Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information

Redox Shuttle Enhances Nonthermal Femtosecond Two-Photon Self-Doping of rGO−TiO_{2-x} Photocatalyst under Visible Light

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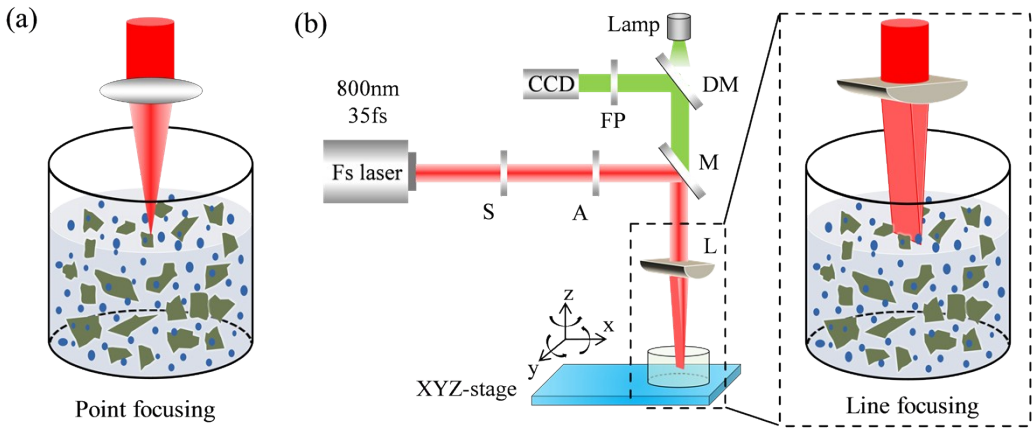

Fig. S1. Schematic diagram of experimental setup for synthesizing rGO−TiO_{2-x} nanocomposite photocatalyst under visible light by (a) point focusing condition, and (b) line focusing condition. Direct laser writing was conducted using a cylindrical lens (f = 50 mm) setup equipped with a NIR femtosecond (fs) laser (800 nm, 35 fs, 1 kHz, Specta Physics, Inc.). When the incident spot size was fixed at about 8 mm, the processing regions are estimated to be about 1256 μm^2 (circle with about 20 μm in diameter) in (a) and 1.6×10^5 μm^2 (approximate rectangle with about 8 mm in length and 20 μm in width) in (b). That is, the effective processing regions in (b) can be significantly improved over two orders of magnitude (~ 127 fold) greater than that in (a). S is the shutter, A is the attenuator to control the laser power, FP is the filter plate, DM is the dichroic mirror, M is the ultrafast mirror, and L is the cylindrical lens.

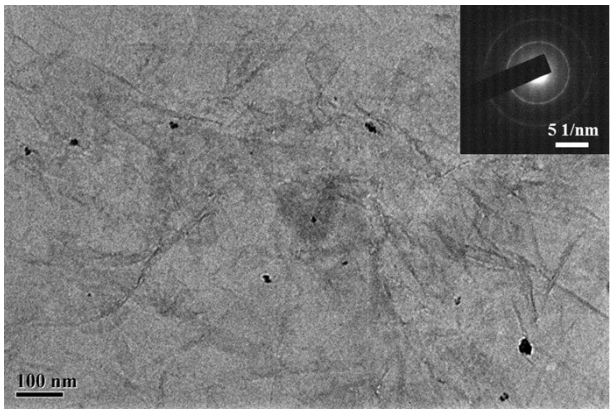

Fig. S2. TEM image of GO nanosheets before irradiation. The insets are the corresponding selected-area electron diffraction (SAED) patterns.

