Syntheses, Crystal Structure, and Photochromic Properties of a New Stable Ti (IV) Complex

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EXPERIMENTAL SECTION

Materials and Methods. All the chemical reagents used in this work were purchased from Aladdin and used without further purification. Fourier-transform IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer in the range of 4000-400 cm^{-1}. Thermogravimetric analyses (TGA) plots were conducted on a Perkin-Elmer TGA-7 from 25-1000 °C in an N_2 atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418Å) in a 2θ range of 3-70° at room temperature. The micro morphology and the energy dispersive spectroscopy (EDS) of the samples were observed by a Quanta 250 scanning electronic microscope (SEM, FEI Company, US). The fluorescence spectra for the solid samples were measured at room temperature on an FL3-P-TCSPC spectrophotometer with a xenon lamp as the light source. The XPS spectra were recorded at room temperature using Al-Ka radiation (1486.6 eV). Diffuse reflectance UV spectroscopy was recorded on a Varian Cary 50 spectrophotometer using a Harrick Scientific Video Barrelino probe. Powder EPR experiments were performed at room temperature using a Bruker EMX Micro EPR spectrometer operating at X-band (ca. 9.84 GHz). The photochromism experiments were performed at room temperature using PLS-SME400E H1 Xenon Lamp or UV lamp (365 nm).

Photochemical Degradation of Dye. A 300 W halogen lamp, positioned 15 cm over the surface of the reaction solution, is employed as light source. The aqueous dispersions of catalysts are prepared by addition of 50 mg Ti-PDA to 30 mL aqueous solutions containing the dye of Methyl Orange (MO) (10 mg/L). Prior to irradiation, the suspensions are magnetically stirred in the dark for ca. 1.0 h to ensure the establishment of adsorption/desorption equilibrium of dye on the surface of the microcrystals. The dispersions are added H_2O_2 (0.016 %, 5 μL) before irradiation. At given time intervals, 2 mL of aliquots are sampled, centrifuged, and then the supernate are analyzed by recording variations of the absorption spectra.

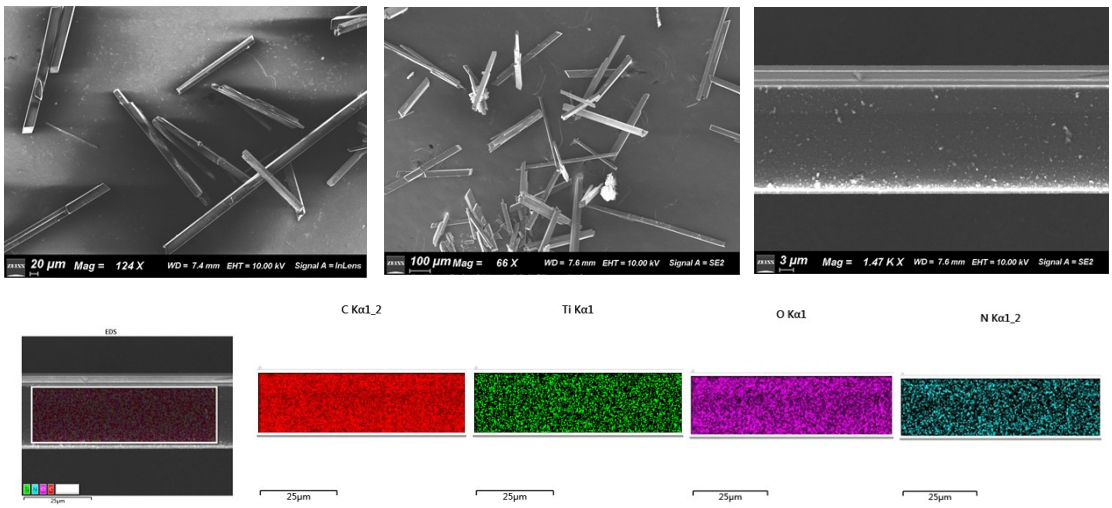

Figure S1. The SEM and EDS elemental mapping image of Ti-PDA.

