Supporting Information

Experimental details:

Materials

Lysozyme from chicken egg white (62971) was purchased from Fluka. Titanium (IV) oxide (634662), tungsten(VI) oxide (550086), titanium(IV)-bis-ammonium-lactato-dihydroxide (TiBALDH) (388165), titanium(III) chloride solution (14010), ammonium thiocyanate (A7149) and sodium tungstate dihydrate (223336) were purchased from Sigma-Aldrich. Micro BCA Protein Assay Kit (23235) was purchased from Thermo scientific.

Determination of dissociation constant of lysozyme binding to TiO_2 or WO_3

Lysozyme was dissolved in water to give concentrations of 0, 5, 10, 20, 30, 40, 50, 60, and 70 µg/ml. 3 mg of TiO_2 or WO_3 particles were incubated with 1 ml of each lysozyme solution for 1 h on a mixer (SLRM-22M Intelli mixer, Seoulin Bioscience, Korea). Following the incubation, the TiO_2 or WO_3 particles were collected by centrifugation (8000*g*, 5 min), and the lysozyme concentration in the supernatant was determined using Micro BCA Protein Assay Kit according to the manufacturer's protocol.

Mineralization of TiO_2 and titanium-tungstate hybrid metal oxides

To synthesize TiO_2, lysozyme was dissolved in water to give 3 mg/ml of protein solution. 36 ml of lysozyme solution was incubated with 4 ml of 1 M TiBALDH (used as TiO_2 precursor) solution for 30 min on the mixer. To synthesize hybrid metal oxides of varying composition, the order of biomineralization for each metal oxide (i.e. the sequence of adding individual precursors to lysozyme solution) was controlled as follows: 36 ml of lysozyme solution was first incubated with 2 ml of 1 M TiBALDH solution for 30 min and this mixture was further incubated with 2 ml of 1 M sodium tungstate (used as WO_3 precursor) solution for additional 30 min (Case A); the sequence of precursor addition to lysozyme solution in the Case A was inversed (Case B); Mixing of both precursor solutions with lysozyme solution was initiated at the same time and the mixture solution was incubated for 30 min (Case C). The synthesized metal oxides were collected by centrifugation (8000*g*, 5 min), washed three times with deionized water and freeze-dried (EYELA FDU-1200, Japan).

Characterization of biomineralized metal oxides

Various metal oxides were suspended in water, deposited on silicon wafer and air-dried. Platinum sputter coating was performed before images of the metal oxides were taken using SEM (JEOL-JSM7500F, Japan), and the particle size analyzed (no. of particles = 50) using Image J software (version 1.43s, NIH, USA). Weight percentage of lysozyme in freeze-dried Case A, B and C composites was determined by thermogravimetric analysis (Seiko Exstar 6000, Seiko Instruments Inc., Japan) from 20 to 1000°C at a rate of 10°C /min. Metal oxides were calcined under 700°C for 3 h, suspended in water and deposited on a pre-cleaned glass substrate for XRD analysis. XRD analysis was conducted with Cu K radiation using an X-ray diffractometer (Bruker D8 Discover, Germany) at 40 kV. The scan rate was 4°/min from 2Θ value of 20° to 70°. PL spectra were measured using luminescence spectrometer (AMINCO•Bowman Series 2, USA) with excitation wavelength of 300 nm. The spectra range was from 350 to 550 nm. Transmission electron microscopy (TEM) and elemental mapping observations were performed on an electron microscope (JEOL, JEM-2100F, Japan). The Ti or W content of the hybrid metal oxides was analyzed by ICP-OES (Inductively

Coupled Plasma-Optical Emission Spectrometry, Varian 720-ES, Varian, USA). The surface areas of composites were measured by BET surface area measurement analyzer (ASAP 2000, Micromeritics Instrument Corporation, USA).

