

## Supporting Information

### **Enhanced Visible Light Response of a WO<sub>3</sub> Photoelectrode with an Immobilized Fibrous Gold Nanoparticle Assembly Using an Amyloid- $\beta$ Peptide**

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## Materials and methods

### Instruments

High-performance liquid chromatography (HPLC) analyses were performed on a Shimadzu UPLC AC20 system with a reversed-phase analytical column (YMC, YMC-Pack Pro C18, 250 mm x 20 mm I.D.,  $S = 20 \mu\text{m}$ ). ESI-TOF MS analyses were performed on a Bruker micrOTOF focus III mass spectrometer. UV-vis spectra were measured using a Shimadzu UV-3150 or UV-2550 spectrophotometer equipped with a thermostated cell holder or on a Shimadzu BioSpec-nano spectrophotometer. Diffuse transmission spectroscopy was performed using a JASCO V670 instrument equipped with an integral sphere (JASCO, ISN-723). The pH values were monitored using an F-52 Horiba pH meter. Electrochemical measurements were conducted using a CompactStat potentiostat (Ivium Technologies, The Netherland) using a platinum mesh as a counter electrode and standard Ag|AgCl as a reference electrode. Atomic force microscopy (AFM) measurements were performed using an MFP-3DTM-SA microscope (Asylum Research). The surface topography of the photoelectrodes was analyzed by scanning electron microscopy (JSM-6335, JEOL, Japan) equipped with an energy dispersive X-ray analyzer (JED-2300F, JEOL, Japan). ICP-AES was conducted using a Shimadzu ICPS-7510 instrument. Visible light was supplied from USHIO Optical Modulex SX-U1501XQ system (500W xenon arc lamp) with a UV and IR cut-off filter (Super Cold Filter, Asahi Spectra:  $\lambda = 390\text{--}750 \text{ nm}$  pass-through) and a UV cut filter (Sigma Koki,  $\lambda < 420 \text{ nm}$  cut-off). Monochromatic light was obtained by passing light through a monochromator (Shimadzu, SPG-120S). The power of light was determined using a power meter (Thorlabs, PM120VA) with sensor modules of either Si-sensor (Thorlabs, S120VC) or a thermal power sensor (Thorlabs, S302C). Ultrapure water ( $>18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) was demineralized using a Merck Milli-Q integral 3 system

### Materials

All reagents were used without purification unless otherwise noted. Citrate-protected AuNP was prepared according to the literature.<sup>S1,S2</sup> Tungsten trioxide ( $\text{WO}_3$ , 99 %) was purchased from Wako Pure Chemical Industries.

**AuNP and A $\beta$ -AuNP.** A $\beta$ -functionalized AuNPs (A $\beta$ -AuNPs) were prepared according to our previously reported method.<sup>S3</sup> Trisodium citrate dihydrate (114 mg, 0.39 mmol) in 10 mL water was added to a boiling aqueous solution of  $\text{HAuCl}_4$  (41.2 mg, 0.10 mmol) in 100 mL and the solution was refluxed for 20 min. A $\beta$  peptide (1.05 mg, 0.46  $\mu\text{mol}$ ) in 25 mL of 20% sodium dodecyl sulfate was added to the reaction mixture at 25 °C and further incubated for 24 h.  $\alpha$ -Lipoic acid (LA) (1.02 mg, 4.6  $\mu\text{mol}$ ) in 2 mL of methanol was added to the mixed solution at 25 °C and incubated for 30 min.

