Supplementary Material (ESI) for Chemical Communications
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Constructing Ultrathin Film with “Memory” Photocatalytic Activity from Monolayered Tungstate Nanodots

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1. Experimental details

Preparation of monolayered tungstate nanodots: The monolayered tungstate nanodots were prepared via exfoliation of layered tungstate nanocrystals according to a previous report.[1] In a typical synthesis process of the layered tungstate nanocrystals, 300 mL aqueous solution of 20 mM sodium tungstate (IV) dehydrate ($Na_2WO_4 \cdot 2H_2O$) and 10 mM cesium carbonate (Cs_2CO_3) was poured into 300 mL 0.1 M hydrochloric acid (HCl) at room temperature. The mixture was aged for 4 days and then the precipitates were collected by centrifuge and dried at room temperature. 1 g of the dried tungstate nanocrystals was then proton-exchanged in 100 mL HCl (1 M) for 3 days. The HCl was refreshed every 24 hours. After proton-exchange, the tungstate nanocrystals were washed with copious water and dried at room temperature. Then 1g of the proton-exchanged tungstate nanocrystals were dispersed in 250 mL tetrabutylammonium hydroxide (TBAOH) solution ($7.05*10^{-3}$ wt%) and stirred for over 10 days. The as-prepared monolayered tungstate nanodots suspension has a concentration of ca. 1 g/L.

Lay-by-layer assembly of tungstate nanodots: Before the layer-by-layer assembly, all substrates were immersed into 0.1 M HCl, acetone, ethanol and H_2O and sonicated for 20 mins respectively. The substrates were dried by an air blow gun before being dipped into polydiallyldimethylammonium chloride (PDDA) solution (20 g/L) for 20 mins. Then the substrates were cleaned with copious water and dried by an air blow gun, after which the substrates were dipped into the monolayered tungstate nanodots suspension (0.08 g/L) for 20 mins. The dipping processes were then repeated until the number of desired (tungstate-PDDA) bilayers was achieved.

Photoelectrochemical test: All photoelectrochemical tests were conducted in a quartz cell using a CH instruments 660E electrochemical workstation. The light source is a 300 W Xe lamp (Beijing Trusttech Co. Ltd., PLS-SXE-300UV).In a three-electrode set-up, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. In the electrochemical discharging process, a two-electrode set-up was used with Pt as both the counter electrode and reference electrode.

Characterisation: The as-prepared samples were characterized by X-ray diffraction (XRD, Rigaku Miniflex), UV-Vis spectrometer (Shimadzu UV-2600), X-ray photoelectron spectroscopy (AXIS Ultra DLD, Kratos Analytical Inc., Manchester, UK), transmission electron microscopy (TEM, FEI Tecnai G2 T20), scanning electron microscopy (SEM, FEI Nova NanoSEM 450), atomic force microscope (AFM, Bruker Dimension Icon), Zeta potential (Malvern Instruments, Nano ZS Zetasizer).

Antibacterial test in dark condition: *E. coli* O1:K1:H7 (ATCC 11775), as an indicator for bacteria contamination, was inoculated in Luria Bertani (LB) medium and cultured at 37 °C in a shaking water bath until the culture reached optical density of 0.5 at 600 nm. To prepare the bacterial suspension, *E. coli* cells were harvested by centrifugation, washed, and then diluted with sterile phosphate saline buffer solution (PBS, pH 7, 0.1mol L^{-1}). The bactericidal activity was investigated by the drop test method with some modification.[2, 3] A 20 μL aliquot of *E. coli* suspension (10^5

cells·mL^{-1}) was dropped onto the charged or discharged film surface. For each film, four independent replicates were done. After the exposure of the film for certain time at room temperature, the *E. coli* suspension was collected by thoroughly flushing it to centrifuge with 2 mL PBS buffer. 100 µL of the diluted suspension was then transferred onto a LB medium plate and incubated for 18 h at 37 °C. Survival ratio of *E. coli* was evaluated on the basis of the number of colonies formed.

For TEM imaging of *E. coli* cells, 0.5 ml of *E. coli* suspension (~109 CFU/ml) was dropped onto the unilluminated and illuminated films. After 6 h, the cell pellets were washed off from the films by 2 ml buffer solution and then collected by centrifugation (8000 rpm, 10 min). The detailed procedure to prepare the E. coli samples for TEM is described in our previous study.[4]

Antibacterial test under irradiation: Antibacterial tests under irradiation were performed similar to those in dark conditions except that the light source was a solar simulator (Newport) equipped with a AM1.5 filter and the reaction time was set to be 10 min.

