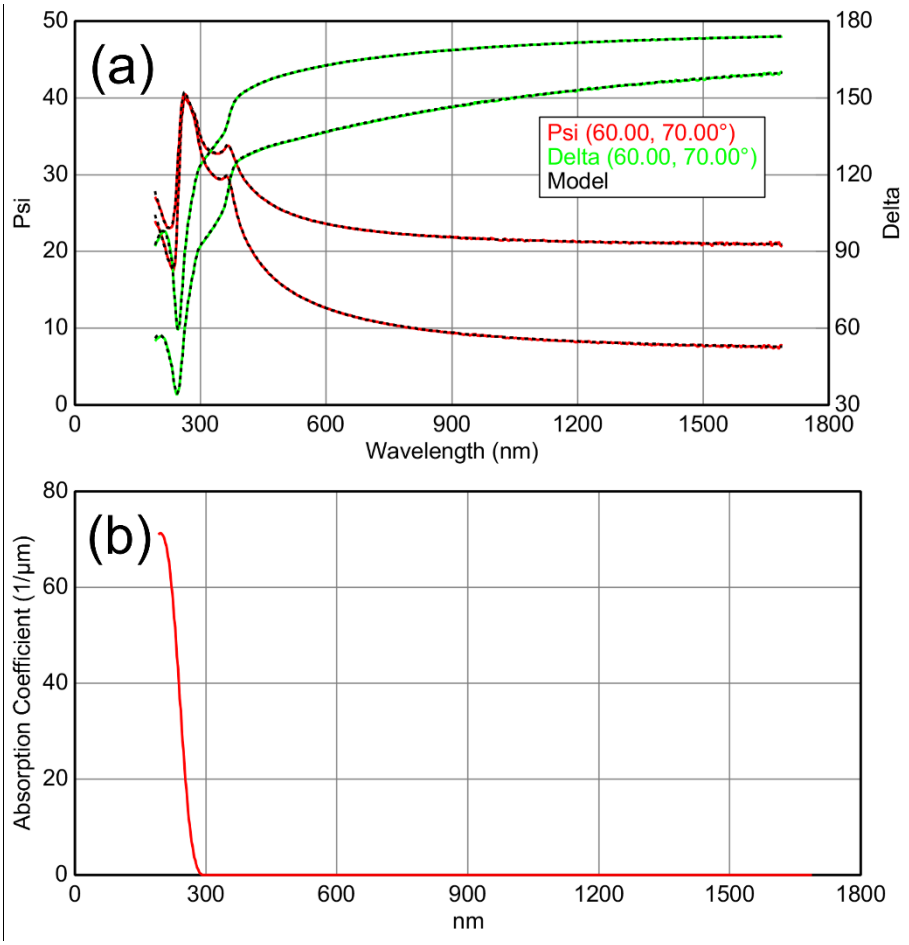


Fig. S6 (a) Typical fitting results of Ψ and Δ. (b) Absorption coefficient (α) of Ta_2O_5

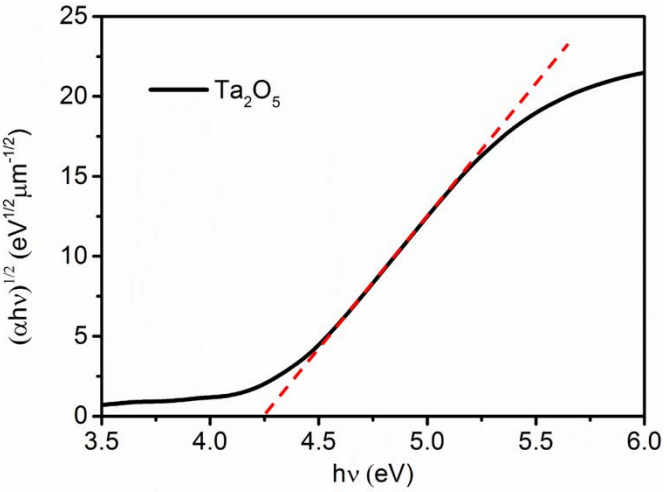


Fig. S7. Tauc plot of ALD Ta_2O_5 thin film on Si substrate extracted from ellipsometry. Intercep of red dashed line: Band gap of Ta_2O_5 (4.25 eV).

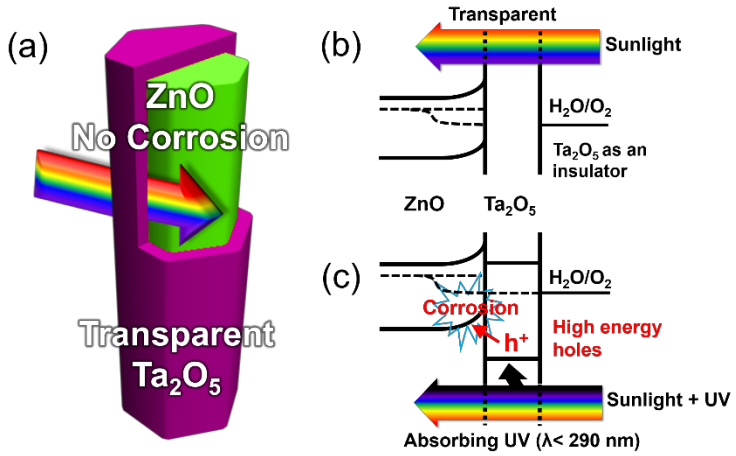


Fig. S8. A schematic of the behavior of ZnO/Ta_2O_5 under illumination with and without UV photons ($\lambda < 290$ nm).

(a): A ZnO/Ta_2O_5 model under AM 1.5G illumination.

(b): Under AM 1.5G illumination, Ta_2O_5 is completely transparent to the incident light and behaves as an insulator, therefore no holes would be generated from Ta_2O_5. Meanwhile, holes generated in ZnO tunnel through Ta_2O_5 layer into electrolyte for water oxidation. The transparent Ta_2O_5 protective layer greatly suppress the photo-corrosion of ZnO (trace ii in Fig. 3).

(c): When UV photons ($\lambda < 290$ nm) are incorporated by deliberately removing AM 1.5G filter, Ta_2O_5 would be activated by high energy UV light as a semiconductor. Since the valence band top of Ta_2O_5 lies in a much lower position, holes generated in Ta_2O_5 hold a much higher energy, which aggravate the degradation of ZnO (trace iii in Fig. 3).

References

1 S. Öztürk, N. Kılınç, N. Taşaltin and Z. Z. Öztürk, *Thin Solid Films*, 2011, **520**, 932.