Supporting Information for

A new-type noncovalent surface-π stacking interaction occurring on peroxide-modified titania nanosheets driven by vertical π-state polarization

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Materials and Methods Chemicals

TiCl₃ aqueous solution, TiCl₄, 3-phenylpropanol (PPL, purity > 99%) and cinnamyl alcohol (CAL, purity > 99%), L-tryptophan (Trp, \geq 98.5%), Rhodamine B (RhB, > 99%), indole (Ind, > 99%) hydrogen peroxide (H₂O₂, ~30wt % in water) were purchased from Aladdin. Benzyl alcohol (BAL, > 99%) and benzoic acid (BA, > 99%) were purchased from Xiqiao Science Co., Ltd. All reagents were of analytical grade and used without further purification. Deionized (DI) water was used in all experiments.

Material preparation:

Synthesis of PMT and PFT nanosheets: $TiCl_3$ solution and $30wt\% H_2O_2$ solution (1.0 mL) were mixed with 30 mL of DI water in a beaker¹. The solution was heated at 80 °C in an electric oven for 90 minutes, which directly yielded titania nanosheets in-situ modified by peroxide ligands (PMT). The product was washed 3 times with water and dried at 60 °C. Peroxide-free titania (PFT) nanosheets were prepared by washing PMT with 1.0 M NaOH solution for 2 min, and washed with water three times.

 $TiO_2(B)$ nanosheets were prepared by hydrolyzing $TiCl_4$ (1.0 mL) in the mixture of ethylene glycol (30 mL) and water (1 mL) at 145 °C for 10 h in a pressure tube. The materials were washed with water and ethanol four times and dried at 60 °C overnight.

Peroxide modification and re-modification of $TiO_2(B)$ and PFT materials were conducted by sonicating titania nanosheets (0.30 g) in 1% H₂O₂ solution for 2 min, and then separated by centrifugation and washed with H₂O three times.

Characterizations

The morphology of PMT nanosheets was characterized on FEI Tecnai F30 transmission electron microscope (TEM) under an acceleration voltage of 300 kV. Crystalline phases of the materials were characterized with powder X-ray diffraction (XRD) on a Bruker D8 diffractometer using Cu K α radiation (1.5418 Å), which were operated at 40 kV and 40 mA with a scanning rate of 6 degree/min. Optical diffuse reflection spectra (DRS) were collected from 1200 nm to 250 nm on a Shimadzu UV-3600 spectrometer equipped with an integrating sphere. The quantitative adsorption results of aromatic molecules on PMT and PFT were determined with UV-Vis absorption spectrophotometer (Shimadzu UV-3600), high performance liquid chromatography

(HPLC, Agilent,1260 equipped with Carbon eighteen reverse polarity column) and gas chromatography with an FID detector (GC-FID, Agilent 7890B equipped with a FFAP 30 m \times 250 μ m \times 0.25 μ m column). XPS measurements were performed on a Thermo ESCALAB 250XI photoelectron spectrometer using Al Ka (1486.6 eV) radiation. H-NMR data of Trp samples were collected on a Bruker 600-M NMR spectrometer, in which Trp molecules were dissolved in D₂O.

NEXAFS data of Ti-L_{2,3} edge was collected on the 4B9B beamline of Beijing Synchrotron Radiation Facility (BSRF) with the mode of total electron yield (TEY). The energy resolution power ($E/\Delta E$) of about 1500. The analysis chamber is equipped with a VG Scienta R4000 electron energy analyzer with a pressure of 1×10⁻¹⁰ mbar. Ti-L spectra were collected between 450 and 480 eV with a step width of 0.1 eV. All the spectra were scanned once without averaging.

XAFS measurements of Ti K-edge were collected on the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF). Ti K-edge XAFS measurement beamline is equipped with Si (111) double crystal monochromator, ion chambers for measuring incident and transmitted beam intensity. The typical energy of the storage ring was 2.5 GeV with a maximum current of 250 mA. The samples (5 mg) were diluted with BN (50 mg), pressed into pellets, and measured in transmission mode. EXAFS data were analyzed using the Demeter software package ².

Adsorption experiments:

Concentration-dependent equilibrium adsorption (n_e): Varied amounts of RhB, Trp and BA were dissolved in 8.0 mL of water in centrifugation tubes to prepare solutions with initial concentrations (c_0) of 0.10 to 1.00 mol/L at pH=7.0, then 40.0 mg of PMT or PFT was added into the solutions. The mixtures were shaken for 30 min to reach equilibrium adsorptions. Finally, the materials were separated by centrifugation, and the supernatants were analyzed to determine the equilibrium adsorptions (n_e). RhB was characterized with UV-Vis absorption, Trp was analyzed with HPLC, and BA was analyzed with GC-FID. The equilibrium adsorptions of the molecules by 40.0 mg of PMT and PFT were calculated according to $n_e = n_0(c_0-c_e)/c_0$, where c_0 and c_e are initial concentration and equilibrium concentration of the molecules in 8.0 mL of their solutions.

Instantaneous adsorption:_The instantaneous adsorption capacities (n_i) of RhB, Trp, Ind, Min, CAL, BAL, PPL, BA and 2-phenylpropionic acid were determined in 8.0 mL of 0.20 mmol·L⁻¹ solution at pH=7.0. At 25 °C, PMT or PFT (40.0 mg) were added into the solutions and vigorously shaken for 1 min, then the adsorbents were immediately separated by centrifugation. The remained

concentrations of the molecules in the supernatants were analyzed to determine instantaneous adsorption capacities (n_i) .