2. Results of Characterizations

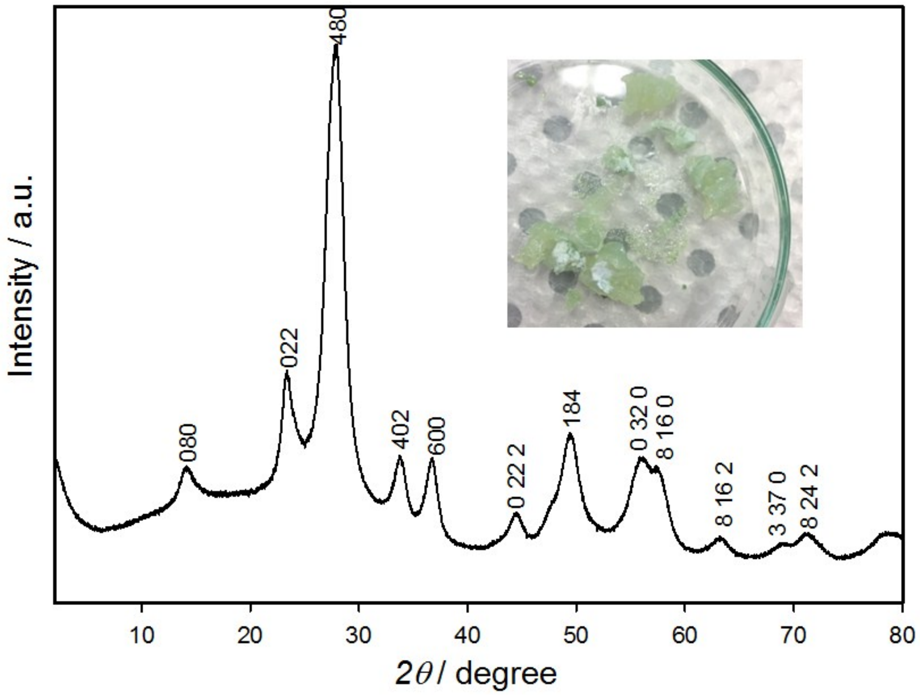

Figure S1. XRD pattern of the layered tungstate nanocrystal precursor $A_{1.2}Cs_{2.8}W_{11}O_{35}\cdot xH_2O$ (A = Na^+ and H^+, $x < 10.5$). The inset is a photograph of the tungstate nanocrystals dried at room temperature.

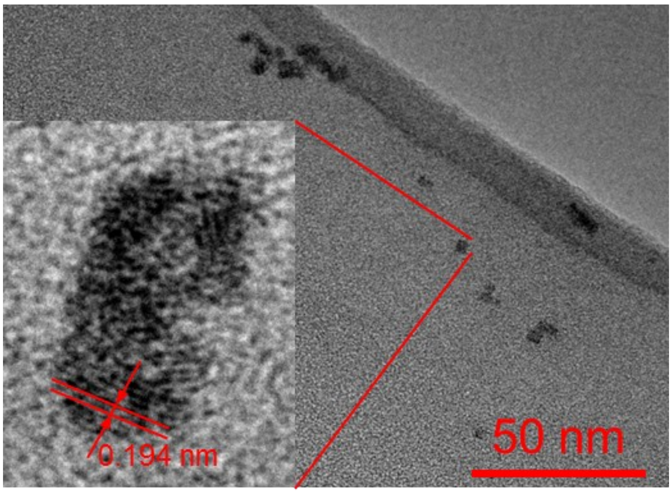

Figure S2. TEM image of the layered tungstate nanocrystals $A_{1.2}Cs_{2.8}W_{11}O_{35}\cdot xH_2O$ (A = Na^+ and H^+, $x < 10.5$). Inset shows the HRTEM image of a layered tungstate nanocrystal.

The observed lattice fringes of 0.194 nm in the High resolution TEM (HRTEM) image of tungstate nanocrystals corresponded to the (004) plane of tungstate (inset of Figure S2).

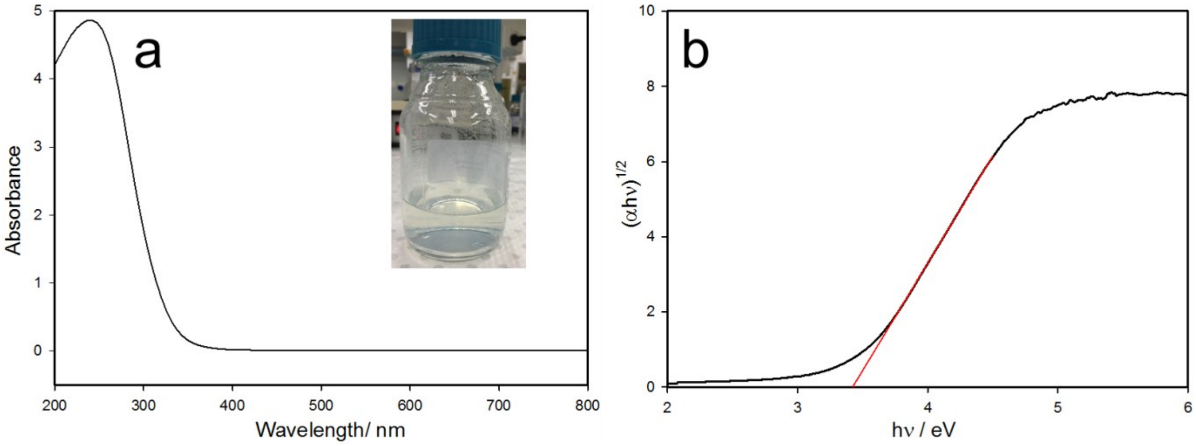

Figure S3. a) UV-Visible absorption spectrum of the monolayered tungstate NDs suspension. Inset is a photograph of the NDs suspension. b) Tauc plot of the monolayered tungstate NDs.