A $\beta$ -AuNP was purified by repeating centrifugation (14800 rpm, 20 min, 4 °C), and washing with NaOH<sub>aq</sub> (pH 10.2) three times, and stored in the same solution. The purity of A $\beta$ -AuNP was confirmed by agarose gel electrophoresis using 0.5% agarose gel in 44.5 mM Tris-borate buffer including 1 mM EDTA at 4 °C. The A $\beta$ -AuNPs with different A $\beta$ -ligand/LA ratios were prepared by changing the amount of A $\beta$ -ligand at the initial modification of citrate-stabilized AuNPs. LA-modified AuNPs were prepared in the same procedure without addition of A $\beta$ -ligand. The concentrations of AuNPs were determined according to the reported extinction coefficient ( $\epsilon_{520} = 2.47 \times 10^8 \text{ cm}^{-1} \text{ M}^{-1}$ ).<sup>S4</sup>

**Atomic Force Microscopy (AFM).** The assembly of A $\beta$ -AuNP was visualized by acoustic mode AFM in air with a SiN<sub>4</sub> tip (AC240TS, Olympus). A glass plate was thoroughly cleaned with SC-1 solution (25% ammonia/30% H<sub>2</sub>O<sub>2</sub>/deionized water = 1/1/5) before use. The A $\beta$ -AuNP solution (10 nM per particle) in 5 mM sodium acetate (NaOAc) pH 4.5, 5 mM potassium phosphate (pH 7.0), or 5 mM potassium phosphate (pH 11.0) was cast onto the glass plate and incubated at 37 °C for 12 h. After the supernatant was removed, the sample was dried under reduced pressure for 6 h and rinsed with deionized water to remove the unbound samples and salts. The glass plate was dried again before the measurement. The images were recorded at a scan rate of 1 Hz with a resolution of 256 pixels per line. All AFM measurements were performed at ambient temperature.

**Small Angle X-ray Scattering (SAXS).** The SAXS data were obtained using the BL-6A beamline<sup>S5</sup> in the Photon Factory of KEK, Tsukuba with an X-ray energy of 8.27 keV (the wavelength of X-ray was 0.150 nm). PILATUS 2M (DECTRIS) was used as a 2-dimensional detector that was set at a position of 162.0 cm apart from the sample position. The solution samples were measured in a quartz capillary (inner diameter: 2mm, thickness of quartz: 0.01mm, length: 80mm; Hilgenberg GmbH, Germany). The solution samples which were drop-cast and dried on a thin polyimide film (TORAY DuPont Kapton film, Du Pont - Toray Co., Ltd., Tokyo, Japan; 25  $\mu\text{m}$ -thick) were subjected to the SAXS measurements with a measurement period of 30 s. For the drop-cast specimens, the 2d-SAXS measurements were conducted by sending the incident beam from the normal direction of the film specimens (through view setting). The 2d-SAXS patterns were converted to a one-dimensional (1d-SAXS) profile by conducting the circular average. Furthermore, the scattering of the empty cell was subtracted from each of the 1d-SAXS profiles. Then, the scattering intensity,  $I(q)$ , was plotted as a function of the scattering vector,  $q$  ( $q = 4\pi/\lambda \sin(\theta/2)$  where  $\lambda$  and  $\theta$  denote the wavelength of X-ray and the scattering angle, respectively).

The 1d-SAXS profiles for solution specimens can be attributed directly to particle scattering of the AuNP. Therefore, a spherical shape was assumed and the theoretical particle scattering intensity for spherical particles with a distribution of sizes can be calculated.<sup>S6</sup> As shown in Fig. S3, the measured

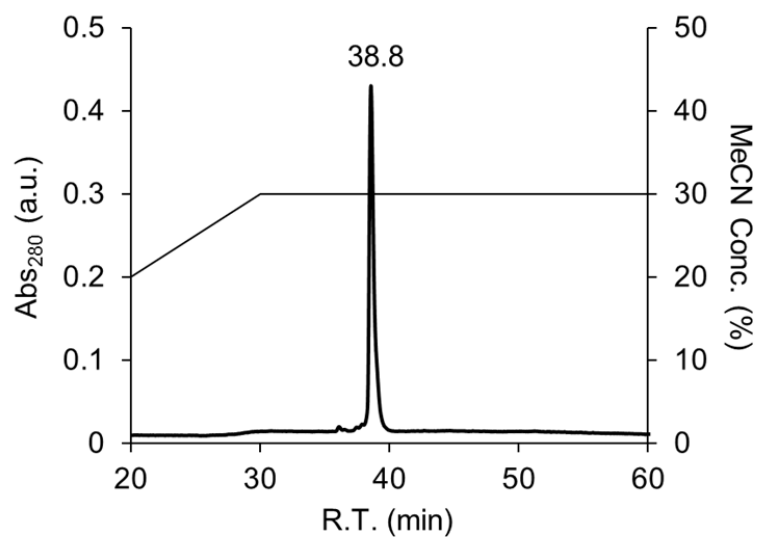
(black) and calculated (red) profiles are coincident with each other. The size (radius of spheres) distribution evaluated is shown in the inset of each panel of the 1d-SAXS profile in Fig. S3.

