# **Electronic Supplementary Information**

# Synthesis of Ag<sub>2</sub>O decorated hierarchical TiO<sub>2</sub> templated by double comb copolymers for efficient solar water splitting

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### 1. Materials and Experimental methods

#### Material

Commercial polyvinylidene chloride (PVDC) was purchased from Goodfellow. 1, 1, 4, 7, 10, 10-hexamethyltriethylenetetramine (HMTETA; >97%), copper(I) chloride (CuCl; >99.995%), poly(ethylene glycol) methyl ether methacrylate (POEM;  $M_n \sim 500$  g / mol), titanium butoxide (TBT>97%), sodium hydroxide, and titanium (IV) isopropoxide (TTIP>97.0%) were purchased from Sigma Aldrich. Hydrochloric acid and silver nitrate (AgNO<sub>3</sub>) were purchased from Thermo Fischer. FTO glass was obtained from Solaronix. All solvents were purchased from J. T. Baker.

#### **Experimental Methods**

### Synthesis of double comb copolymer (PVDC-g-POEM)

PVDC (6 g) was dissolved in 50 ml of NMP in a 100 ml capacity of the round flask with stirring at 500 rpm for 4 h. After PVDC was homogeneously dissolved, 36ml of POEM, 0.1 g of CuCl, and 0.23 mL of HMTETA were added to the polymer mixture and the round flasks were sealed with a rubber septum. Then, the reaction mixture was purged with N<sub>2</sub> gas for 90 min. The reaction was carried out at 90 °C while stirring at 500 rpm for 24 h. The synthesized double comb copolymers were reprecipitated into methanol/hexane mixture several times. The polymer was redissolved in NMP, then reprecipitated into methanol. Finally, the obtained copolymer was dried in a vacuum oven at 50 °C for 12h. The double comb copolymers were obtained in a powder form.

#### Synthesis of TiO<sub>2</sub> nanorod (TiO<sub>2</sub> NR)

Before hydrothermal synthesis, FTO glass was cut into  $3 \times 4 \text{ cm}^2$  and washed with acetone, ethanol, and DIW for 30 min. TiO<sub>2</sub> NRs were deposited on FTO glass using simple hydrothermal synthesis<sup>1</sup>. 0.8g of titanium butoxide (TBT) was dissolved into 60mL of HCl (37%) / H<sub>2</sub>O (v/v = 1:1). After solution becomes a homogeneous state, TBT / HCl / H<sub>2</sub>O solution was transferred into 100 mL capacity of a Teflon-lined steel autoclave. The Teflon bottle was sealed in an autoclave and was heated in an oven at 150 °C for 6 h. After hydrothermal reaction, the autoclave was cooled naturally then obtained TiO<sub>2</sub> NRs were cleaned with deionized water and dried in air.

#### Preparation of Hierarchical TiO<sub>2</sub> nanorod (HNR)

The as-synthesized 0.1g of double comb copolymer (PVDC-*g*-POEM) was dissolved in 1.5 mL of THF. Meanwhile, TiO<sub>2</sub> precursor solution was prepared by mixing of TTIP, HCl, and H<sub>2</sub>O (2:1:1). Then 0.1 mL of TTIP / HCl / H<sub>2</sub>O solution was added slowly in a prepared double comb copolymer solution under vigorous stirring and aged 3h. The solution was dropped onto prepared TiO<sub>2</sub> NR and was spin coated at 1500 rpm for 20 s. Upon calcination at 500 °C and 550 °C for 1 h, the organic chemicals were removed.

#### Preparation of Ag<sub>2</sub>O decorated hierarchical TiO<sub>2</sub> nanorod (Ag<sub>2</sub>O@HNR)

Silver oxide deposition on HNR was conducted by modifying previously reported papers<sup>2</sup>. First, 0.3 mmol of AgNO<sub>3</sub> was dissolved in 120 mL DIW, 50 mL EtOH mixture. The prepared HNR films were placed in solution with the conductive side facing up. Then, 2 mL of 1M NaOH solution was added while sonication treatment for 1, 2, 5, 10 min, respectively. FTO glasses were cleaned with DIW three times. Finally, an ultraviolet LED (365nm) was irradiated to reduce remaining Ag ions.