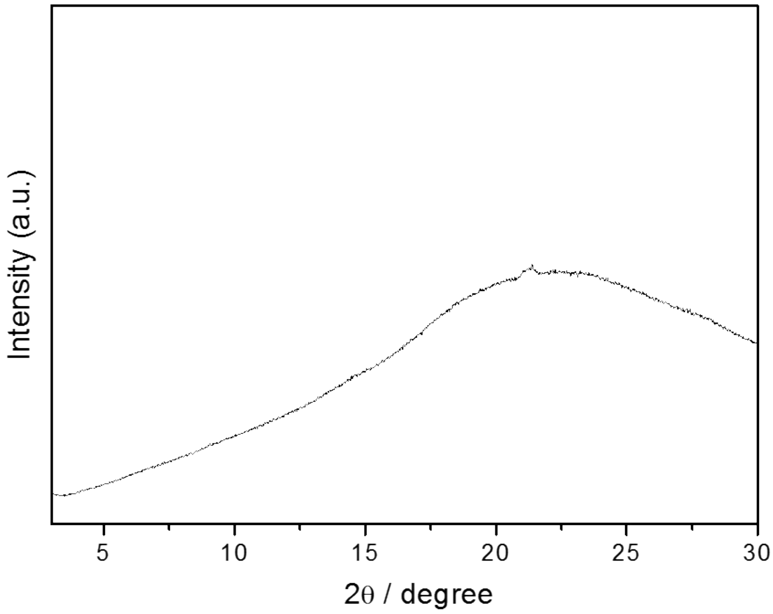

Figure S4. XRD pattern of the monolayered tungstate nanodots deposited onto a glass substrate.

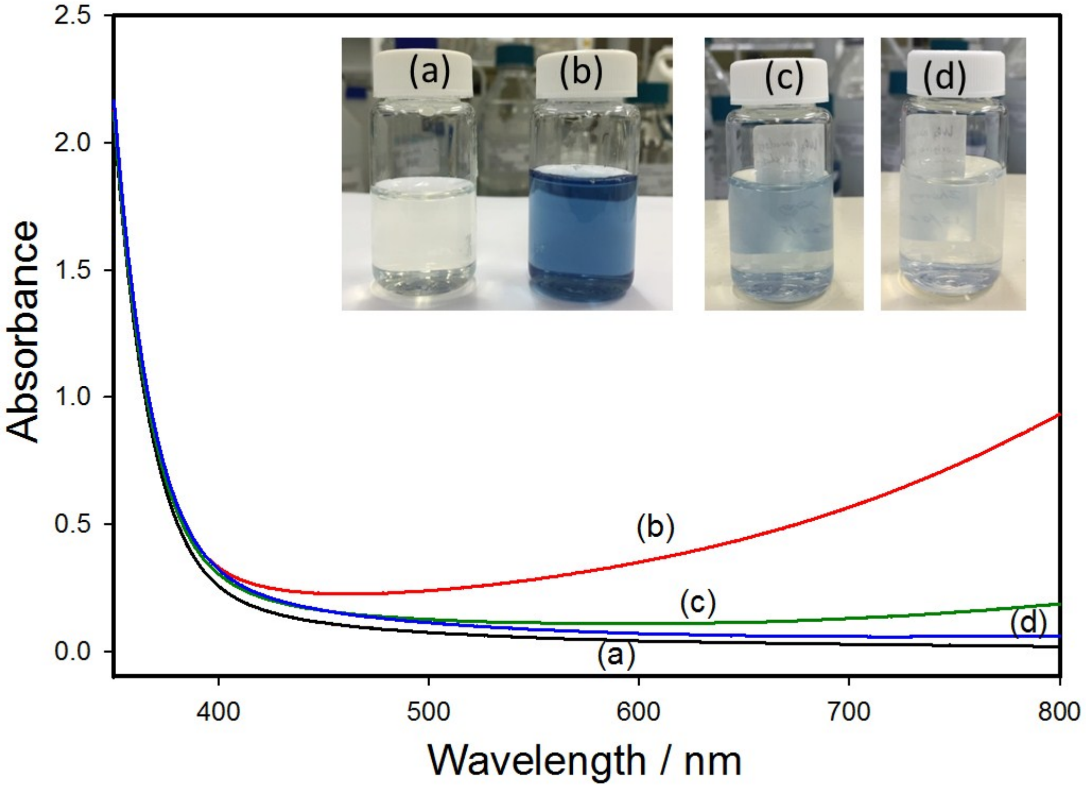

Figure S5. UV-Visible absorption spectra and photographs of (a) the as-prepared tungstate NDs suspension, (b) the NDs suspension after 10 mins of irradiation, and stored in dark for (c) 3 days and (d) 6 days.

The as-prepared monolayered tungstate NDs showed obvious photochromic phenomenon. The colour of NDs colloidal suspension quickly turned from light greenish to deep blue within 10 mins of UV irradiation, and then gradually shifted back to initial state under dark condition in a week. The reversible coloration/bleaching was repeated over three times to verify the photochromism effect of the NDs.