**WO<sub>3</sub>/FTO electrode immobilizing A $\beta$ -AuNP.** FTO-coated glass plates (9.79  $\Omega$ /sq., AGC Fabritech Co., Ltd) was washed with SC1 for 30 min and thoroughly rinsed with deionized water and ethanol. WO<sub>3</sub> suspended in water (100 mg/mL) containing 0.5% diacetyl cellulose was homogenized using ball-mill (AN1-515, Nitto Kagaku) for 24 h, and spin-coated on the clean FTO (10 x 25 mm). The electrode was heated to 450  $^{\circ}$ C and incubated for 2 h to afford the WO<sub>3</sub>-immobilized FTO electrode (WO<sub>3</sub>/FTO). WO<sub>3</sub>/FTO was immersed in an A $\beta$ -AuNP solution (20 nM per particle, 200  $\mu$ L) for 24 h at room temperature and gently rinsed with deionized water three times. The electrodes were dried in reduced pressure for 6 h at room temperature to afford the A $\beta$ -AuNP-immobilized WO<sub>3</sub> electrode (A $\beta$ -AuNP@WO<sub>3</sub>).

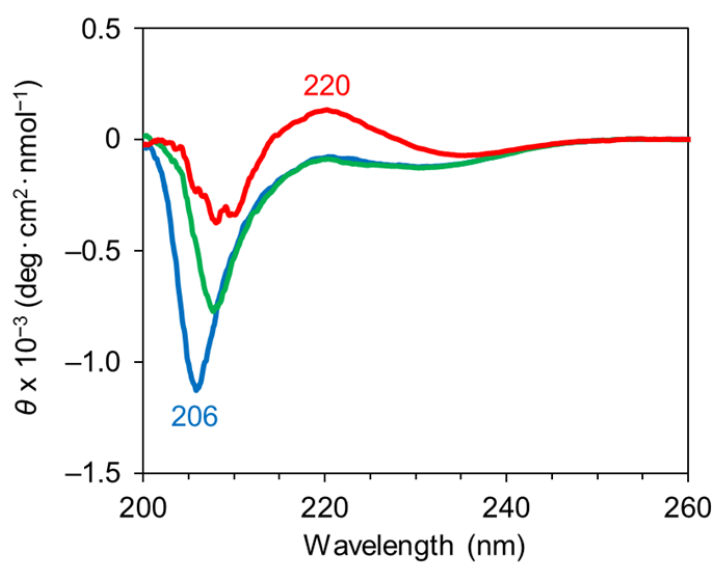
**ICP-AES measurement.** Gold content (Au wt%) of AuNP immobilized on WO<sub>3</sub> was determined using the WO<sub>3</sub> composite prepared without FTO: Twenty microliters of WO<sub>3</sub> solution (500 mg/mL) was mixed with A $\beta$ -AuNP (100 nM per particles) in 200  $\mu$ L of buffer. The mixture was incubated for 24 h at room temperature, and the precipitates were washed with deionized water three times. The composite was dried under reduced pressure. The composite (10 mg) was suspended in 500  $\mu$ L of aqua regia (HNO<sub>3</sub>/HCl = 1/3) and the mixture was sonicated at 60  $^{\circ}$ C for 3 h. After the AuNPs were dissolved, the solution was used before the ICP-AES measurements were conducted. The quantification of Au wt% was determined in quadruplicate for each sample.

