**Supporting information**

Marimo Bead-Supported Core-Shell Nanocomposites of Titanium Nitride and Chromium-Doped Titanium Dioxide as Highly Efficient Water Floatable Green Photocatalyst

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Figure S1.Optical images of the fabricated samples.

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Figure S2.Schematic representation of the synthesis steps of SiO2 layer onto TiN NPs.

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Figure S3.SEM images of (a) TiO2 (b) Cr-TiO2 (c) TSCT, and (d) TiN. Each scale bar represents 200 nm.

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Figure S4.XRD plot of B-Cr-TiO2 NPs. “A” and “R” stands for anatase and rutile, respectively.

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Figure S5. XRD pattern of TiN NPs (TiN: JCPDS, No. 06-4909) and TSCTwith varying SiO2/TiN wt%.

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Figure S6. Raman spectra of TiN and B-Cr-TiO2.  “A” and “R” stand for anatase and rutile, respectively.

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Figure S7. Nitrogen adsorption desorption isotherm of TSCT, TiN, TiO2, Cr-TiO2, and B-Cr-TiO2.

Table S1.Crystallite size andBET surface area of TiO2,Cr-TiO2, B-Cr-TiO2, TiN, and TSCT samples.

|  |  |  |
| --- | --- | --- |
| Sample | Particle size (nm) | SBET (m2/g) |
| TiO2 | 7.81 | 104.778 |
| Cr-TiO2 | 9.14 | 70.624 |
| B-Cr-TiO2 | 10.43 | 75.829 |
| TiN | 30.88 | 206.89 |
| TSCT | 75 | 149.3 |

Note S1.The average crystallite size (*D*XRD) was calculated using the Debye– Scherrer formula1;

*D*XRD = 0.9 *λ*/ (*β*cos*θ*),

where Scherrer constant is taken as 0.9, *λ* is the wavelength of incident X-ray, *β* is the full width at half height of the diffraction peak and *θ* is the diffraction angle.

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自動的に生成された説明

Figure S8. (a) TEM image of Cr-TiO2 and electron diffraction pattern in the inset. (b) HRTEM image of Cr-TiO2, and (c), (d) enlarged images of the marked areas in image (b).

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Figure S9.TEM image of B-TiO2 and electron diffraction pattern in the inset. (b) HRTEM image of B-TiO2, and (c), (d) enlarged images of the marked areas in image (b).

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Figure S10. TEM images and particle size distributions of (a) TiO2 (b) Cr-TiO2 (c) TiN, and (d) TSCT.

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Figure S11. High resolution XPS spectra of (a) Ti 2p (b) O 1s (c) Cr 2p, and (d) Si 2p of TSCT.

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Figure S12. EPR spectrum of TiN NPs at room temperature.

Table S2.Comparison of photocatalytic degradation of MB dyes by various nanomaterials reported in the literatures. Here efficiency represents the dye degradation efficiency.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Photocatalyst** | **Conc** | **photocatalytic**  **conditions** | **Dye Conc.** | **Efficiency** | **Period**  **(min)** | **Rate**  **constant**  **(min-1)** | **Ref.** |
| **TSCT** | **2 mg mL−1** | **100 mW/cm-2** | **1 ×10−5 M**  **or 3 mgL−1** | **99%** | **10** | **0.23** | **Our work** |
| Cu0.26Zn0.05Fe0.26S0.43 NCs | 0.4 mg mL−1 | day light | 10mgL−1 | >95% | 30 | 0.108 | 2 |
| CdS/MoS2  heterostructure | 0.6 mg mL−1 | illuminated by 300 W Xe arc lamp, > 420 nm | 2 ×10−5 M | >80% | 50 | 0.0058 | 3 |
| N-TiO2/g-C3N4  composites | 0.4 mg mL−1 | illuminated by 300 W xenon arc lamp | 10mgL−1 | 69 % | 60 | 0.070 | 4 |
| Ag2CO3 rods | 1 mg mL−1 | illuminated by a 300 W Xe arc lamp | 10mgL−1 | 95% | 40 | NA | 5 |
| Au/TiO2  superstructure | 1 g L−1 | illuminated by a 500 mW  cm−2 Xe lamp,460 nm- 700 nm | 1.0 × 10−5 M | NA | NA | 0.25 | 6 |
| Graphene oxide  modified Ag2O  nanocomposites | 0.5 mg mL−1 | irradiated under 500 W tungsten lamp | 10mgL−1 | 95% | 100 | 0.035 | 7 |
| Zinc sulfide–  graphene  nanocomposites | 0.12 mg mL−1 | irradiated under 4 W UV lamps with wavelength 254 nm | 10ppm | 96.7% | 80 | NA | 8 |
| AgCl:Ag  Plasmonic NCs | NA | irradiated under 150 W quartz halogen lamp | 20mgL−1 | >90% | 60 | 0.07 | 9 |
| Cu2S-Pd4S  Hybrid nanoplates | 25 ppm | irradiated under 100 W halogen lamp | 100mM | over  80% | 30 | NA | 10 |

