

Supporting information for

**High Performance Photocatalytic Metal Oxide Synthetic Nanosheets
Formed by Atomic Layer Deposition**

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1. Experimental details

Sacrificial Polymer layer: Polyacrylic acid (PAA, $M_w = 1,800$ g/mol) and polyvinyl alcohol (PVA, $M_w = 16,000$ g/mol) were purchased from Sigma-Aldrich and Acros Organics, respectively and used without further purification. They were dissolved in deionized (DI) water with a concentration of 2 wt% followed by spin-coating onto a Si/SiO₂ substrate for 30 s at 3000 rpm. For the results shown in this manuscript, nanosheets were prepared with an PVA sacrificial layer.

Atomic Layer Deposition (ALD): The precursors for ZnO and Al₂O₃ films are diethylzinc (DEZ, 95%) and trimethylaluminum (TMA, 98%), respectively. For TiO₂ films, titanium tetrachloride (TiCl₄, 99%) was used as a precursor. All precursors were purchased from Strem Chemicals, Inc. ALD was performed in a custom hot wall viscous flow tube reactor where each precursor was dosed sequentially with DI water as the oxidant. The partial pressures for DEZ, TMA, and DI water was 0.1–0.2 torr at the deposition temperature of 90 °C while TiO₂ ALD was performed with partial pressure 0.03 torr of TiCl₄ at deposition temperature of 100 °C. The operating pressure was 2 torr for all ALD processes. Growth per cycles (GPC) were 1.3, 1.7, and

0.4 Å/cycle for Al₂O₃, ZnO, and TiO₂, respectively. The as-deposited Al₂O₃ and TiO₂ films have amorphous, and ZnO film is polycrystalline.^[1,2]

Film Separation: After coating the PVA sacrificial layer with ALD, the films were cut with a razor blade while still on the silicon substrate to facilitate dissolution of the sacrificial layer. Next, the wafers were immersed in DI water heated to 60 °C. After several minutes, metal oxide nanosheets were separated from the substrate and became dispersed in aqueous solution.

For AFM, SEM, or TEM investigations, the nanosheets were collected on a substrate dipped in solution. To collect nanosheets more effectively, carbon tetrachloride was added to the nanosheet dispersion followed by shaking. When a substrate such as oxidized silicon was introduced vertically in the solution, nanosheets were collected on the substrate densely to minimize total interface energy of the system.^[3] For AFM, samples collected on flat SiO₂ were annealed in air at 300 °C for 1 h to remove any residual polymer. For TEM, annealing was also performed at 300 °C to 450 °C for 1 h to crystallize the material.

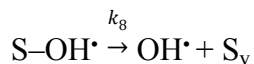
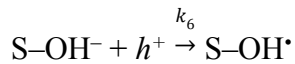
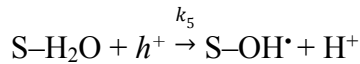
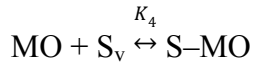
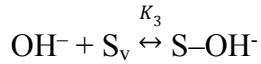
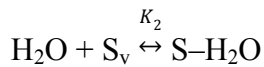
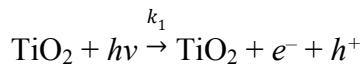
Characterization: ALD film thickness was measured with ellipsometry (Alpha-SE Ellipsometer, JA Woollam Co., Inc.) using a reference Si/SiO₂ substrate. Atomic force microscopy (AFM, DI 3000) and scanning electron microscopy (SEM, JEOL 6400) with energy dispersive X-ray analysis (EDX) was used to image nanosheets, measure thickness and analyze composition. Transmission electron microscopy (TEM, Hitachi HF 2000) operated at 200 kV was used to characterize crystallinity.

