

Electronic supplementary information (ESI)

Plasmon resonances in semiconductor materials for detecting photocatalysis at single-particle level

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Supplementary note 1. X-Ray photoelectron spectroscopy (XPS; ESCALab250) was used to determine the oxidation state and the ratio between Ti^{3+} and Ti^{4+} . In O 1s spectra (Fig. S1a), the main peak located at 529.6 eV represents the lattice oxygen of TiO_2 , while the shoulder peak at 531.5 eV corresponds to the oxygen vacancy- Ti^{3+} surface state very clearly, also known as Ti_2O_3 . Quantitative analysis of the XPS data indicates that the ratio between O^{2-} in TiO_2 and defective oxides in Ti_2O_3 is close to 2:3. And in Ti 2p spectra (Fig. S1b), small peaks at 458.6 eV and 464.6 eV are assigned to the $2p_{3/2}$ and $2p_{1/2}$ core levels of Ti^{4+} , while the red-shifted peaks at 458.0 eV and 463.5 eV mean obvious Ti^{3+} signals. And the ratio between Ti^{4+} and Ti^{3+} is 1:2. Therefore, the self-doping TiO_{2-x} can be regarded as $\text{TiO}_{1.67}$. And X-Ray diffraction (XRD; D/MAX-2200, Rigaku) spectra were collected from as-synthesized

TiO_{1.67} and treated sample after annealing at 500°C (Fig. S1c). Although three strong diffraction peaks at 36.2°, 41.3° and 54.5° indexed to the characteristic peaks of rutile TiO₂ (JCPDS card File No.650192) can be observed in both TiO_{1.67} and rutile TiO₂, the diffraction peaks in rutile TiO₂ are much stronger and narrower. What is more, two weak diffraction peaks can only be observed in TiO_{1.67} samples, which can be indexed to the (110) and (003) crystallographic planes of Ti₃O₅ (JCPDS card File No.110217). It demonstrates the existence of defects in as-synthesized TiO_{1.67}. Raman scattering spectrometry (Renishaw, with a laser source of 514 nm) was also used to demonstrate the existence of oxygen vacancies. In Fig. S1d, compared with annealed rutile TiO₂, an obvious blue shift (~15 cm⁻¹) and broadening of the E_g band were clearly observed due to the photon-confinement effects induced by the lattice defects from non-stoichiometric TiO_{1.67} NPs as a result of oxygen vacancies. More analysis can be found in our published work (*Nanoscale* 2016, **8**, 8826).

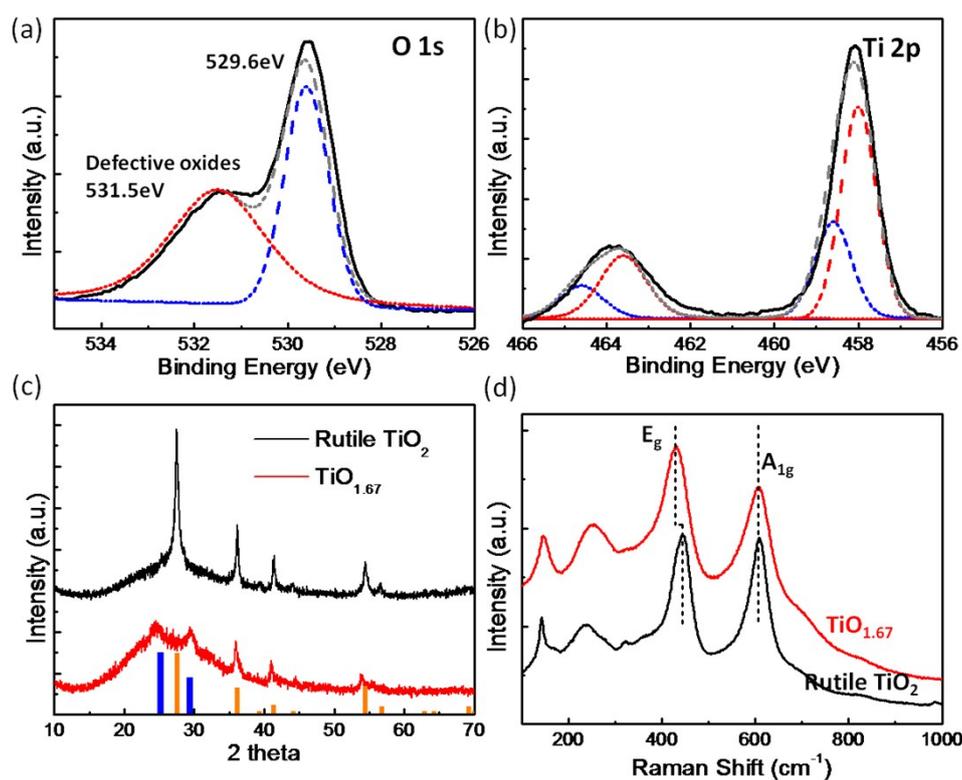


Figure S1. (a) O 1s XPS spectra of the titanium oxide. The black curve is the experimental result resolved into two peaks at 529.6 eV (blue dashed curve) and 531.5 eV (red dashed curve) with the area ratio 2:3. The grey dashed curve is the summation of the two decomposed peaks. (b) Ti 2p XPS spectra of the as-synthesized $\text{TiO}_{1.67}$ NPs. Black curve is the experimental result. And the grey dashed curve is the summation of four decomposed peaks at 458.6eV ($\text{Ti}^{4+} 2p_{3/2}$), 464.6eV ($\text{Ti}^{4+} 2p_{1/2}$), 458.0 ($\text{Ti}^{3+} 2p_{3/2}$) and 463.5eV ($\text{Ti}^{3+} 2p_{1/2}$). (c) XRD patterns of pristine $\text{TiO}_{1.67}$ NPs and the rutile TiO_2 obtained after annealing treatment at 500°C. Blue bars represent the diffraction peaks of Ti_3O_5 (JCPDS #11-0217), and orange bars are typical peaks of rutile TiO_2 (JCPDS #65-0192). (d) Raman spectra of $\text{TiO}_{1.67}$ (red curve) and rutile TiO_2 (black curve).