### 2. Characterization

#### **Material Characterization**

Gel permeation chromatography (GPC) was conducted to estimate the molecular weight of PVDC, and double comb copoylmer (PVDC-g-POEM) at 25 °C in THF flow rate of 1 mL min <sup>-1</sup> using a YL9112 isocratic pump, YL9131 column, YL9170 refractive index detector (YL instruments, Korea). <sup>1</sup>H-NMR measurements were conducted with a high resolution of 600 MHz spectrometer (AVANCE 600, Bruker, Germany). Fourier transform infrared spectrometer (Spectrum Two, PerkinElmer, USA) was employed to ascertain the functional group of the synthesized double comb copoylmer (PVDC-g-POEM), pristine PVDC, and POEM in the frequency range of 4000-650 cm<sup>-1</sup> the mode for attenuated total reflection (ATR). The thermal properties of the copolymers were determined by thermal gravimetric analysis (TGA; TG209 F3, NETZSCH). The TGA and DSC measurements were performed under an air and Argon gas from room temperature to 550 °C at a rate of 10 °C/min. TEM images were obtained from a Philips CM30. X-ray diffractometer (Rigaku, Japan) with Cu-ka was used to identify crystal phase and materials on FTO glass at an incident angle of 1 theta. The morphology of HNR was attained using a field emission-scanning electron microscope (FE-SEM) (Hitachi SU 8010, Hitachi, Japan). UV-visible absorbance spectra were obtained by UV-vis spectrometer (Mega-900, Scinco, Korea) equipped with an integrating sphere from 300 to 800 nm. The photoelectrochemical characteristics were obtained under one sun illumination (100 mWcm<sup>-2</sup>). The EIS measurements were performed at frequencies ranging from 100,000 Hz to 0.1 Hz using a CompactStat electrochemistry analyzer (Ivium Technologies). The IPCE measurements were performed using a light source, which is 150 W Xenon arc lamp source with filter wheel and 600 grooves/mm 500nm blazed wavelength. The crystal structure of the samples was analyzed by X-ray diffractometer (XRD, Smartlab, Rigaku) using CuKa radiation. Surface compositions and oxidation states of the materials were investigated by X-ray photoelectron spectroscopy (XPS) using a VG Scientific K-alpha spectrometer equipped with an Al X-rays  $(K\alpha = 1486.6 \text{ eV})$  as excitation source was employed.

## Photoelectrochemical measurement

For the three-electrode measurements, as prepared photoanode, Ag/AgCl electrode and Pt coil were employed as the working electrode, reference electrode, and counter electrode, respectively. The electrolyte was 1 M KOH solution. Linear sweep voltammetry was conducted under light irradiation (AM 1.5 illumination, 100 mW cm<sup>-2</sup>) with a scan rate of 5 mV s<sup>-1</sup>. In the

case of the chopper system, the light on-off cycle was 5 s. The electrochemical impedance spectra (EIS) were measured under illumination at an open-circuit potential (OCP) with a signal of 10 mV amplitude over a frequency range of  $10^5$  to 0.1 Hz. I-t curves were obtained by using transient chronoamperometry at 1.23V vs. RHE. Before all electrochemical measurements, the reference electrode was calibrated through several standard electrodes and converted with the RHE scale by using Nernst equation:  $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} (1M \text{ KOH}) + E^{0}_{Ag/AgCl}$ , where  $E_{RHE}$  is the converted potential,  $E^{0}_{Ag/AgCl} = 0.1976 \text{ V}$  at 25 °C, and  $E_{Ag/AgCl}$  is the applied potential vs reference electrode. Cyclic voltammograms (CV) with various scan rates without illumination in the potential window from 0 to 0.1 V vs. Hg/HgO to prevent photoanode from electrochemical reaction.

## **3. Supplementary Results**

Figure S1. FT-IR spectra of PVDC, POEM, and double comb copolymer (PVDC-*g*-POEM).



**Figure S2.** TGA curve of PVDC, POEM, and double comb copolymer (PVDC-*g*-POEM) under Air condition, (b) DSC curves of PVDC, POEM, and double comb copolymer (PVDC-*g*-POEM).



**Figure S3**. <sup>1</sup>H-NMR spectra of the PVDC and double comb copolymer (PVDC-*g*-POEM).



**Figure S4.** SEM images of (a) low-magnified Ag<sub>2</sub>O@HNR, EDX mapping of Ag<sub>2</sub>O@HNR (b) Ti, (c) Ag, and (d) O.



Figure S5. Low magnified SEM images of (a) mesoporous TiO<sub>2</sub>, (b) Ag<sub>2</sub>O@HNR.



Figure S6. XPS spectra of Ag<sub>2</sub>O@HNR (a) survey, and (b) Ag 3d.



**Figure S7.** Linear sweep voltammograms of TiO<sub>2</sub> NR 500 °C, TiO<sub>2</sub> NR 550 °C, HNR 500 °C and HNR 550 °C (a) without chopper, (b) under chopped illumination, transient photocurrent plots under illumination at a constant potential of 1.23 V vs. RHE (c) TiO<sub>2</sub> NR 500 °C, HNR 500 °C, and (d) TiO<sub>2</sub> NR 550 °C, HNR 550 °C.