Photocatalysis Measurement: Methyl orange was purchased from Sigma-Aldrich. Nanosheets were prepared on Si/SiO₂ substrates (2 × 2 cm²/ea) using a PVA sacrificial layer. A fixed volume of 10 ml DI water was used to dissolve the sacrificial layers and disperse the nanosheets directly without further annealing. Following dispersion, 10 ppm of methyl orange

was added to the volume. The concentration of TiO₂ nanosheets was controlled by changing the number of substrates dissolved in the DI water. For comparison, 10 ppm aqueous solution of methyl orange without nanosheets was also tested. UV-light irradiation was achieved using a shuttered UV-light flood system (Intelli-Ray 400, Uvitron International). The Pyrex vial was placed under the UV-lamp with constant stirring. UV-intensity was varied from 122.5 $\mu\text{W}/\text{cm}^2$ to 245 $\mu\text{W}/\text{cm}^2$. After irradiation, absorbance of the solution was measured by sampling every 30 min with UV-Vis spectrophotometer (Evolution 300, Thermo Scientific Inc.) at 466 nm, which is the major absorbance peak of methyl orange. After sampling, the solution was returned to the vial and irradiation was continued. This procedure was repeated for 3 h for each sample. Care is taken to maintain uniform and reproducible UV flux conditions during all irradiation measurements, to achieve consistent conditions for each sample analyzed.

2. Photodegradation mechanism

A reasonable elementary reaction scheme for photodegradation of methyl orange on a photocatalytically active surface such as TiO₂ is given by^[4,5]:



Here, MO is methyl orange dye and S_v is a vacant adsorption site on the TiO_2 surface. $S-H_2O$, $S-OH^-$, $S-MO$, and $S-OH^\bullet$ represent adsorbed species on active TiO_2 surface sites. The k 's are rate constants for irreversible reactions, and the K 's represent equilibrium constants for reversible reactions. Generally, the UV photons generate electron-hole pairs in TiO_2 , and the holes migrate to the surface and react with adsorbed water molecules and hydroxyl ions. The resulting hydroxyl radicals oxidize the methyl orange dye.

An overall rate expression is derived from the elementary reaction steps using the overall site balance and the steady-state approximation. The overall site balance is given by:

$$[S_t] = [S_v] + [S-H_2O] + [S-OH^-] + [S-MO]$$

where $[S_t]$ is total adsorption sites on all TiO_2 nanosheets, and $[S_v]$ is vacant adsorption sites on all TiO_2 nanosheets, and the steady state approximation is given by

$$\frac{d[H^+]}{dt} = \frac{d[S-OH^\bullet]}{dt} = 0$$

We also assume: 1) the generation of h^+ and $e^- \gg$ recombination of h^+ and e^- ; 2) photon intensity that reaches each nanosheet surface is equal for all nanosheets in the solution; 3) the adsorption sites on the nanosheet are occupied primarily by H_2O : $[S-H_2O] \gg [S-OH^-]$ or $[S-MO]$; and 4) $[MO]$ is very small and $[H_2O]$ is constant.

The rate of methyl orange decomposition is written as

$$r_{MO} = -\frac{d[MO]}{dt} = k_7[S-OH^\bullet][S-MO] \quad (1)$$

From the steady state approximation:

$$\frac{d[S-OH^\bullet]}{dt} = 0 = k_5[S-H_2O][h^+] + k_6[S-OH^-][h^+] - k_7[S-OH^\bullet][S-MO] - k_8[S-OH^\bullet]$$

$$[S - OH^*] = \frac{k_5[S - H_2O][h^+] + k_6[S - OH^-][h^+]}{k_7[S - MO] + k_8} \quad (2)$$

$$\begin{aligned} \frac{d[H^+]}{dt} &= 0 = k_1[TiO_2][hv] - k_5[S - H_2O][h^+] - k_6[S - OH^-][h^+] \\ &= \frac{k_1[TiO_2][hv]}{k_5[S - H_2O] + k_6[S - OH^-]} \end{aligned} \quad (3)$$