**Photoelectrochemical measurement.** Photocurrent measurements were performed in a typical three-electrode configuration. An Ag|AgCl electrode with a saturated KCl<sub>aq</sub> and Pt-mesh electrode were employed as the reference and counter electrodes, respectively. The WO<sub>3</sub> electrode was mounted at the quartz cuvette as a working electrode. The electrochemical analysis was carried out under Ar atmosphere at 25  $^{\circ}$ C in 1 M KOH aqueous solution including 0.5 M of 2-propanol. The electrolyte was bubbled with pure Ar gas (99.9%) for at least 20 min to expel the dissolved oxygen. A limited area of the electrode sealed with a Teflon O-ring (Echo perfluor,  $\phi$  = 7 mm, Taiwan Air Water Mach Co., Ltd.) was exposed to the electrolyte. The linear sweep voltammogram (LSV) was recorded with a scan rate of 50 mV sec<sup>-1</sup>. The photocurrent response was recorded under potentiostatic conditions with exposure to the visible light (420 <  $\lambda$  < 750 nm, 513  $\pm$  3.4 mW cm<sup>-2</sup>). The electrode was irradiated by the visible light with a distance of 1.5 cm between the cell and the light source. Incident photon-to-electron conversion efficiency (IPCE) was calculated using the following equation.

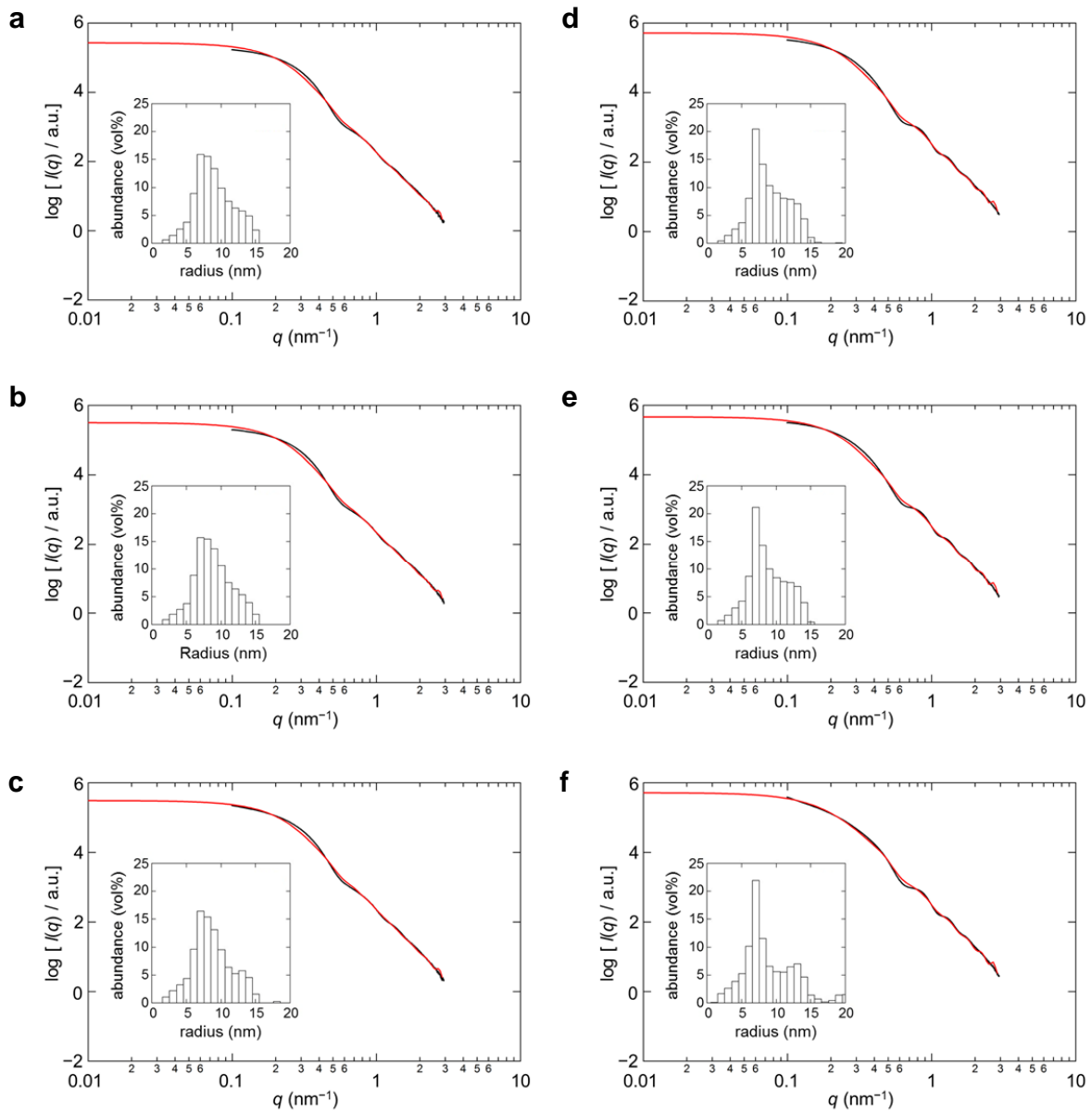
$$\text{IPCE} = [ \{ 1240 \times J \text{ (mA cm}^{-2}\text{)} \} / \{ \lambda \text{ (nm)} \times \text{Power density (mW cm}^{-2}\text{)} \} ] \times 100$$