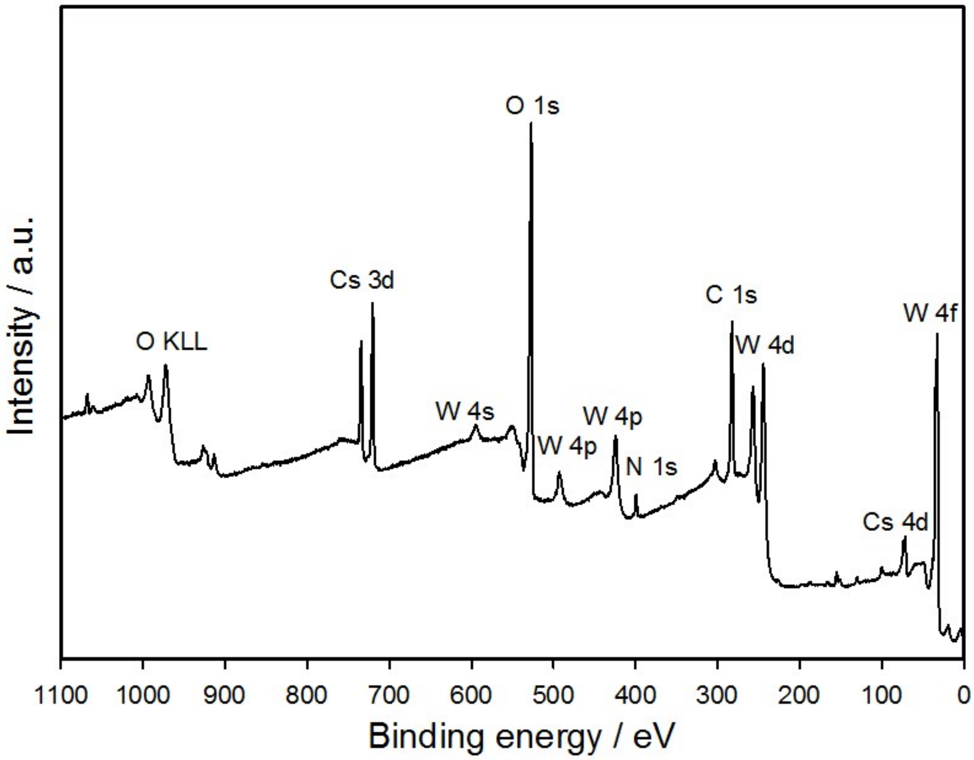

Figure S6. XPS spectrum of the (tungstate-PDDA)$_{10}$ multilayer film.

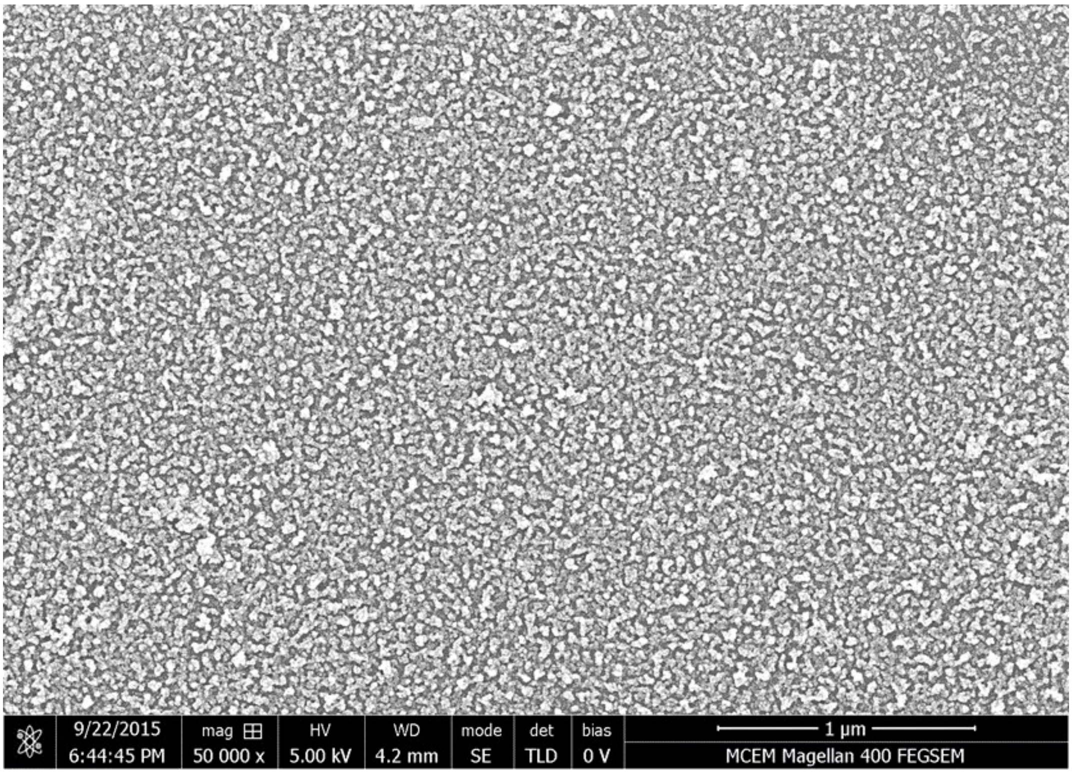

Figure S7. SEM image of (tungstate-PDDA)$_{10}$ multilayer film on glass substrate.