Substituting equation (3) into equation (2),

$$[S - OH^*] = \frac{k_5[S - H_2O] + k_6[S - OH^-]}{k_7[S - MO] + k_8} \times \frac{k_1[TiO_2][hv]}{k_5[S - H_2O] + k_6[S - OH^-]} = \frac{k_1[TiO_2][hv]}{k_7[S - MO] + k_8} \quad (4)$$

And putting (4) into (1),

$$\frac{d[MO]}{dt} = -k_7[S - OH^*][S - MO] = -k_7[S - MO] \frac{k_1[TiO_2][hv]}{k_7[S - MO] + k_8} = \frac{-k_1[TiO_2][hv]}{1 + \frac{k_8}{k_7[S - MO]}} \quad (5)$$

Because the adsorption sites are occupied primarily by H_2O , $[S - H_2O] \gg [S - OH^-]$ or $[S - MO]$ (assumption 3 above):

$$[S_t] = [S_v] + [S - H_2O] + [S - OH^-] + [S - MO] = [S_v] + [S - H_2O]$$

$$K_2 = \frac{[S - H_2O]}{[H_2O][S_v]} = \frac{[S - H_2O]}{[H_2O]([S_t] - [S - H_2O])}$$

$$K_2[H_2O]([S_t] - [S - H_2O]) = [S - H_2O] \rightarrow [S - H_2O] (1 + K_2[H_2O]) = K_2[H_2O][S_t]$$

Therefore:

$$[S - H_2O] = \frac{K_2[H_2O][S_t]}{1 + K_2[H_2O]} \quad (6)$$

The equilibrium constant for the elementary reaction (4) is given by:

$$K_4 = \frac{[S - MO]}{[MO][S_v]} \rightarrow [S - MO] = K_4[MO][S_v] = K_4[MO]([S_t] - [S - H_2O])$$

We next substitute the value for $[S - H_2O]$ from equation (6) into K_4 and obtain:

$$\begin{aligned} [S - MO] &= K_4[MO]([S_t] - \frac{K_2[H_2O][S_t]}{1 + K_2[H_2O]}) = K_4[MO][S_t](1 - \frac{K_2[H_2O]}{1 + K_2[H_2O]}) \\ &= \frac{K_4[MO][S_t]}{1 + K_2[H_2O]} \end{aligned} \quad (7)$$

Substituting (7) into (5), we obtain:

$$\frac{d[MO]}{dt} = \frac{-k_1[TiO_2][hv]}{1 + \frac{k_8}{k_7[S - MO]}} = \frac{-k_1[TiO_2][hv]}{1 + \frac{k_8(1 + K_2[H_2O])}{k_7K_4[MO][S_t]}}$$

Then, since $[MO]$ is small (assumption 4 above),

$$\frac{d[MO]}{dt} = \frac{-k_1k_7K_4[MO][S_t][TiO_2][hv]}{k_8(1 + K_2[H_2O])} = -k'[S_t][TiO_2][hv][MO]$$

where, $k' \equiv \frac{K_4k_7k_1}{k_8(1 + K_2[H_2O])}$

In this expression, $[TiO_2]$ is the surface area of nanosheets per unit volume of solution $[cm^2/cm^3]$ and $[hv]$ is the number of incident photons per unit area that create an electron/hole pair per unit time. The number of electron/hole pairs created per unit volume of solution per unit time is therefore $[TiO_2][hv]$. Using the Beer-Lambert Law, $I = I_0e^{-\alpha D}$ where I is the photon intensity per unit area $[W/m^2]$, α is the absorption coefficient for TiO_2 at a given energy $[nm^{-1}]$ and D is the thickness of the nanosheet $[nm]$, the energy absorbed by a nanosheet within

thickness D per unit area per time is $I_0(1 - e^{-\alpha D})$ [$J/cm^2 \cdot s$]. In the energy region where the absorption coefficient is large, the number of charges generated is estimated by integrating the absorbed intensity across the film thickness D :