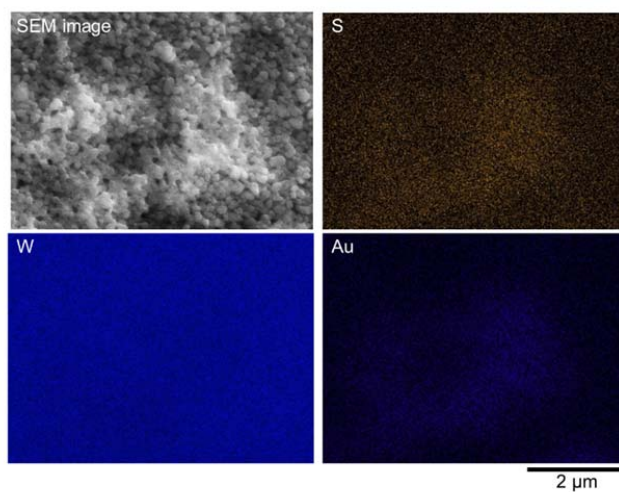
**Fig. S1** Analytical HPLC elution profile of the A $\beta$  peptide.



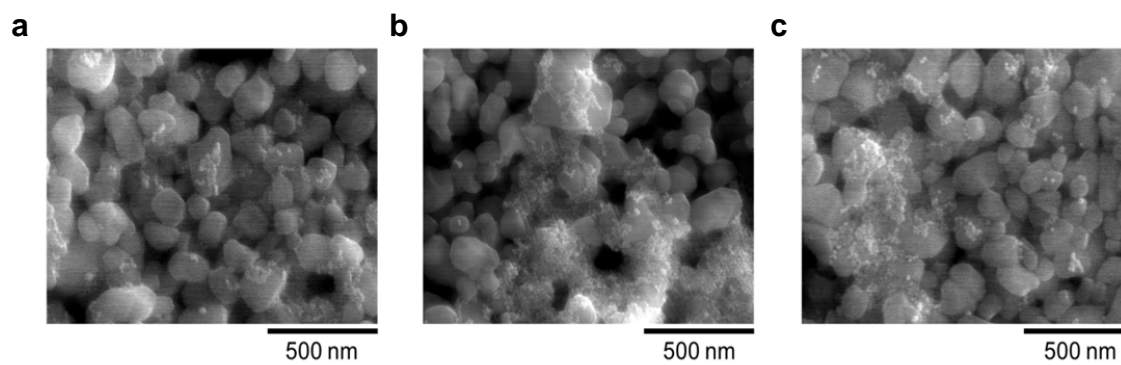
**Fig. S2** CD spectra of the A $\beta$  peptide at pH 11 (blue), 7.0 (green), and 4.5 (red) in 5 mM buffer solution.