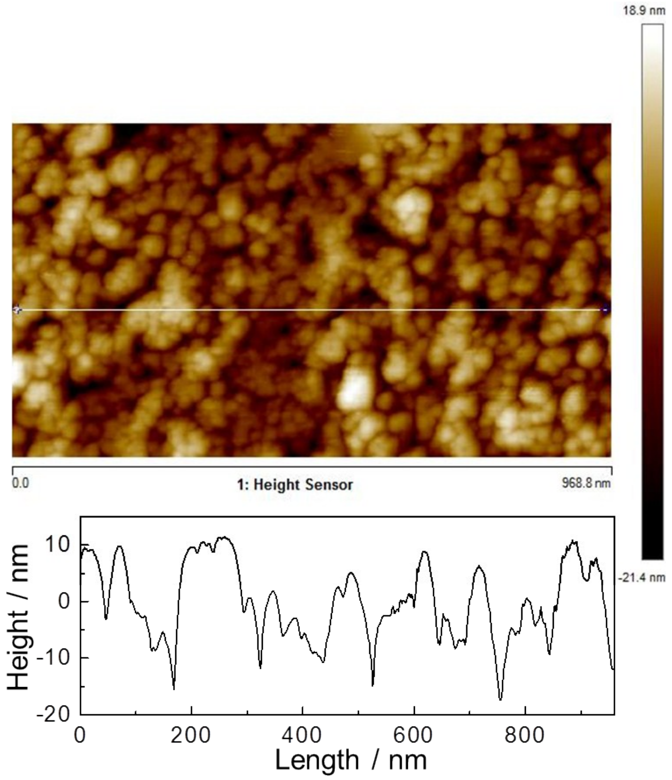

Figure S8. AFM image of (tungstate-PDDA)$_{10}$ multilayer film on glass substrate, and the height profile analysis taken around the white line.

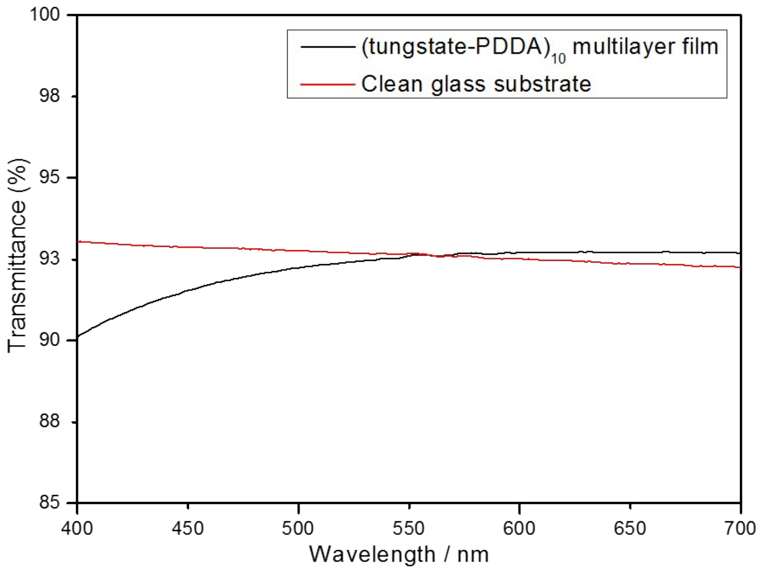

Figure S9. Visible transmittance of clean glass substrate and (tungstate-PDDA)10 multilayer film.

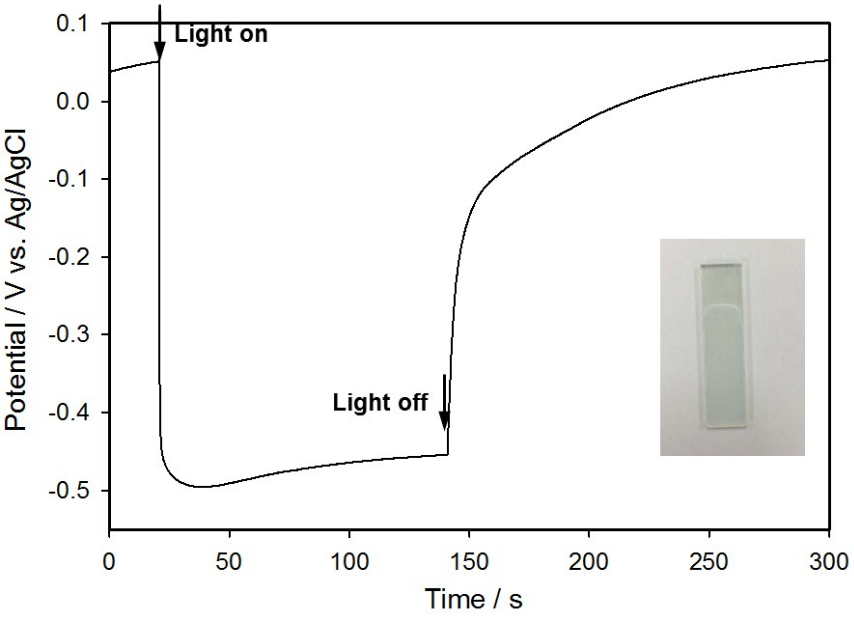

Figure S10. The shift of OCP in response to light on/off for the P25 photoelectrode. Inset is a photograph of the P25 photoelectrode. Experimental condition: a 300 W Xe lamp was used as the light source, and 3wt% NaCl solution (pH=5.0) was chosen as the electrolyte. A total surface area of 1.9 cm^2 of the photoelectrode was illuminated during the measurement.

Generally, when a n-type semiconductor is exposed to irradiation, the photogenerated holes are consumed by the surface absorbed water molecules while the photogenerated electrons accumulate in the conduction band, causing the downshift of potential. However, the accumulated electrons are not stable and often decay very quickly once the illumination is stopped.