Figure S8. Linear sweep voltammograms of  $TiO_2$  NR, and  $Ag_2O@TiO_2$  NR with different deposition time.







Figure S10. OCP decay profiles of HNR and Ag<sub>2</sub>O@HNR.



The open-circuit potential (OCP) decay is a simple and useful tool for evaluating charge recombination. The OCP decay curve represents the behavior of photo-induced electron recombination after blocking of incident light, and the recombination rate can be calculated using the following expression

$$\frac{V - V_{illumination}}{V_{dark} - V_{light}} = 1 - e^{-kt}$$

where V, V<sub>illumination</sub>, V<sub>dark</sub>, k, and t denote OCP values at a given instant, under AM 1.5G illumination, dark condition, pseudo-first order recombination rate constant, and time, respectively.<sup>3,4</sup> As depicted in Figure S10, light was irradiated for up to 20 s and switched to dark using the chopper system . Subsequently, photo-induced charge carriers were observed to disappear exponentially. Post Ag<sub>2</sub>O deposition, an increase in normalized OCP values was observed. This corresponds to a reduction in recombination rate.

**Figure S11.** Applied bias photo-to-current efficiency (ABPE) of TiO<sub>2</sub> NR, HNR, and Ag<sub>2</sub>O@HNR.



Although the applied bias photo-to-current efficiency (ABPE) is not a true measure of solarto-hydrogen conversion, it is commonly used as a diagnostic measurement parameter. ABPE can be expressed as

$$ABPE = \left[\frac{|j_{ph}| \times (1.23 - |V_b|)}{P_{total}}\right]_{AM \ 1.5G}$$

where  $J_{ph}$  denotes the photocurrent density of the sample under the applied bias V<sub>b</sub>.<sup>5</sup> In this study, ABPE of prepared photoanodes was calculated using the *J*–*V* curve plotted in Figure 3. As depicted in Figure S11, the maximum value of ABPE reaches 0.88, 0.53, and 0.41%, respectively.

**Figure S12**. Cyclic voltammograms of (a)  $TiO_2$  NR, (b) HNR, and (c) linear fitting of capacitive currents vs. scan rate.



The electrochemical surface area was calculated to determine the active surface area of  $TiO_2$  NR, and HNR. Double-layer capacitance could be calculated by plotting the difference in current between anodic and cathodic charging and the scan rate, the slope of which equals twice the double-layer capacitance. As depicted in Figures S12(a)–(c), compares to TiO<sub>2</sub> NR, and HNR demonstrates 50% increase in double-layer capacitance, which in turn, leads to improved PEC performance, as discussed above.

Figure S13. UV-Vis diffuse reflectance spectra of the HNR and Ag<sub>2</sub>O@HNR.



The UV-vis absorbance spectrum depicted in Figure S13 demonstrates that HNR mainly absorbs ultraviolet radiations owing to the intrinsic bandgap of rutile  $TiO_2$ . This could be attributed to charge transfer from the valence band of O (2p) to conduction band of Ti (3d).<sup>6</sup> Post Ag<sub>2</sub>O deposition, however, the absorption edge demonstrated a shift to longer wavelengths, thereby resulting in absorption of a wavelength corresponding to the visible-light range of the optical spectrum.

**Figure S14.** IPCE plots of HNR and Ag<sub>2</sub>O@HNR in range of 300 nm to 800 nm (inset) magnification of the main plot over the wavelength range of 400 nm to 800 nm.



The incident photon-to-current conversion efficiency (IPCE) was calculated to investigate the visible-light response of Ag<sub>2</sub>O@HNR, as depicted in Figure S14. Compared to HNR, Ag<sub>2</sub>O@HNR demonstrated higher efficiency over the short-wavelength region. This could be attributed to the observed increase in the number of catalytically active sites and reduced charge recombination due to p–n band alignment between Ag<sub>2</sub>O@TiO<sub>2</sub>.<sup>7</sup> Moreover, as depicted in the inset to Figure S14, the small band gap of Ag<sub>2</sub>O enables Ag<sub>2</sub>O @HNR to absorb radiations within the visible-light region of the spectrum, thereby enhancing photoelectrochemical performance. Also, the IPCE results suggested that the enhanced photo response of Ag<sub>2</sub>O nanoparticle in Ag<sub>2</sub>O@HNR in the visible-light region was due to not only the increased optical absorption of TiO<sub>2</sub> associated with surface plasmon resonance electrical field amplification but also suppress charge recombination, as similar results were reported previously.<sup>8-10</sup>