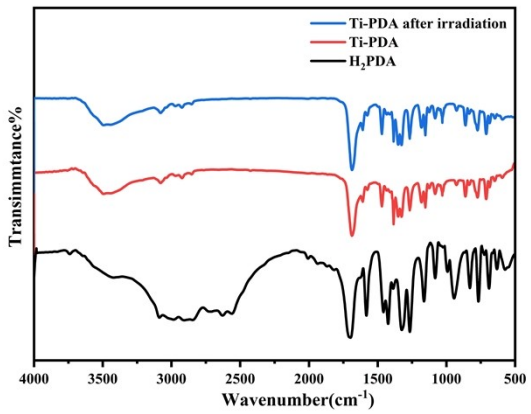

Figure S2. The Infrared spectra of Ti-PDA and H_2PDA.

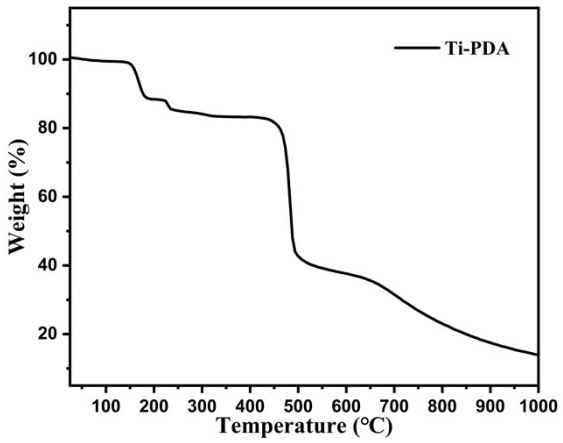

Figure S3. The thermogravimetric (TG) curve of Ti-PDA.

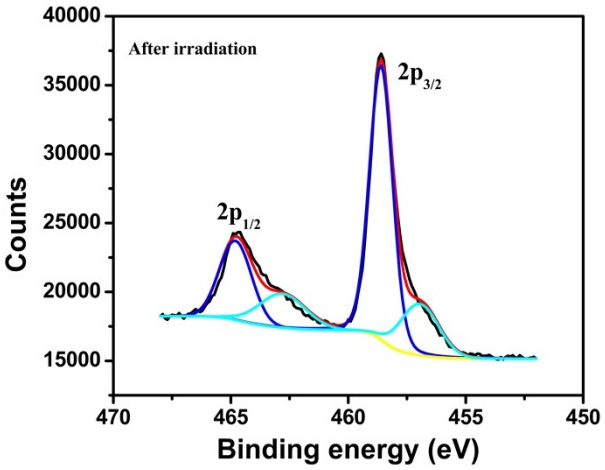

Figure S4. The XPS spectra for Ti 2p of the after irradiation, respectively. Black: experimental date, red curve: fitting of Ti 2p core level by synthetic peaks (blue curves: for Ti(IV) $2p_{1/2}$ and $2p_{3/2}$ spin states, and cyan curves: or Ti(III) $2p_{1/2}$ and $2p_{3/2}$ spin states), yellow curve: Shirley background.

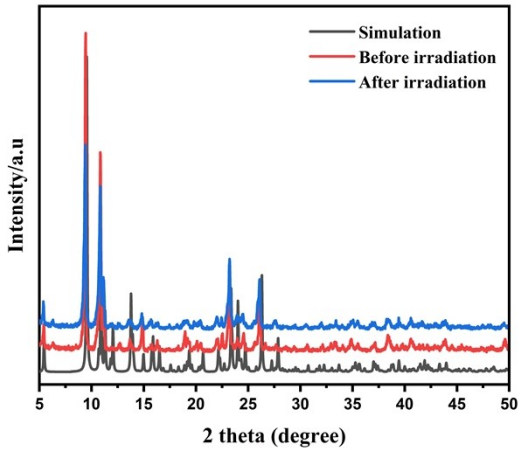

Figure S5. The XRD pattern of Ti-PDA.

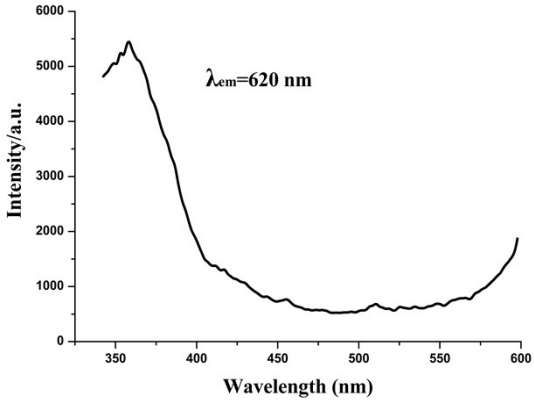

Figure S6. Room-temperature excitation n spectra for the Ti-PDA in the solid State.