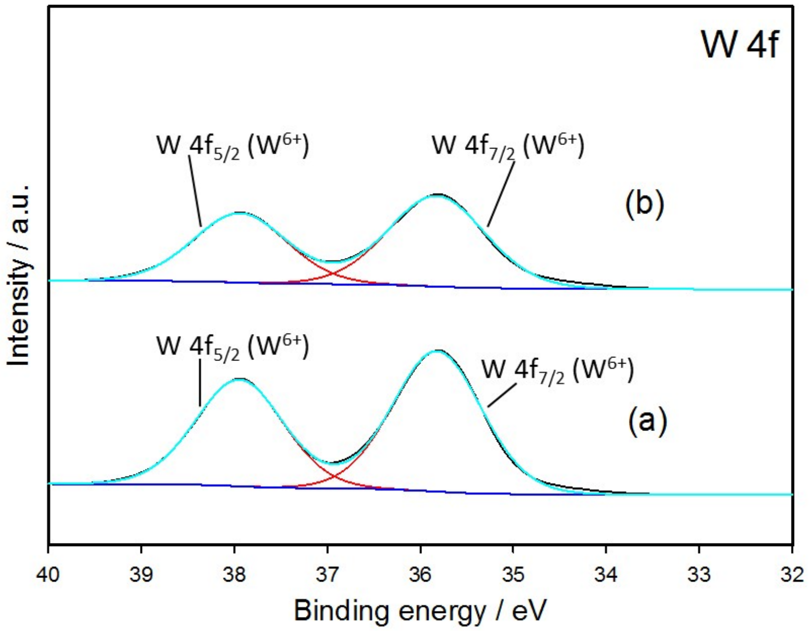

Figure S11. XPS spectra of W 4f measured in (a) the as-prepared (tungstate-PDDA)$_{10}$ film and (b) the illuminated (tungstate-PDDA)$_{10}$ multilayer film after being stored in air for 1 week.

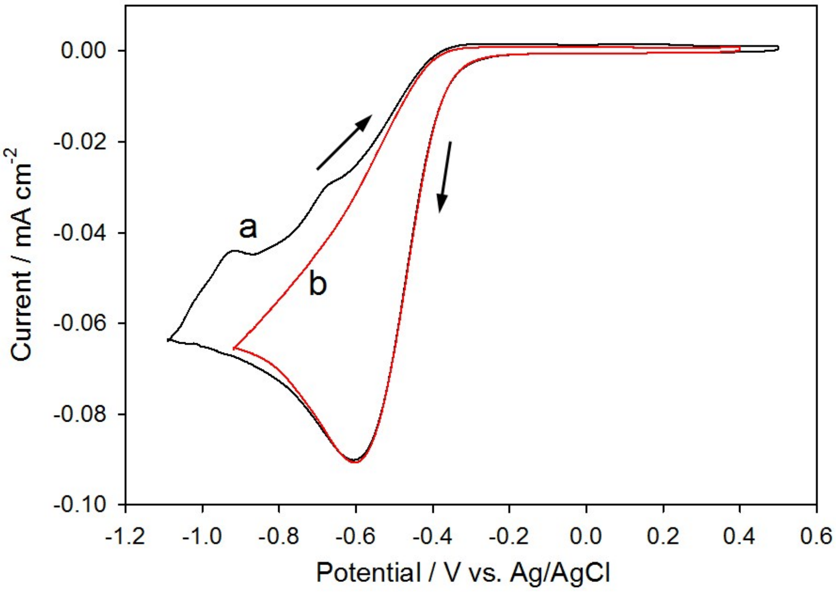

Figure S12. Cyclic voltammogram of the (tungstate-PDDA)$_{10}$ multilayer electrode (a) measured immediately after the photoelectrode was illuminated for 20 mins and (b) measured 5 mins after the first cycle was finished. The black arrows showed the scanning direction. Measurement condition: 0.5 M Na_2SO_4 solution (pH=5.7) was used as the electrolyte, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. During the whole measuring process, a total area of 2 cm^2 of the electrode was illuminated by the Xe lamp.

In the cyclic voltammogram (CV) of (tungstate-PDDA)$_{10}$ photoelectrode measured immediately after 20 mins of photocharging (Figure S11a), an anodic peak at ca. -0.91 V vs. Ag/AgCl associated with the oxidation of W^{5+} to W^{6+} was observed, which disappeared in the second scan cycle (Figure S12b), presumably due to absence of W^{5+}. It should be noted that the anodic peak at -0.68 V and the cathodic peak at -0.6 V were not assigned to the (tungstate-PDDA)$_{10}$ multilayer film. As shown in Figure S13, in the cyclic voltammogram of a bare FTO substrate, those two peaks also appeared.