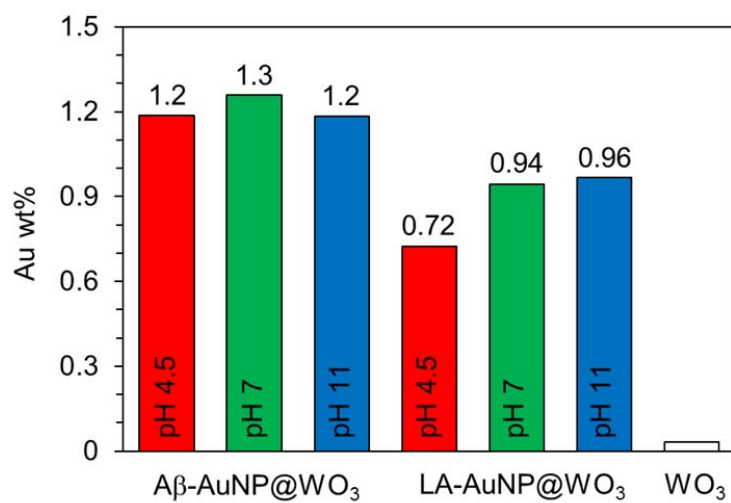
**Fig. S3** SAXS profiles measured (black line) for A $\beta$ -AuNP at (a) pH 11, (b) pH 7.0, (c) pH 4.5 and LA-AuNP (d) pH 11, (e) pH 7.0, (f) pH 4.5 in buffer solution. The simulated profiles in each sample are shown with a red line using the distribution of the particle radius as shown in the inset of each panel of the figures for 1d-SAXS profile.



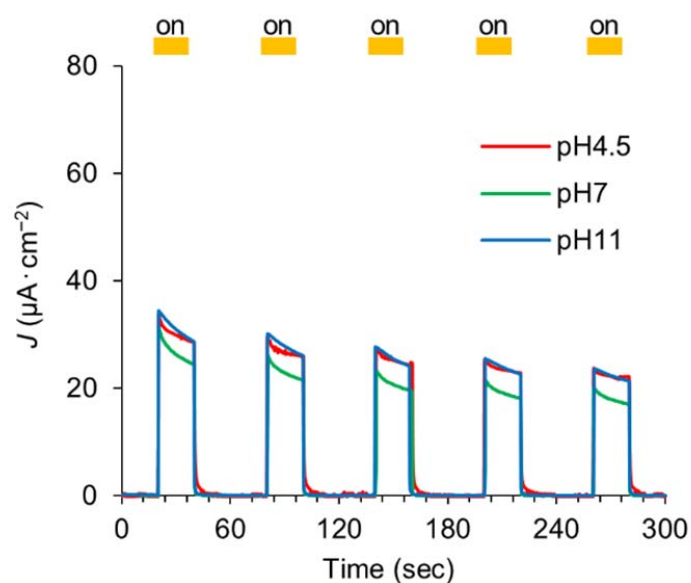
**Fig. S4** Elemental mapping of  $A\beta$ -AuNP<sub>ass</sub>@WO<sub>3</sub>@FTO.



**Fig. S5** SEM images of (a) LA-AuNP@WO<sub>3</sub>, (b)  $A\beta$ -AuNP<sub>ass</sub>@WO<sub>3</sub>, and (c)  $A\beta$ -AuNP<sub>dis</sub>@WO<sub>3</sub> electrodes.