## 4. Charge separation efficiency

The charge separation efficiencies of the photoanode have been established as an effective tool for the performance evaluation of PEC water oxidation applications.<sup>11,12</sup> Charge separation and surface charge transfer efficiency can be calculated using the following equations:

$$\eta_{bulk} = \frac{J_{Na2SO3}}{J_{abs}} \dots (1)$$
  
$$\eta_{surface} = \frac{J_{H2O}}{J_{Na2SO3}} \dots (2)$$

in which  $J_{abs}$  is the theoretical photocurrent density assuming that all absorbed photons can be converted into current (APCE = 100%), and  $J_{H2O}$  and  $J_{Na2SO3}$  are the photocurrent densities obtained in 1 M KOH aqueous solution without and with 1 M Na<sub>2</sub>SO<sub>3</sub>, respectively. According to the previous studies, however, Ag nanoparticle can react with Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as hole scavengers which results in an undesired reaction in PEC water oxidation.<sup>13,14</sup> We agree with reviewer's comments that charge separation efficiency measurements are important and worth measuring but we believe the EIS and OCP decay strongly support our results.

# 5. The Fermi-level variations at the Ag<sub>2</sub>O-TiO<sub>2</sub> heterojunction

The fermi level can be determined by the following equation:

 $E_F = E_c + kT \ln \frac{n_c}{N_c} \dots (3)$ 

Herein  $E_F$  is the fermi level potential,  $E_c$  is the conduction band potential, k is the boltzmann constant, T is the temperature,  $n_c$  is the accumulated electrons and  $N_c$  is the density of states in conduction band.<sup>15</sup> An increase of charge accumulated in the conduction band edge of Ag<sub>2</sub>O-TiO<sub>2</sub> heterojunction under illumination, which would result in a positive shift of Fermi-level.

#### 6. References

1. G. W. An, M. A. Mahadik, W.-S. Chae, H. G. Kim, M. Cho, and J. S. Jang. *Appl. Surf. Sci.*, 2018, **440**, 688-699.

- 2. C. Peng, W. Wang, W. Zhang, Y. J. Liang, and L. Zhuo, Appl. Surf. Sci., 2017, 420, 286-295.
- 3. J. Kim, D. Monllor-Satoca, and W. Choi, Energy Environ. Sci., 2012, 5, 7647-7656.
- 4. Z. Hu, Z. Shen, and J. C. Yu, Chem. Mat., 2016, 28, 564-572.
- 5. Z. Chen, T. F. Jaramillo, T. G. Deutsch, A. Kleiman-Shwarsctein, A. J. Forman, N. Gaillard,
- R. Garland, K. Takanabe, C. Heske, and M. Sunkara, J. Mater. Res., 2010, 25, 3-16.
- 6. G. K. Mor, H. E. Prakasam, O. K. Varghese, K. Shankar, and C. A. Grimes, *Nano Lett.*, 2007, 7, 2356-2364.
- 7. H.-T. Ren and Q. Yang, Appl. Surf. Sci., 2017, 396, 530-538.
- 8. Y.-C. Pu, G. Wang, K.-D. Chang, Y. Ling, Y.-K. Lin, B.C. Fitzmorris, C.-M. Liu, X. Lu, Y. Tong, J. Z. Zhang, Y.-J. Hsu and Y. Li, *Nano letters*, 2013, **13**, 3817-3823.
- 9. R. Takakura, T. Oshikiri, K. Ueno, X. Shi, T. Kondo, H. Masuda and H. Misawa, *Green Chem.*, 2017, **19**, 2398-2405.
- 10. L. Wang, Y. Wang, P. Schmuki, S. Kment and R. Zboril, *Electrochim. Acta*, 2018, **260**, 212-220.
- 11. C. Wang, X. Long, S. Wei, T. Wang, F. Li, L. Gao, Y. Hu, S. Li and J. Jin, *ACS Appl. Mater. Interfaces*, 2019, **11**, 29799-29806.
- 12. L. Gao, F. Li, H. Hu, X. Long, N. Xu, Y. Hu, S. Wei, C. Wang, J. Ma and J. Jin, *ChemSusChem*, 2018, **11**, 2502-2509.
- 13. D. Kal'nyi, V. Kokovkin and I. Mironov, Russ. J. Gen. Chem., 2011, 81, 793-798.
- 14. D. R. Lide, CRC handbook of chemistry and physics, CRC press, 2004.
- 15. V. Subramanian, E. E. Wolf and P. V. Kamat, J. Am. Chem. Soc., 2004, 126, 4943-4950.