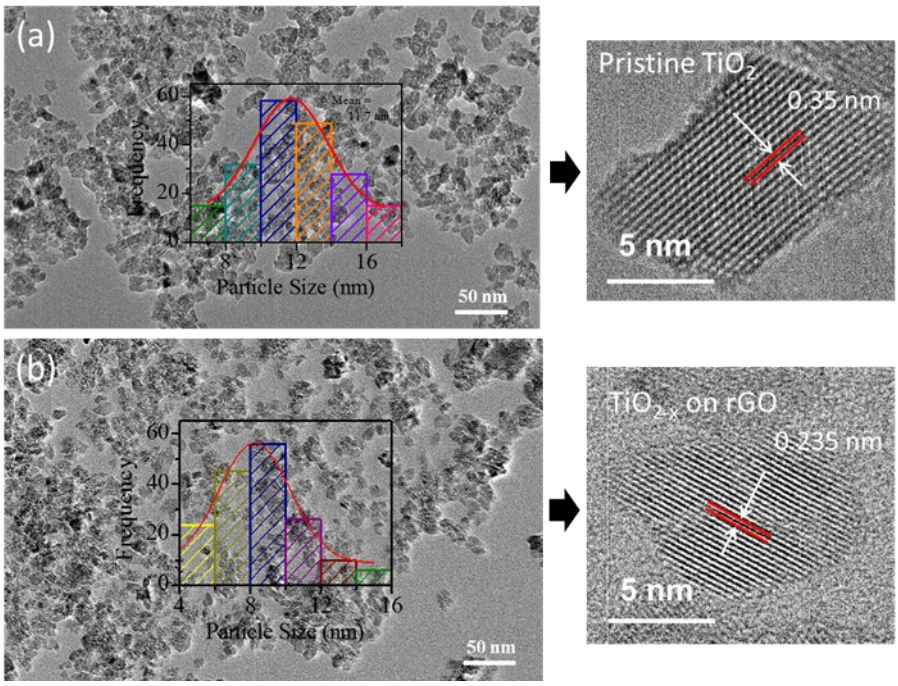

Fig. S3. TEM and HRTEM image of anatase TiO_2 (a) before and (b) after irradiation. The average sizes of TiO_2 before and after irradiation are ~11.7 nm and ~8.2 nm, respectively.

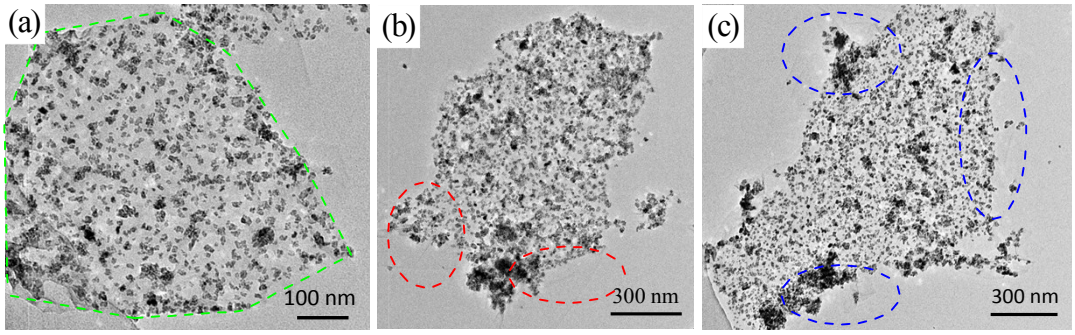

Fig. S4. (a), (b) and (c) are the typical TEM images of as-prepared rGO−TiO_{2-x} nanocomposites after 1 h irradiation at an incident pulse energy of about 1.0 mJ. The rGO nanosheet can be recognized by the dashed lines.

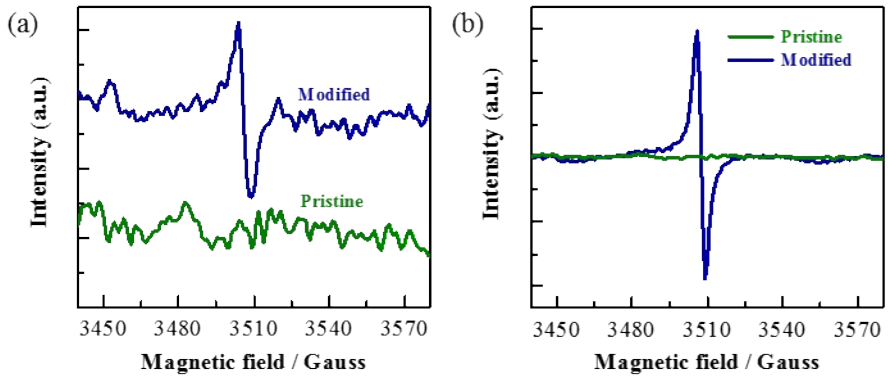

Fig. S5. Comparison of EPR spectra between (a) without and (b) with ethanol and GO to pristine TiO_2. The modified samples are the cases that the given sample were irradiatied for 1 h at pulse energy of 1 mJ. Other form factors were the same. Signal intensity in (b) is markedly larger than that in (a) with respect to the pritine samples. All the tests are conducted at room temperature (298 K).