Measurement of photocurrent density

Chronoamperonmetry measurements were performed to investigate electrochemical responses using a 3-electrode configuration with Pt (counter electrode) and Ag/AgCl (reference electrode) in 0.5 M Na_2SO_4 solution (electrolyte), and these techniques were used at a scan rate of 10 mV/s under 0.6 V of bias. The samples used as photoanodes (working electrode) were illuminated under 1 sun irradiance with a xenon lamp based solar simulator (PECCELL, Yokohama, Japan, PEC-L01: 100 mW/cm^2). The power of the xenon lamp was 150 W and the light intensity of the solar simulator was calibrated prior to each sample measurement using a silicon reference cell (Fraunhofer ISE, Certificate No. C-ISE269).

Measurement of photocatalytic activity

Photocatalytic activity of synthesized metal oxides was determined using rhodamine B solution of initial concentration 10 μM. Before the photocatalytic activity measurement, metal oxides and rhodamine B were kept for 2 h in the dark to allow adsorption/desorption equilibrium. After equilibration, 25 mg of metal oxide in 50 ml of rhodamine B was illuminated using 100 mW/cm^2 of light irradiance from a xenon lamp based solar simulator, and 2 ml solutions were sampled at 20 min-intervals for 120 min. The unreacted rhodamine B was separated from the metal oxides by centrifugation, and the absorbance of the supernatant was measured by UV-vis spectrometer.