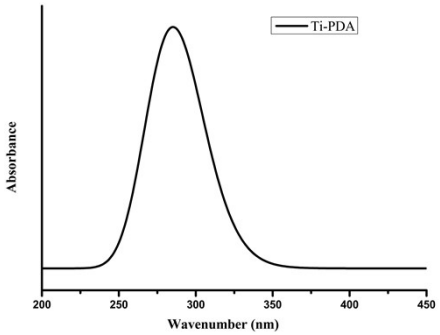

Figure S7. The calculated UV-vis spectrum of Ti-PDA. The absorption edge is calculated to be 450 nm.

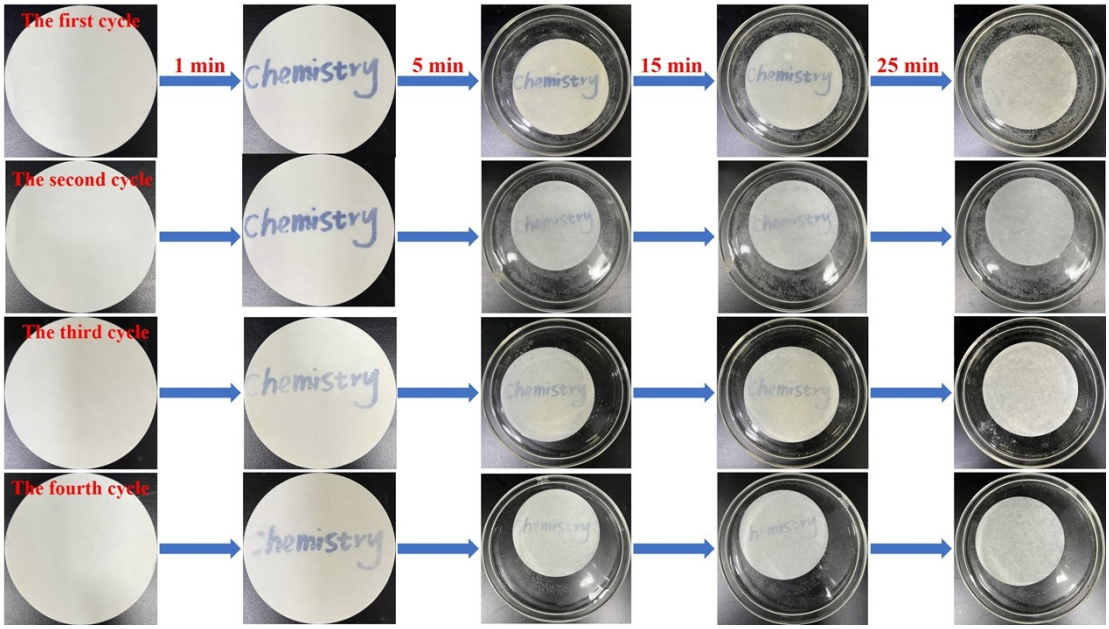

Figure S8. Four inkless and erasable reversible printing process.

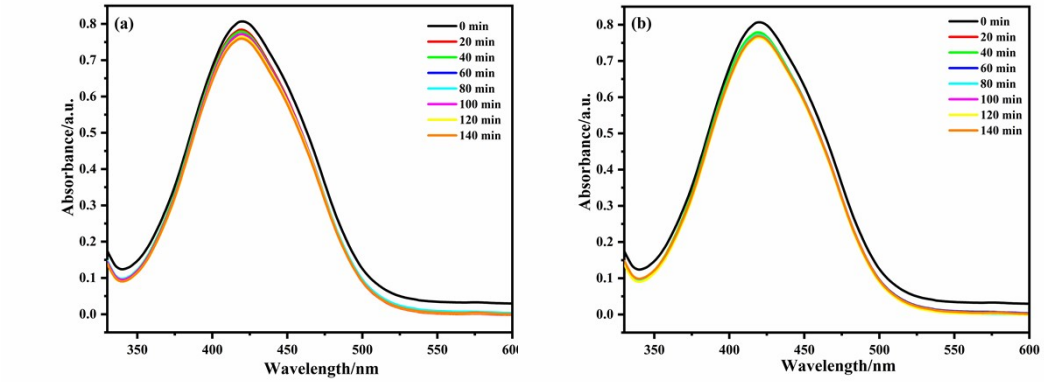

Figure S9. Ultraviolet spectra of MO degradation under darkness (a) or without Ti-PDA (b).

