

## Supplementary Information

Visible-light-induced electron transfer between alternating stacked layers of tungstate and titanate mediated by excitation of intercalated dye molecules.

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## Experimental Procedure

### Synthesis of the RhB intercalated alternating layered structure

The titanium oxide/tungsten oxide alternating layered structure was synthesized as previously reported.<sup>16</sup> Layered tungstate  $\text{H}_2\text{W}_2\text{O}_7$  and layered titanate  $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$  ( $\square$ :vacancy,  $x\approx 0.7$ ) were each separately dispersed in octylamine/heptane. As a result of the intercalation of octylamine, the interlayer distances between the layers of tungstate and titanate were expanded. After the organic modification of the tungstate and titanate layers by 8-octenyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane, respectively, alkene-modified tungstate and thiol-modified titanate were obtained. These samples were ultrasonicated in *N,N*-dimethylformamide (DMF) for 1 h to generate nanosheet dispersions of each oxide. The two nanosheet dispersions were mixed together, and then azobisisobutyronitrile (AIBN) was added to the mixture under nitrogen, followed by stirring of the solution for 24 h at 80 °C. The product, which comprised alternating stacked layers of tungstate and titanate, was collected by centrifugation.

Next, the alternating layered structure (10 mg) was dispersed in a solution of rhodamine B (RhB) in ethanol ( $4.0 \times 10^{-4}$  M, 25 mL). The suspension was then stirred for 24 h, after which time the product was collected via centrifugation. The centrifuged product was dried under vacuum, and the RhB-intercalated titanium oxide/tungsten oxide alternating layered structure was obtained as a powder.

### Characterizations

X-ray diffraction (XRD) analyses were carried out using a Philips X'Pert MPD-OEC diffractometer with bent crystal monochromated  $\text{CuK}\alpha$  radiation. UV-Vis absorption spectra were recorded on a JASCO V-570.

### Visible-light-induced electron transfer

A double-faced tape (5 mm  $\times$  5 mm) was attached to a glass substrate, and the RhB-intercalated sample was then dispersed on its top surface. The sample-coated substrate was irradiated with 400 nm monochromatic light for 5 min. During irradiation, near-infrared diffuse reflectance spectroscopic measurements were taken once per minute. After 400 nm irradiation, the substrate was irradiated with 570 nm monochromatic light for 8 min. During irradiation, near-infrared diffuse reflectance spectroscopic measurements were collected every 2 minutes. Light irradiation was carried out using a MAX-303 Xe light source (equipped with 400 nm and 450–650 nm (every 10 nm) band-pass filters (Asahi Spectra Co., Ltd.)). Near-infrared diffuse reflectance spectroscopy was performed using a JASCO V-570 instrument equipped with an integrating sphere JASCO ISN-470 near-infrared spectrometer.

### Calculation method of vertical axis of action spectrum (Fig.4)

$K_{5min}$  was K-M value of the RhB-intercalated sample after irradiation with 400 nm light for 5 min.

$K_{7min-\lambda}$  was K-M value of the sample after irradiation with 400 nm light for 5 min then irradiation with  $\lambda$ (=450-650) nm monochromatic light for 2 min.

$E_{\lambda, nm}$  was the energy which the sample absorbed by irradiation with  $\lambda$  nm light.

Then, vertical axis values of Fig.4 were given by

$$\frac{K_{5min} - K_{7min-\lambda}}{\lambda E / hc}$$

where the denominator was the number of photons the sample absorbed, and the numerator was  $\Delta$  K-M value from 5 min to 7 min. A scale of  $\Delta$  K-M value should be proportionate to the number of electrons in the tungstate conduction band.