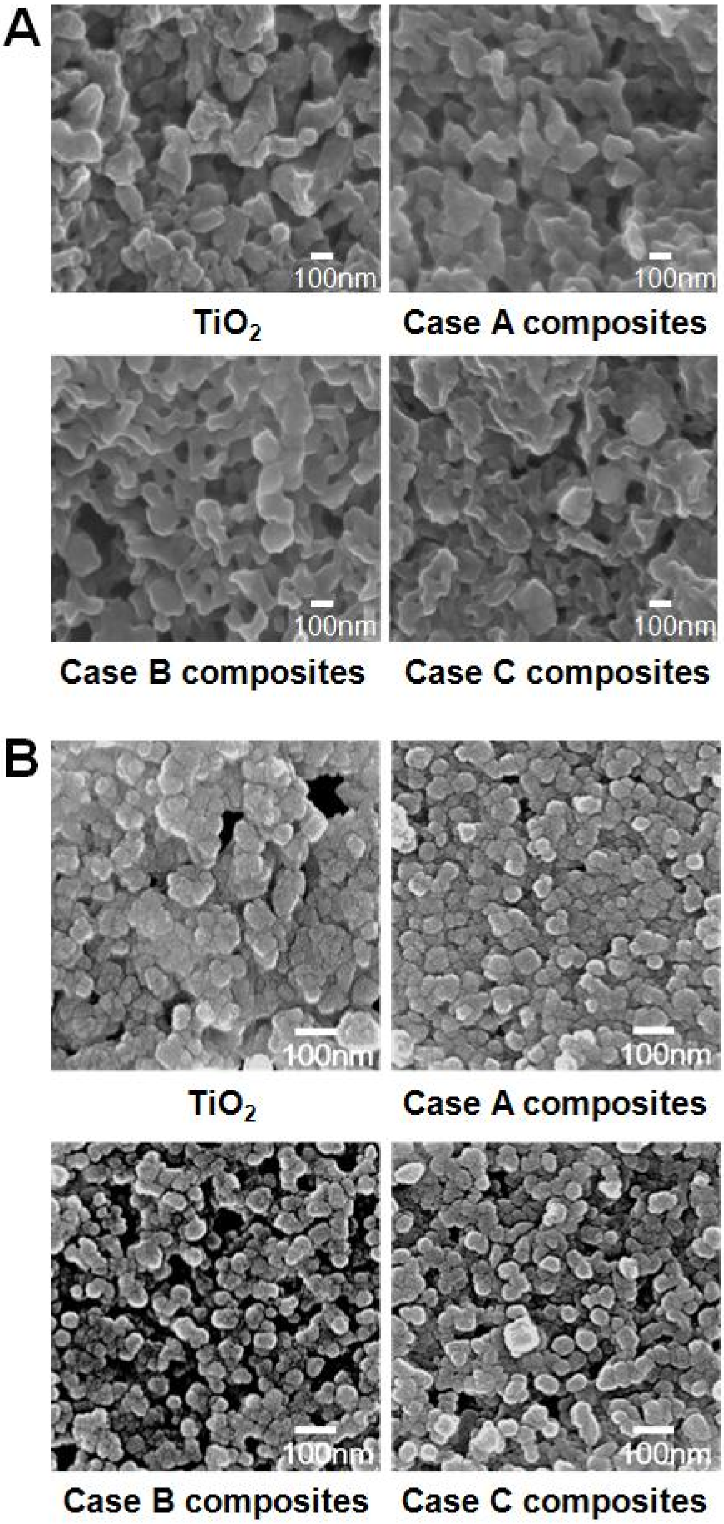

Fig. S1 SEM images of TiO_2 and titanium-tungstate composites produced from biomineralization Cases A, B and C before (A) and after (B) calcination.

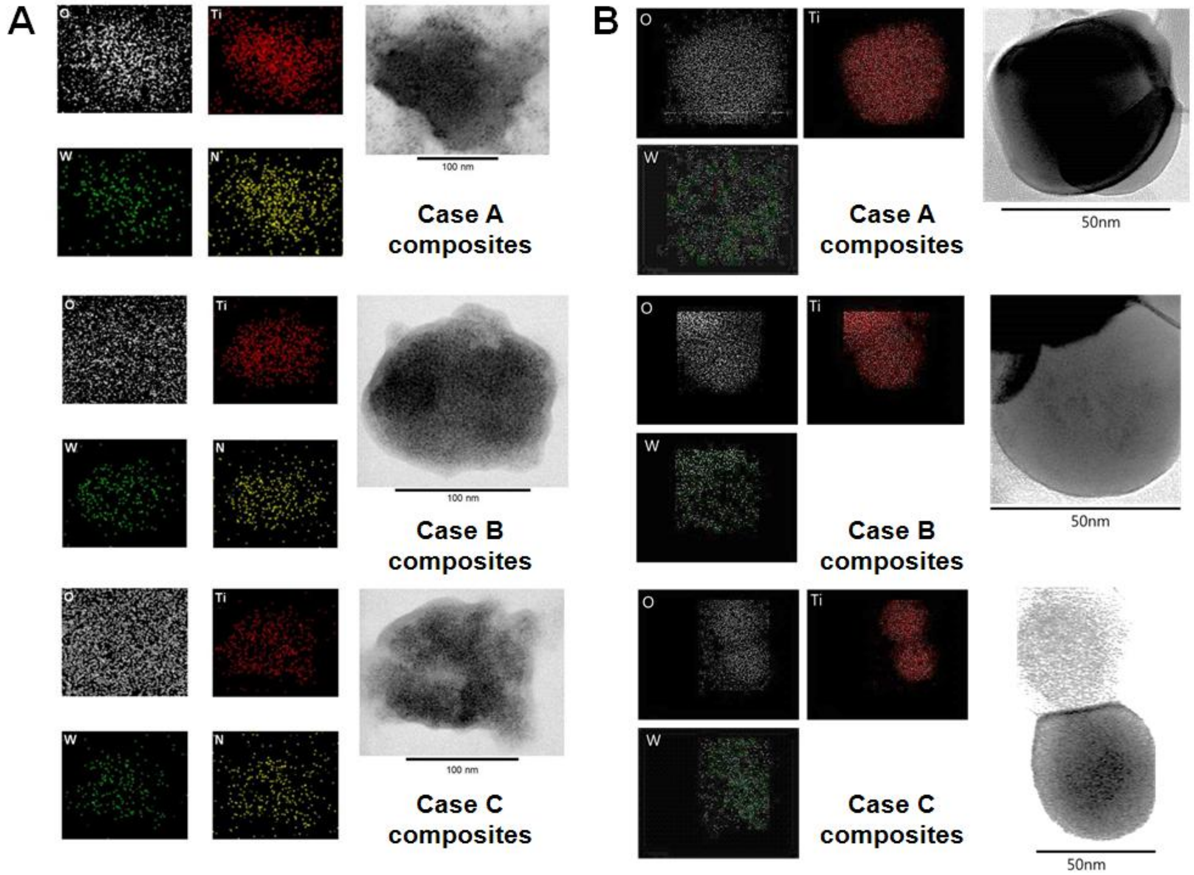

Fig. S2 TEM images and elemental mapping images of titanium-tungstate composites produced from biomineralization Cases A, B and C before (A) and after (B) calcination. Ti, W and N represent the presence of TiO_2, WO_3 and lysozyme (protein), respectively.