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Figure S13.MB dye degradation rate of TSCT with (a) different ratio of TiN NPs in TSCT, (b) as a function of catalyst loading, and (c) under the illumination of UV component, visible light component, and full spectrum of the simulated solar light.

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Figure S14.Pictures of synthesized P-Marimos (a) without NPs loading, (b) loaded with TiO2, (c) with Cr-TiO2 and (d) with TSCT.

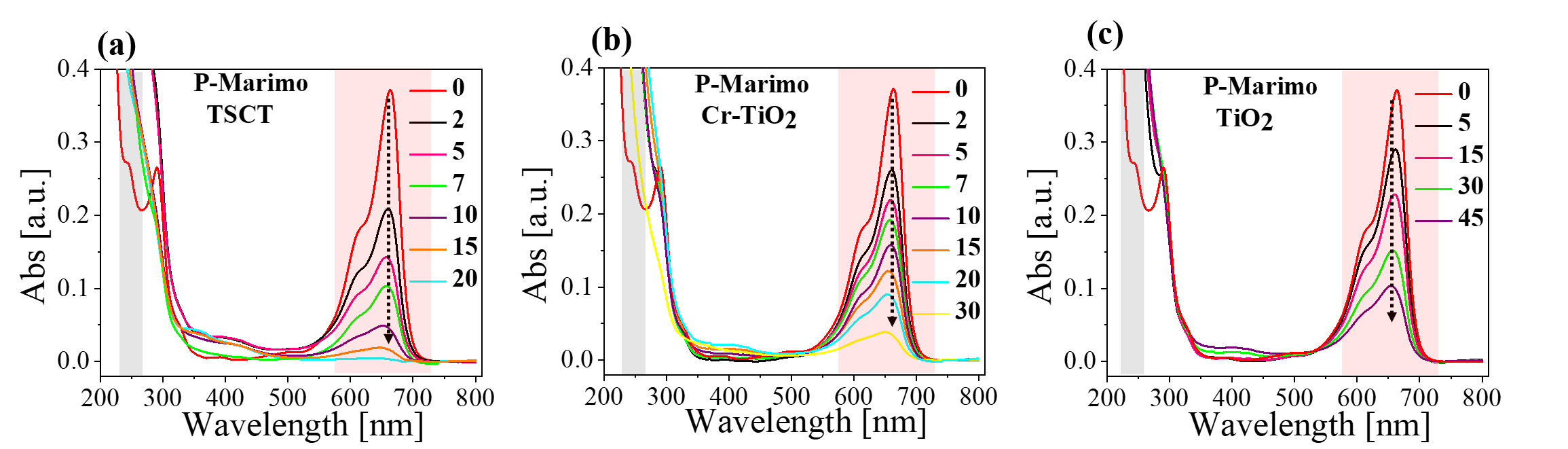


Figure S15.Absorbance spectra of MB dye degradation for (a) TSCT (b) Cr-TiO2, and (c) TiO2. Note that the pink and grey regions in the absorbance spectra represent the absorbance regions of MB and leuco methylene blue, respectively.