$$\int_0^D I_0(1 - e^{-\alpha D}) dD = aI_0 \left(D + \frac{1}{\alpha} e^{-\alpha D} - \frac{1}{\alpha} \right) = I_0 D$$

where for large very α and small D , $\left(\frac{1}{\alpha} e^{-\alpha D} - \frac{1}{\alpha} \right) \rightarrow 0$. The photon flux versus photon energy is related to the irradiance of the light source. If a is the fraction of photons in the incident light with $h\nu > E_g$, then when D is small relative to $1/\alpha$, the number of photons that create electron hole pairs in the nanosheets present in solution is given by

$$[TiO_2][h\nu] = aI_0 D S / 2 \text{ } [\mu W \text{ nm}]$$

where S is the total surface area (front plus back) of all nanosheets in solution, and the factor of 2 arises since photons are incident on only one side of the nanosheet. Therefore:

$$\frac{d[MO]}{dt} = -k[S_t][TiO_2][h\nu][MO] = -ak'S_t I_0 D \frac{S}{2} [MO]$$

Since $[S_t]$ is proportional to S , and we can write $k'' = ak'/2$, we obtain

$$\frac{d[MO]}{[MO]} = -k'' S^2 I_0 D dt$$

where, the final substitution $K \equiv k'' S^2 I_0 D$ [s^{-1}] gives

$$\boxed{\ln \frac{C}{C_0} = -Kt}$$

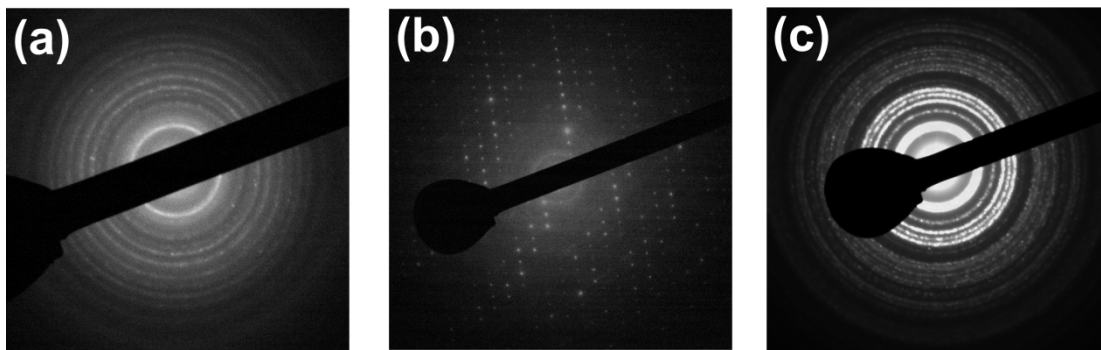


Fig. S1 Diffraction pattern obtained from TEM images. (a) and (b) are from light gray and dark gray domains of TiO_2 nanosheet shown in Figure 2(e), respectively. (c) is from ZnO nanosheet shown in Figure 2(f).