Adsorption kinetics of RhB by PMT: 40.0 mg of PMT was mixed with 20 mL of 1.0 mmol/L RhB solution. The mixture was shaken at 25 °C and sampled every 5 min to quantify the time-dependent adsorption behaviors.

Adsorptions of TMB and oxTMB by PMT: TMB was first dissolved in acetone to prepare a stock solution with TMB concentration of 1.0 mg·mL⁻¹. Then 0.50 mL of CeO₂ nanocatalyst in water, 0.10 mL of TMB stock solution and 0.10 mL of 3.0 wt% H₂O₂ solution were added into 2.30 mL of 0.20 mol·L⁻¹ HAc/NaAc buffer solution (pH = 4.0) to prepare oxidized TMB (oxTMB). After the solution turned blue, the catalyst was separated by filtration. PMT (5.0 mg) was added into the mixed solution of TMB and oxTMB and vigorously shaken for 1 min, then the adsorbents were immediately separated by centrifugation. The concentrations of remained TMB and oxTMB in the supernatant were quantified with UV-Vis absorption³.

Controlled RhB separation by PMT membrane: PMT nanosheets (0.20 g) were first dispersed in H_2O (50 mL) in a beaker, and deposited through filtration.



Figure S1. Synthetic results of PMT and PFT nanosheets. (a) TEM image of PMT nanosheets. (b) XRD patterns of PMT and PFT. (c) N_2 adsorption and desorption curve of PMT nanosheets. (d) The multipoint curve to calculate BET surface area of PMT. The BET surface area of PMT nanosheet is 204.4 m²/g. (e) TEM image of PFT nanosheets. (f) The multipoint curve to calculate BET surface area of PFT nanosheet is 204.3 m²/g.



Figure S2. Adsorption results of RhB by peroxide-modified and raw TiO₂(B) nanosheets and TiO₂ NPs. (a) TEM image of peroxide-modified TiO₂(B) nanosheets, which were first prepared by hydrolyzing TiCl₃ in ethylene glycol at 140 °C and then mixed with H₂O₂ to realize surface modification ^{4,5}. (b) The adsorption results of RhB on peroxide-modified and raw TiO₂(B) nanosheets. The results show that raw TiO₂(B) nanosheets cannot adsorb RhB but the peroxide-modified material can, meaning the noncovalent attraction can also occur between RhB and peroxide-modified TiO₂(B) nanosheets. (c) TEM image of TiO₂ nanoparticles with an average size of 32 nm. (d) The adsorption result of RhB by TiO₂ nanoparticles in the presence of H₂O₂. The result shows that TiO₂ nanoparticles can be surface modified by H₂O₂ to become yellow, and cannot adsorb RhB from the aqueous solution.



Figure S3. Adsorption results of RhB by PMT and PFT nanosheets. (a) Concentrationdependent UV-vis absorptions of RhB in water and (b) the linear standard curves at 554 nm absorbance for quantitative analysis. (c) and (d) are the adsorption kinetics of RhB on PMT. (e) and (f) are the raw data to measure the concentration-dependent equilibrium adsorption capacities of RhB on PMT.



Figure S4. Raw data of concentration-dependent equilibrium adsorption of Trp on PMT nanosheets characterized with HPLC.



Figure S5. Raw data of concentration-dependent equilibrium adsorption of BA on PMT and PFT nanosheets characterized with GC-FID.



Figure S6. The instantaneous adsorption results of Rhodamine B (RhB), tryptophan (Trp), indole (Ind), 2-methylindole (Min), cinnamyl alcohol (CAL), benzyl alcohol (BAL), phenyl propanol (PPL), benzoic acid (BA) and 2-phenylpropionic acid by PMT and PFT nanosheets.



Figure S7. Adsorption isotherms of Trp on PMT nanosheets at 25 °C. (a) shows concentrationdependent adsorption isotherm of Trp at 25 °C. The equilibrium adsorption capability (Q_e) increases with the equilibrium concentrations (C_e), and becomes saturated at high concentrations. The isotherm is fitted with Langmuir (b) and Freundlich (c) adsorption models. The adsorption of Trp on PMT more matches Langmuir adsorption, according to the greater linear correlation coefficients (R^2) of 0.9929 than 0.9885.



Figure S8. Adsorption of TMB and oxTMB on PMT characterized with UV-vis absorption.



Figure S9. XAFS data of PMT, PFT, peroxide-modified PFT and Trp-adsorbed PMT in energy space (**a**) and *k* space (**b**).



Figure S10. XPS spectra of PMT, PFT and PFT+H₂O₂ samples. (a) O1s spectra. (b) Ti2p spectra.



Figure S11. The interaction of Trp with PMT and hydrogen peroxide (HPO). H-NMR result of pure Trp (a), desorbed Trp from PMT (b) and (c) the overlapped curves in (a) and (b). (d) UV-vis absorptions of Trp and indole in water and H_2O_2 . The results show that Trp and indole cannot absorb visible light when they are directly mixed with H_2O_2 , suggesting no interactions occur.

PH <i>Tela potential(mV)</i>	3.0	7.0	12.0
PMT	-2.7	-41.7	-46.4
PFT	-7.7	-34.4	-43.4

Table S1. Zeta potentials of PMT and PFT measured at pH = 3.0, 7.0 and 12.0.

Movie S1.

Controlled separation of RhB from water by PMT membrane through filtration and elution with NaOH solution.

References:

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