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Figure S16. (a) MB degradation performance of TSCT. The MB with TSCT was pre-illuminated for 2 minute and kept in the dark for 1 day and heated at 50 °C for 15 min. Absorbance spectra of MB with TSCT before heating, MB without TSCT, and MB without TSCT and heated at 50 °C were also plotted. (b) Absorbance spectra of MB with TSCT and Cr-TiO2 that were pre-illuminated for 2 minute and stored in the dark environment for 1 year. Absorbance spectrum of MB is also shown. (c) Optical images of; 1. MB with TSCT 2. MB with Cr-TiO2, and 3. MB without any catalysts.

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Figure S17.MO dye degradation by TSCT. (a) Absorbance spectra of the samples under solar light by varying the illumination time. (b) Absorbance spectra of the samples which were pre-illuminated and kept in the dark environment for one hour where the pre-illumination time was varied.

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Figure S18. Photocatalytic activity comparison of typical IPA oxidation by TSCT, Cr-TiO2 and TiO2.

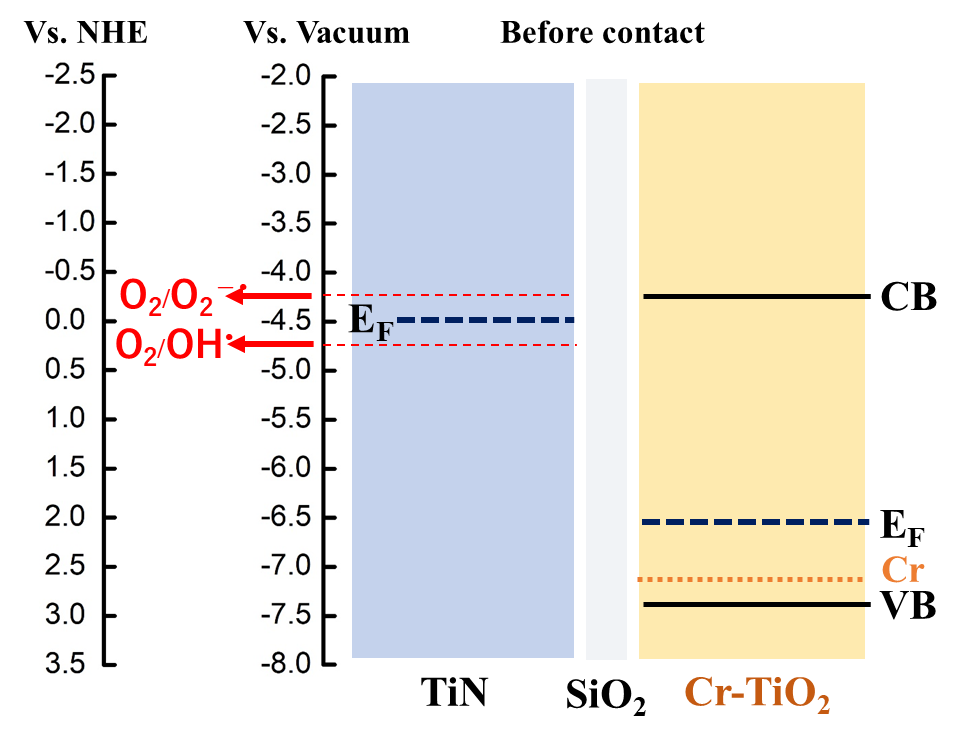


Figure S19. (a) Another possible example of an energy level diagram of TSCT (before charge transfer) and standard redox potential of different oxidative species with respect to vacuum energy levels and NHE.

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Figure S20. Degradation efficiency of MB (10 µM) by P-Marimo TSCT in successive cycles of uses.

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