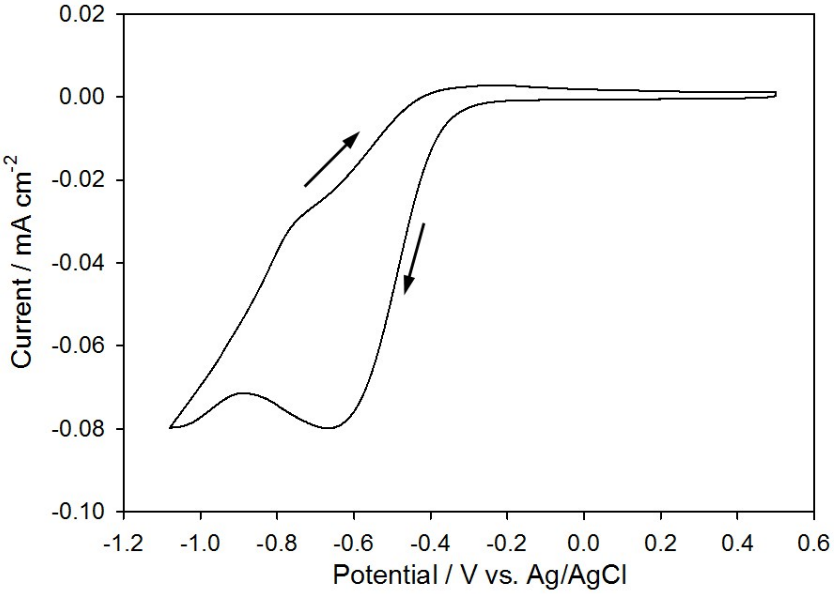

Figure S13. Cyclic voltammogram of a bare FTO substrate. The black arrows showed the scanning direction. Measurement condition: 0.5 M Na_2SO_4 solution (pH=5.7) was used as the electrolyte, Pt was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. During the whole measuring process, a total area of 2 cm^2 of the electrode was illuminated by the Xe lamp.

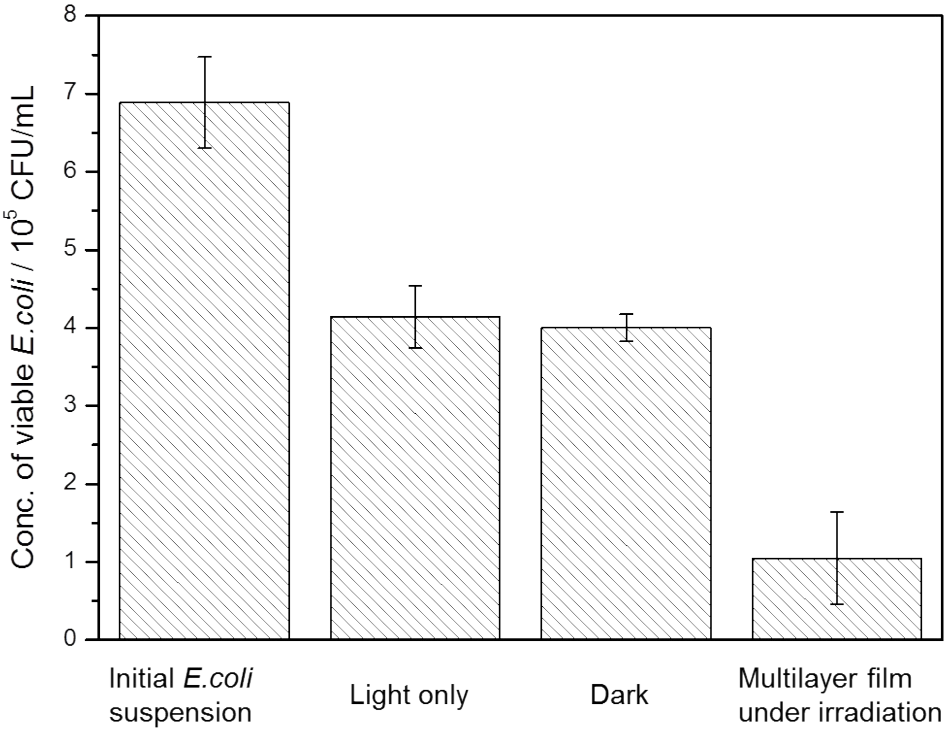

Figure S14. Comparison of concentrations of viable E. coli in the initial suspension, after 10 min reaction under irradiation only without multilayer film, after 10 min reaction with multilayer film under dark conditions and after 10 min reaction with multilayer film under irradiation. Light source: Solar simulator (100 W) equipped with AM1.5 filter.