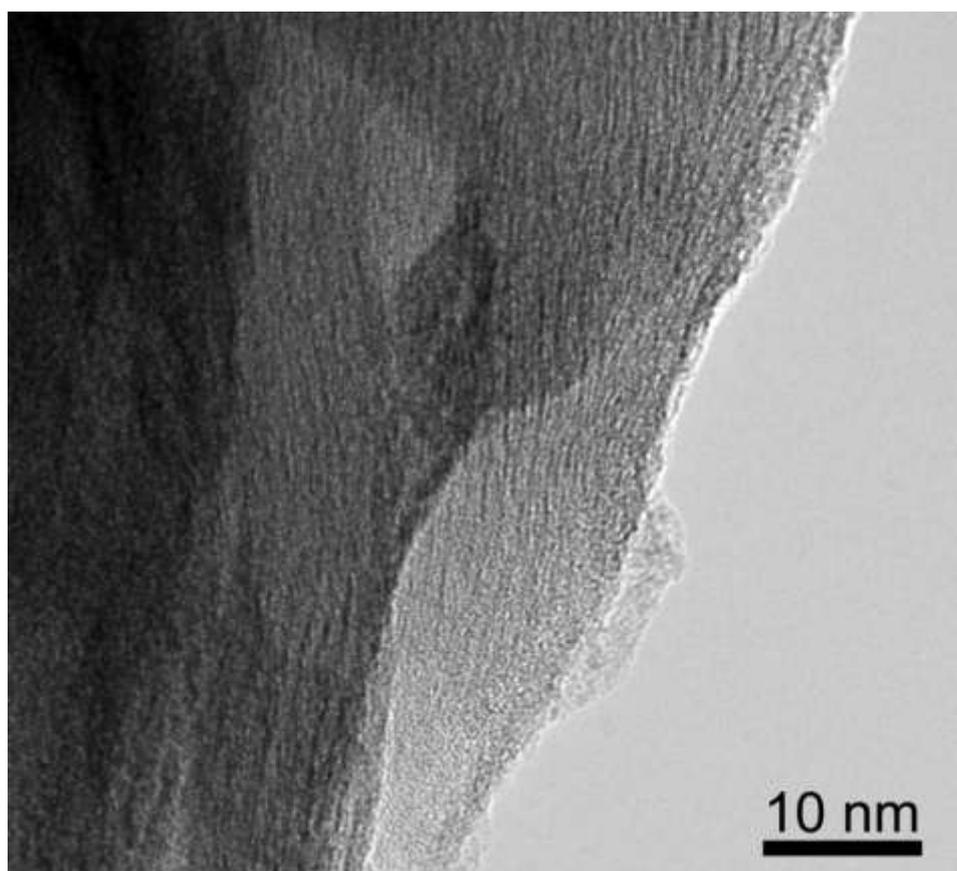


Fig. S1 TEM image of alternative stacking structure.

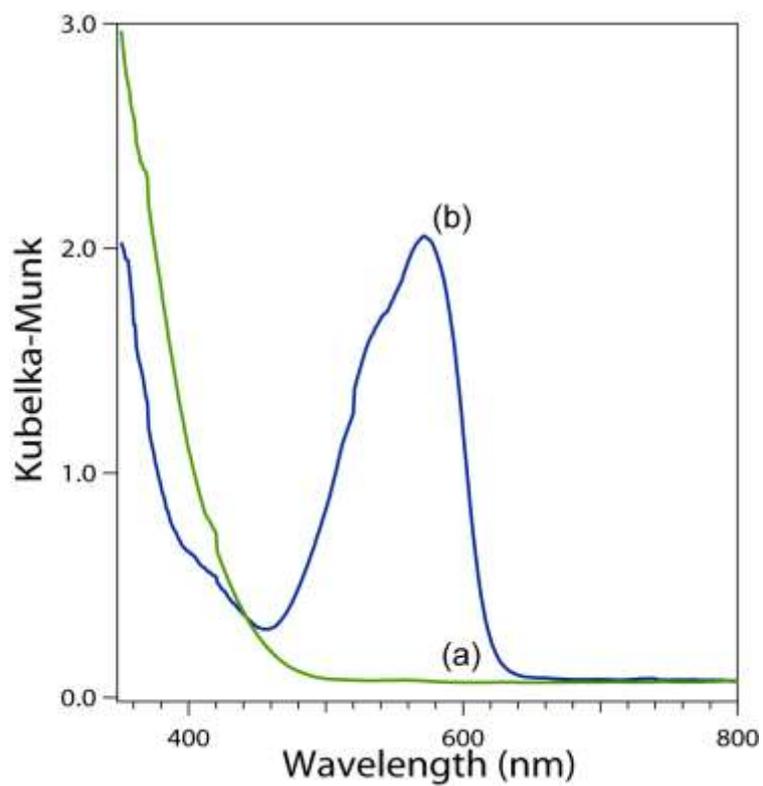


Fig. S2 UV-Vis diffuse reflectance spectra: (a) Alternating stacked layers of tungstate and titanate. (b) RhB-intercalated sample. The peak at  $\lambda = 570$  nm originates from RhB.