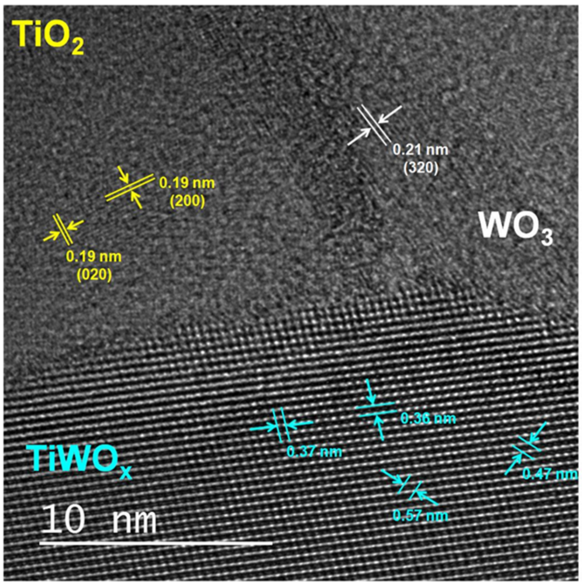

Fig. S3 HR-TEM images of Case C composites shown in Fig. 1F after calcination.

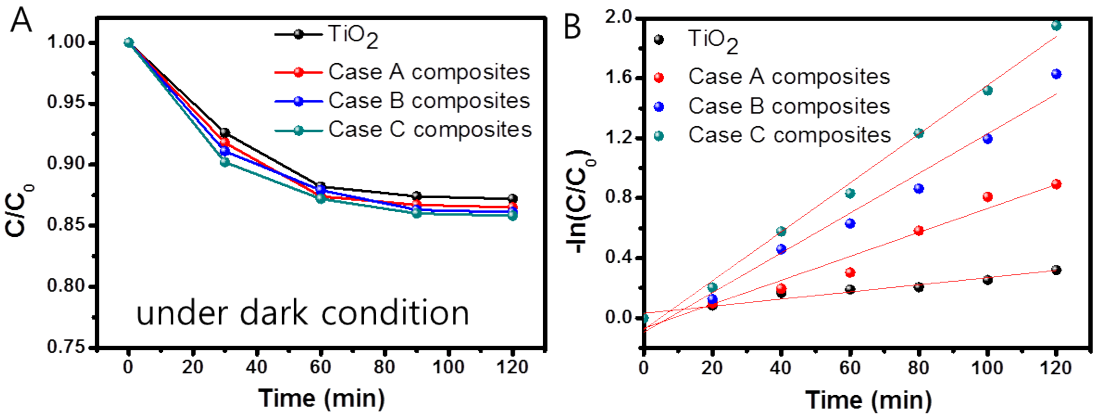

Fig. S4 Concentration changes in rhodamine B solution under the dark condition for adsorption/desorption equilibrium (A) and natural logarithmic plots for the study of kinetics of rhodamine B photodegradation profiles shown in Fig. 4C (B). Note that the differential kinetics of rhodamine B photodegradation is unlikely affected by the surface area of each composites as all the composites used in the experiments were found to have 11 - 12 m^2/g of BET surface area (data now shown).

Table S1 First order reaction rate constants for photodegradation of rhodamine B estimated by calculating the slopes for the natural logarithmic plots in Fig. S4B.

	TiO_2	**Case A**	**Case B**	**Case C**
Rate constant, k (min^{-1})	0.0038	0.0050	0.0094	0.0128

Rate constant values were calculated by $C/C_0=\exp(-kt)$, where k is the apparent rate constant, t is the irradiation time, C_0 is the initial and C is the residual concentration of rhodamine B, respectively.