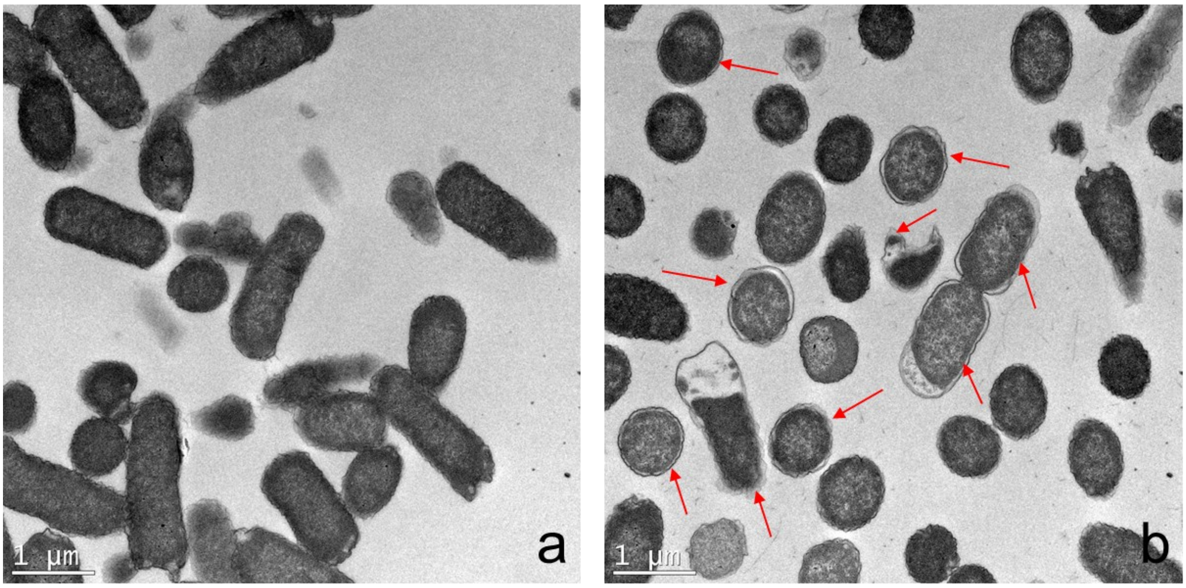

Figure S15. TEM images of *E. coli* cells reacted with a) unilluminated and b) pre-illuminated multilayer film for 6 h. The red arrow in b) indicates the cells with destroyed cell structure. For some cells, a remarkable electron-light region occurs on the edge, and in other cells, missing cytoplasm and big gap between the cytoplasm membrane and the cell wall can be clearly seen.

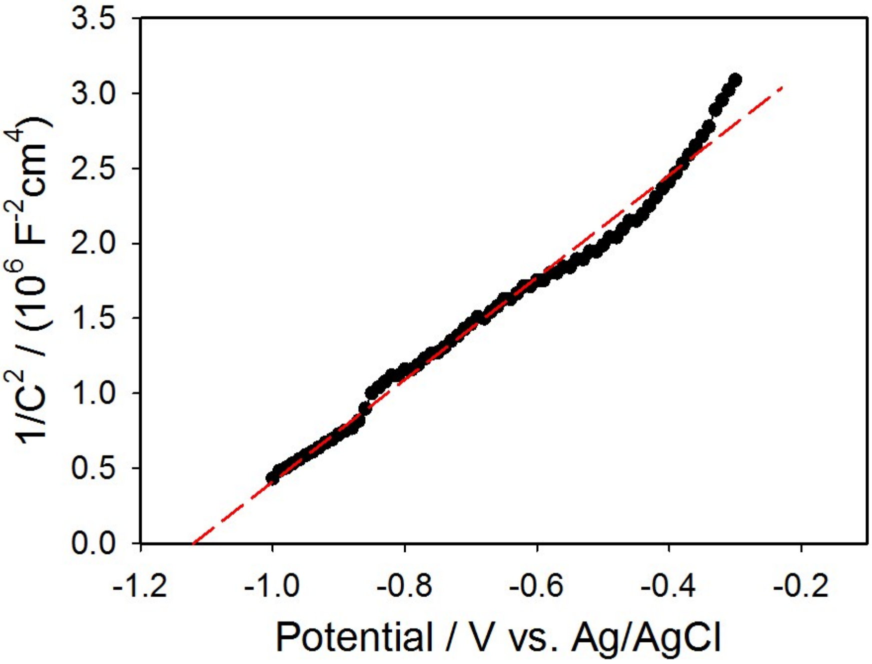

Figure S16. Mott-Schottky plot of monolayered tungstate nanodots. The potential was measured against an Ag/AgCl reference electrode in a 0.1 M NaH_2PO_4/Na_2HPO_4 solution (pH=7). The red dash line shows the linear fit of the plot.

Mott-Schottky equation is:

$$\frac{1}{C^2} = \frac{2}{e_0 \varepsilon \varepsilon_0 N_d}\left(V - V_{FB} - \frac{kT}{e_0}\right)$$

Where C is the interfacial capacitantce, e_0 is electron charge, $\boldsymbol{\varepsilon}$ is the permittivity of vacuum, $\boldsymbol{\varepsilon}_0$ is the dielectric constant, N_d is the dopant density, V is the applied potential, V_{FB} is the flat band potential, k is the Boltzmann's constant and T is the absolute temperature.

The flat band potential of monolayered tungstate nanodots can be determined by extrapolating the linear fit of the Mott-Schottky plot to the horizontal axis intercept. The flat band potential was calculated to be -1.12 V vs. Ag/AgCl at pH=7. To convert the obtained flat band potential vs. Ag/AgCl to it vs. RHE (NHE at pH=0), the following equation is used:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}{}^{0} (E_{Ag/AgCl}{}^{0} =+ 0.199V)$$

The converted NHE flat band potential is -0.51 V vs. NHE, which is more negative than both O_2/O_2^- (-0.284 vs. NHE) and O_2/H_2O_2 (+0.682 V vs. NHE). This indicated the fact that the electrons stored in the monolayered tungstate NDs can reduce O_2 to form both O_2^- and H_2O_2.

References:

1. K. Nakamura, Y. Oaki and H. Imai, *J. Am. Chem. Soc.*, 2013, **135**, 4501-4508.

2. T. Tatsuma, S. Takeda, S. Saitoh, Y. Ohko and A. Fujishima, *Electrochem. Commun.*, 2003, **5**, 793-796.
3. I. Y. Kim, S. Park, H. Kim, S. Park, R. S. Ruoff and S. J. Hwang, *Adv. Funct. Mater.*, 2014, **24**, 2288-2294.
4. X. K. Zeng, D. T. McCarthy, A. Deletic and X. W. Zhang, *Adv. Funct. Mater.*, 2015, **25**, 4344-4351.