Supplementary note 2. The absorption spectrum of $\text{TiO}_{1.67}$ NPs was measured by a UV-Vis-NIR spectrophotometer (Lambda, PerkinElmer Company). The typical Tauc plot derived from the UV-vis absorption spectrum was used to determine the bandgap.

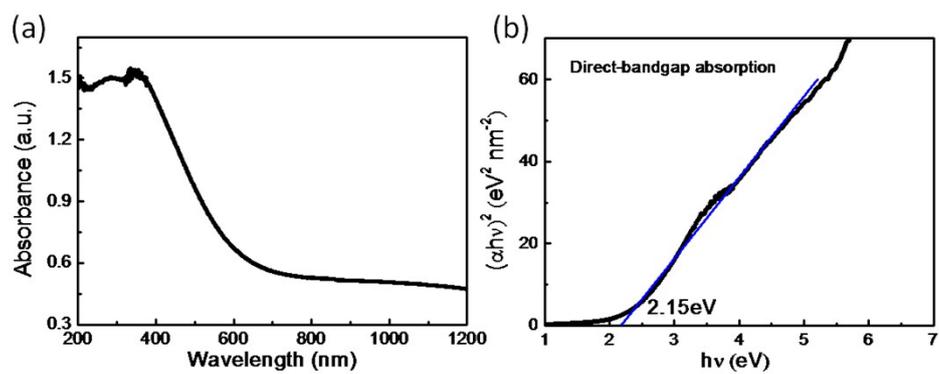


Figure S2. (a) Absorbance of $\text{TiO}_{1.67}$ NPs colloidal suspension. (b) The typical Tauc plot derived from the UV-vis absorption spectrum.

Supplementary note 3.

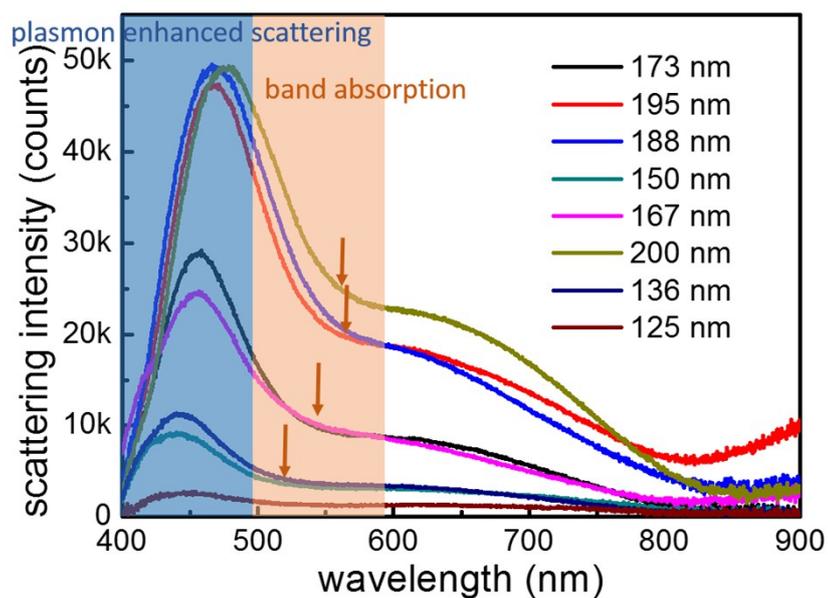


Figure S3. Scattering spectra of TiO_{1.67} nanoparticles with varied diameters. Arrows show the scattering dips. Orange and blue regions mean the “band absorption” region and the “plasmon enhanced scattering” region.

Supplementary note 4. In dark-field scattering measurement process, the light source spectrum was measured through the reflected light from a mirror.

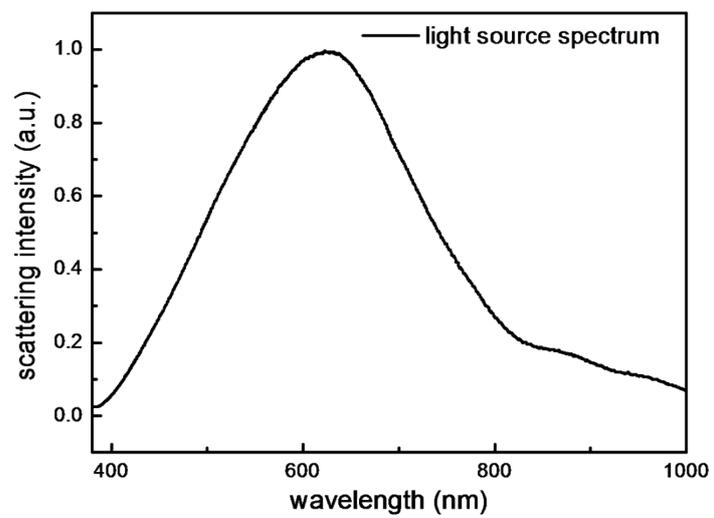


Figure S4. Light source spectrum measured through the reflected light from a mirror.