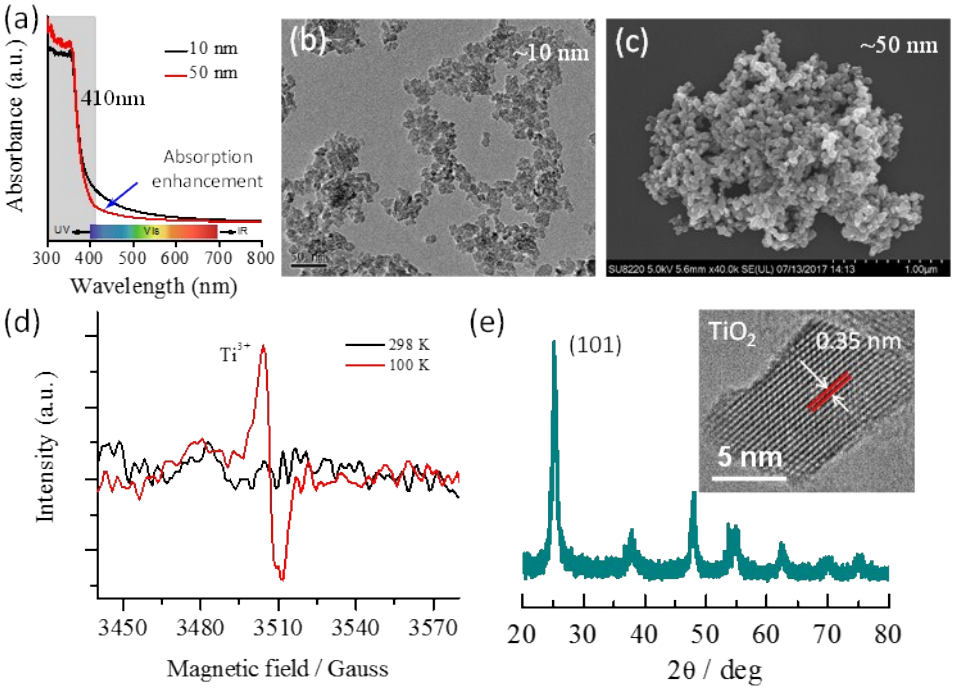

Figure S6. (a) UV-vis diffuse reflectance spectra of different sizes of anatase TiO_2. Enhanced absorption of visible photons can be distinguished. (b) TEM of ~10 nm TiO_2, and (c) SEM of ~50 nm TiO_2.TEM and HRTEM images of pure TiO_2. (d) Electron paramagnetic resonance (EPR) spectra of pristine TiO_2 under different temperature (100 K, red, and 298 K, black). Ti^{3+} species can be detected using low temperature EPR test (100 K). (e) XRD of pure TiO_2, and

the inset HRTEM image is the active (101) facets of anatase TiO_2. All of them attribute to the photocatalytic activity of pure TiO_2 in the present work.

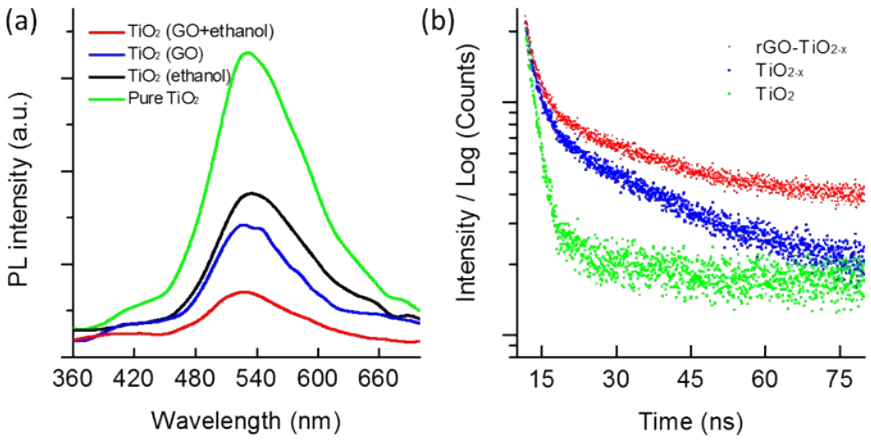

Figure S7. (a) PL and (b) TR-PL spectra of anantase TiO_2 irradiated by femtosecond laser at different surrounding mediums. The excited wavelength is 325 nm.