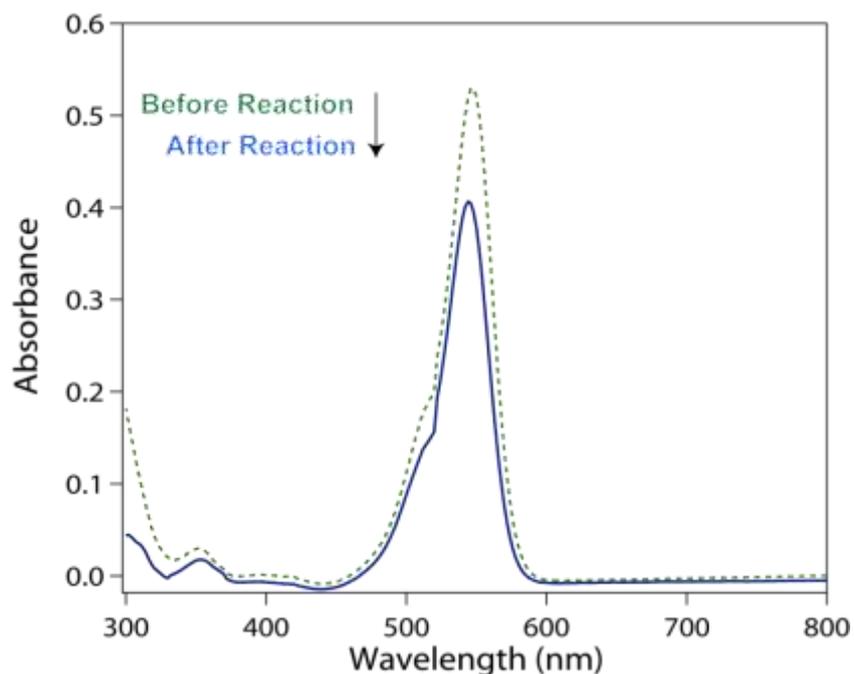


Fig. S3 UV-Vis absorption spectrum of an ethanol solution of RhB. The green dotted line is the spectrum of the RhB solution before intercalation. The blue solid line is the spectrum after RhB intercalation. The amount of intercalated RhB was calculated on the basis of the decrease in the absorbance of RhB.

Table S1 Chemical composition of the products

Elemental Analysis(Carbon,Hydrogen,Nitrogen) was carried out using a YANACO CHN CORDER MT-6.

|                                     | Mass<br>%C | Mass<br>%N | Octylamine<br>molecules/nm <sup>2</sup> | RhodamineB<br>molecules/nm <sup>2</sup> | Click-reacted organic chain<br>molecules/nm <sup>2</sup> |
|-------------------------------------|------------|------------|---|---|--|
| Alternate layered<br>nanostructure  | 13.53      | 2.03       | 4.2                                     | -                                       | 0.50   |
| Rhodamine B<br>-intercalated sample | 13.88      | 1.24       | 1.3                                     | 0.6                                     | 0.50   |

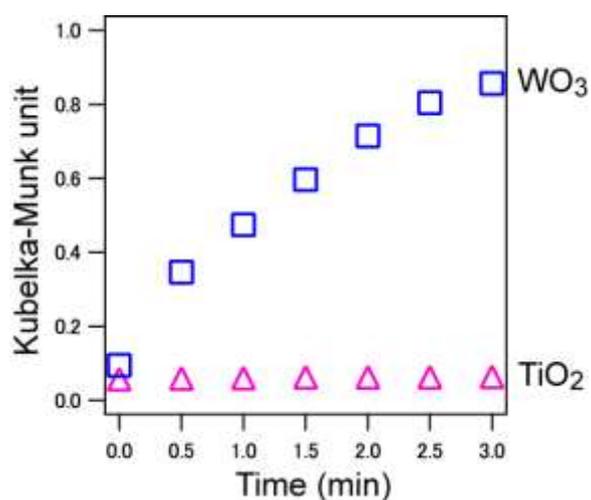


Fig. S4 Time variation plots of the Kubelka-Munk values at 1500 nm. (blue: tungsten oxides irradiated with 400 nm monochromatic light. Pink: titanium oxides irradiated with 305 nm monochromatic light.)

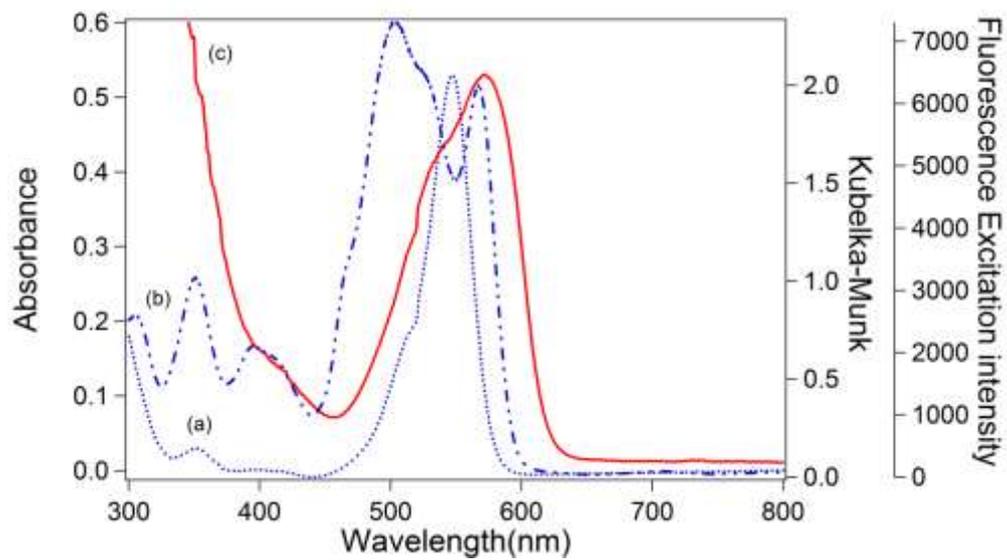


Fig. S5 (a) UV-Vis absorption spectrum of a hydrochloric acid solution (pH = 2) of 0.03 mM RhB (left axis); (b) Fluorescence excitation spectrum of a hydrochloric acid solution (pH = 2) of 0.03 mM Rh B (furthest right axis); and (c) UV-Vis diffuse reflectance spectrum of the RhB-intercalated sample (right axis).