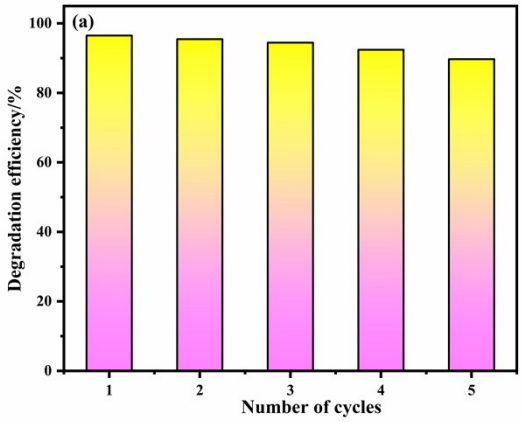

Figure S10. Five cycles photocatalytic degradation of MO**.**

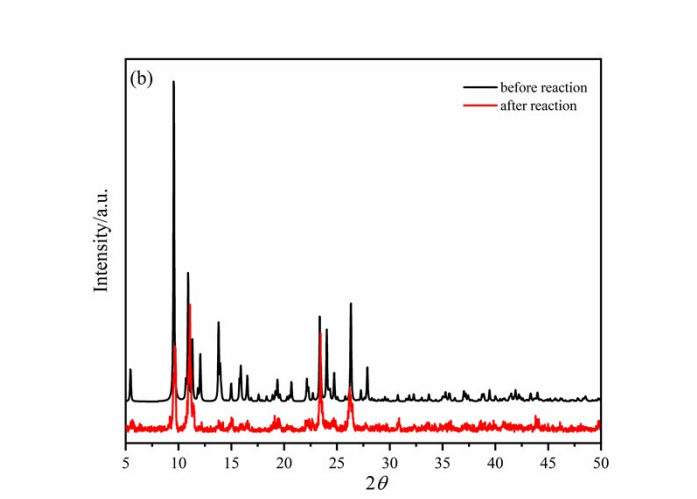

Figure S11. XRD spectra of before and after Ti-PDA photocatalytic degradation.

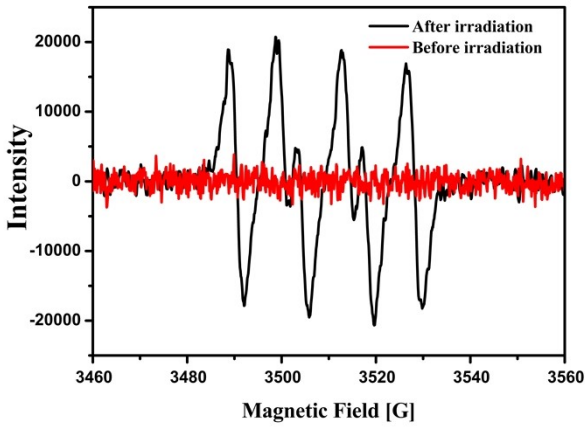

Figure S12. The detected EPR signal of superoxide anion radicals ($\cdot O_2^-$) before and after irradiation.

Table S1. Selected Bond Lengths (Å) and Bond Angles (deg) for Ti-PDA.

Ti-PDA			
Ti1—O2	2.024 (2)	O2—Ti1—N3	75.04 (8)
Ti1—O7	2.0219 (18)	O2—Ti1—N4	75.62 (8)
Ti1—O6	2.0020 (19)	O2—Ti1—N2	140.99 (8)
Ti1—O3	1.9952 (18)	O2—Ti1—N1	72.28 (8)
Ti1—N3	2.228 (2)	O7—Ti1—O2	97.32 (8)
Ti1—N4	2.232 (2)	O7—Ti1—N3	140.55 (9)
Ti1—N2	2.206 (2)	O7—Ti1—N4	72.14 (8)
Ti1—N1	2.221 (2)	O7—Ti1—N2	75.17 (8)