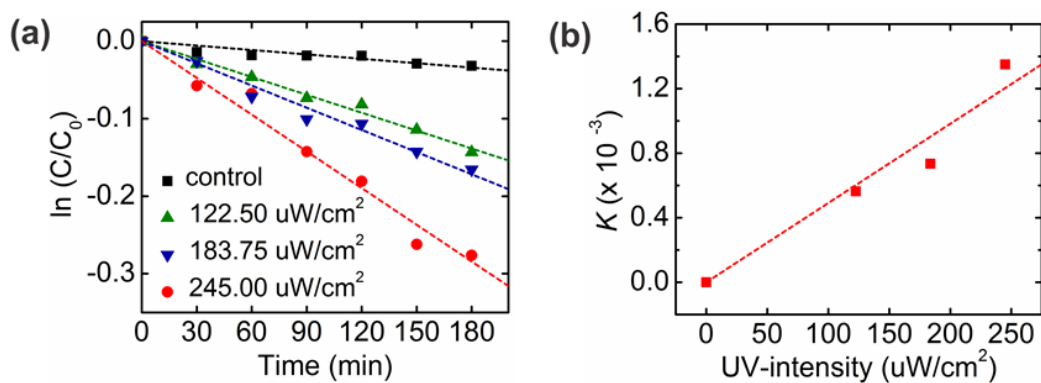


Fig. S2 Dye degradation rate depending on UV intensity. (a) Degradation of methyl orange using photocatalytic TiO_2 nanosheets under varying UV intensity (122.50, 183.75, and 245.00 $\mu\text{W}/\text{cm}^2$). (b) Values of K obtained from the fits in (a) versus UV intensity. The value of k'' is $3.8 \times 10^{-11} \text{ s}^{-1}\text{cm}^{-2}\mu\text{W}^{-1}\text{nm}^{-1}$.

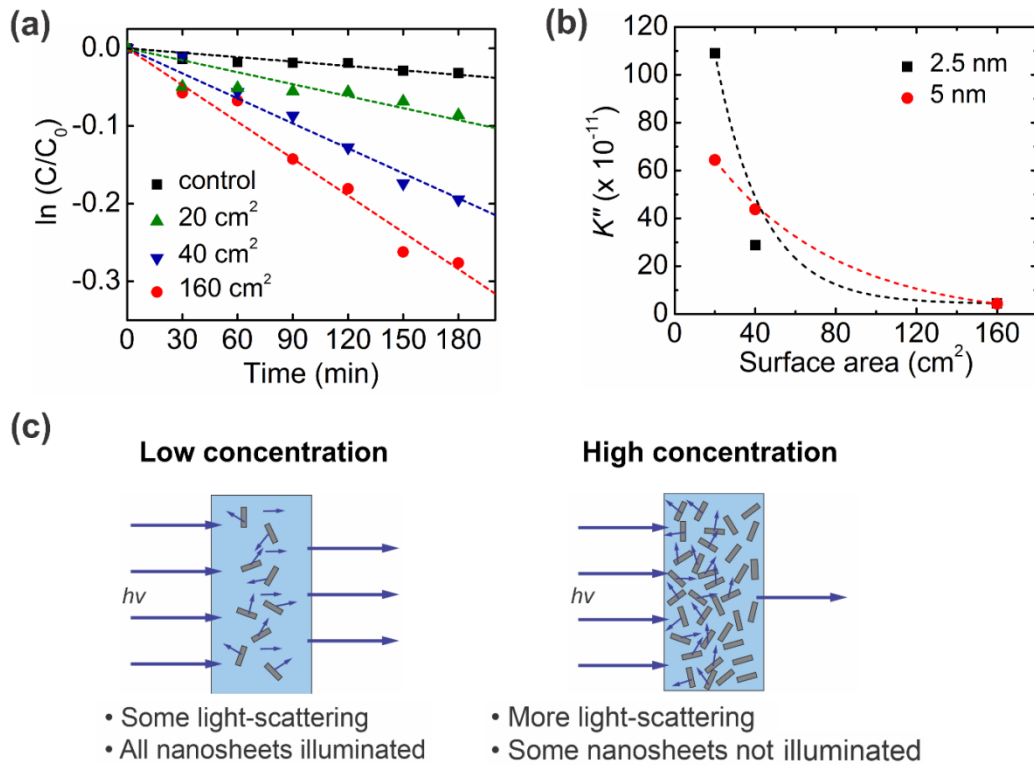


Fig. S3 (a) Degradation of methyl orange using photocatalytic TiO₂ nanosheets under varying surface area of nanosheets (20, 40, and 160 cm²). (b) k'' values versus S for 2.5 nm (black square) and 5 nm (red circle) thickness. The k'' is expected to decrease with increasing S due to scattering effects. The dashed lines are guides for the eye. (c) Illustration that shows how surface area of nanosheets affects UV light scattering.

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