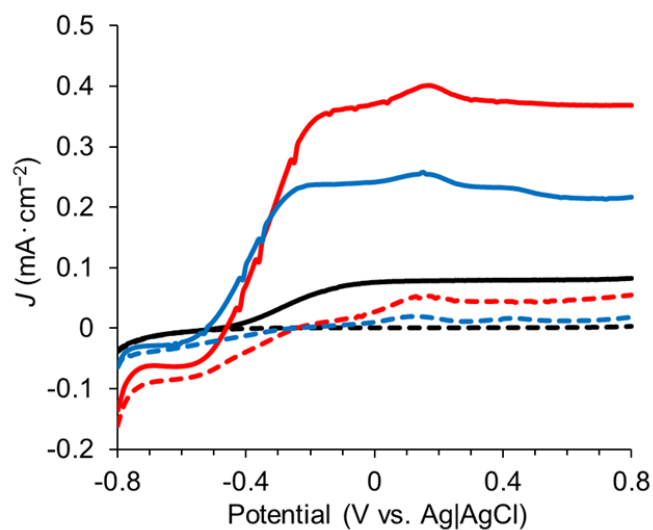


**Fig. S6** Gold contents (Au wt%) of the WO<sub>3</sub> composites determined by ICP-AES analysis.

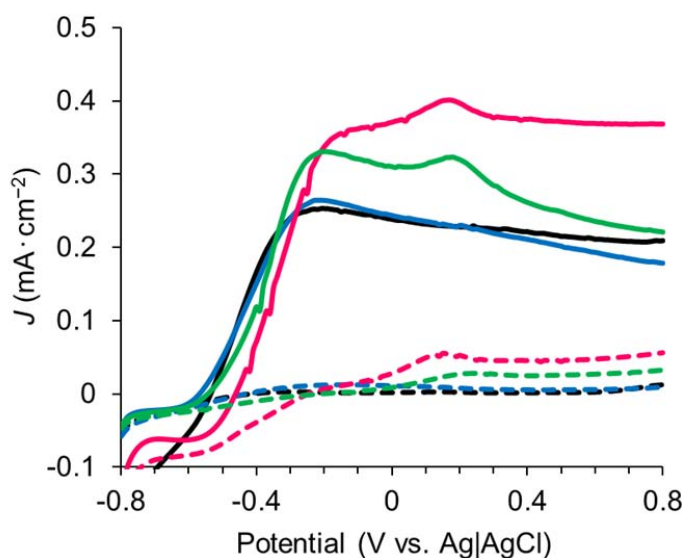


**Fig. S7** Photocurrent responses of the WO<sub>3</sub>/FTO electrode during the on/off cycle of visible light irradiation. The WO<sub>3</sub>/FTO electrodes were immersed in buffers at different pH before conducting the photocurrent measurement.





**Fig. S8**  $I$ - $V$  curves of  $\text{WO}_3/\text{FTO}$  (black),  $\text{A}\beta\text{-AuNP}_{\text{dis}}@/\text{WO}_3/\text{FTO}$  (blue), and  $\text{A}\beta\text{-AuNP}_{\text{ass}}@/\text{WO}_3/\text{FTO}$  (red). The curves were collected in the dark (bold lines) and upon visible light irradiation (dashed lines).



**Fig. S9** (a)  $I$ - $V$  curves of  $\text{A}\beta\text{-AuNP}_{\text{ass}}@/\text{WO}_3/\text{FTO}$  electrode immobilizing different concentrations of AuNPs. The  $\text{WO}_3/\text{FTO}$  electrode was prepared in solutions of  $\text{A}\beta\text{-AuNP}$  at 1 nM (black), 10 nM (blue), 100 nM (red), and 500 nM (green)  $\text{A}\beta\text{-AuNP}$ . The curves were generated from the measurement made in the dark (bold lines) and upon visible light irradiation (dashed lines).

## References

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