Supporting Information

One Step in situ Synthesis of Core-shell Structured Cr₂O₃:P@Fibrous-Phosphorus Hybrid Composites with Highly Efficient Full-spectrum-response Photocatalytic Activities

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1. Supplementary figures

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1. Supplementary figure

**Figure S1** XRD patterns of (a) Cr$_2$O$_3$:P@f-P with different P content fired at 700 °C; (b) comparison of XRD patterns for Cr$_2$O$_3$:P@f-P (m=2.5) and Cr$_2$O$_3$:P@f-P (m=2.5) annealed in N$_2$ for 2 h; (c) XRD patterns of Cr$_2$O$_3$:P@f-P (m=2.5) calcined at 600 °C, 700 °C and 900 °C.
Figure S2 (a-c) SEM, TEM and HRTEM images of pure Cr$_2$O$_3$; (d-e) FESEM image and corresponding EDS spectra of Cr$_2$O$_3$:P@f-P (m=2.5).
Figure S3 (a) survey XPS spectra of Cr₂O₃:P@f-P (m=2.5) prepared at different temperature; (b) The high resolution P2p XPS spectra of Cr₂O₃:P@f-P (m=2.5) calcined at 600 °C, 700 °C and 900 °C, respectively.
**Figure S4** the XRD pattern of possible phosphate impurities for Cr$_2$O$_3$:P@f-P (m=2.5) after TGA measurements in the N$_2$ and air atmosphere.
Figure S5 Photocatalytic degradation activities of the Cr$_2$O$_3$:P@f-P composites prepared with different molar ratio (m) of P to Cr$_2$O$_3$ under visible light irradiation (pH = 7).
<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Target pollutants</th>
<th>Light source</th>
<th>Light density (mw/cm²)</th>
<th>Catalyst dosage (mg)</th>
<th>Pollutants concentration (mg/L)</th>
<th>Activity (min)</th>
<th>Degradation efficiency (%)</th>
<th>Ref (year)</th>
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<tbody>
<tr>
<td>Cr₂O₃:P@f-P</td>
<td>MO</td>
<td>300 W Xe lamp, &gt; 800 nm</td>
<td>95</td>
<td>20</td>
<td>10</td>
<td>300</td>
<td>100%</td>
<td>This work</td>
</tr>
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<td>WS₂</td>
<td>MO</td>
<td>5 W NIR LED, (800-900 nm)</td>
<td>95</td>
<td>50</td>
<td>20</td>
<td>300</td>
<td>80%</td>
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<td>α-NaYF₄:Yb, Tm/TiO₂/rGO</td>
<td>MO</td>
<td>2 W LED laser, 980 nm</td>
<td>-</td>
<td>65</td>
<td>15</td>
<td>720</td>
<td>70%</td>
<td>[2] (2016)</td>
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<tr>
<td>α-NaYF₄:Yb, Tm/TiO₂</td>
<td>MO</td>
<td>1 W LED laser, 980 nm</td>
<td>-</td>
<td>5</td>
<td>20</td>
<td>1500</td>
<td>70%</td>
<td>[3] (2013)</td>
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<tr>
<td>α-NaYF₄:Yb, Tm/ZnO</td>
<td>RhB</td>
<td>2 W LED laser, 980 nm</td>
<td>2000</td>
<td>0.5</td>
<td>20</td>
<td>1800</td>
<td>55%</td>
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<tr>
<td>Cu₂(OH)PO₄</td>
<td>2,4-DCP</td>
<td>&gt; 800 nm</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>360</td>
<td>90%</td>
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<tr>
<td>Er³⁺/Yb³⁺-(CaF₂ @TiO₂)</td>
<td>MO</td>
<td>500 W Xe lamp, 720-1100 nm</td>
<td>-</td>
<td>50</td>
<td>10</td>
<td>720</td>
<td>30%</td>
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<td>Cs₅WO₃</td>
<td>MB</td>
<td>200 W NIR lamp, &gt;800 nm</td>
<td>42.7</td>
<td>100</td>
<td>50</td>
<td>360</td>
<td>37%</td>
<td>[10] (2016)</td>
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**Table S1** Comparison of NIR photocatalytic performance for Cr₂O₃:P@f-P hybrid composites with other NIR photocatalysts
Figure S6 The XRD patterns of core-shell structured Cr$_2$O$_3$:P@f-P (m=2.5) hybrid composites before and after photodegradation process.
Figure S7 the COD removal efficiency of MO under 300 mW/cm² light density.
Figure S8 (a) The photoluminescence spectra (PL) of pure Cr$_2$O$_3$ and core-shell structured Cr$_2$O$_3$:P@f-P (m=2.5) hybrid composites upon 290 nm light excitation; (b) EIS Nyquist plots of pure Cr$_2$O$_3$ and core-shell structured Cr$_2$O$_3$:P@f-P (m=2.5) hybrid composites in the 0.2M Na$_2$SO$_4$ solution.
Figure S9 (a-c) The SEM image of nano rod, nano rod/ flake and flake morphology fibrous phase P on the surface of TiO$_2$; (d) The comparison of Raman spectra of fibrous phase P grown on Cr$_2$O$_3$ and TiO$_2$.

Figure S9(a-c) shows the SEM images of fibrous phase P grown on Cr$_2$O$_3$ and TiO$_2$, respectively. The results imply fibrous phase P can be different morphologies such as nanorod, nanoflake synthesized on different particles via adjusting experimental conditions. The Raman spectra for all the samples can be well indexed to fibrous phase P.
2. Theoretical calculations

The theoretical calculations were carried out with the Vienna ab initio simulation package (VASP) based on density-functional theory (DFT) using projector augmented wave (PAW) potentials. The electron exchange correlation interaction was described by Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. The LSDA+U (i.e., PBE+U) method was performed for antiferromagnetic (AFM) Cr$_2$O$_3$, with a small effective on-site Coulomb energy $U_{\text{eff}}$ of 3.3 eV for the chromium d electrons. The plane wave kinetic energy cutoff was set at 520 eV, and a $9 \times 9 \times 9$ uniform Monkhorst-Pack k-grid was used for all calculated cells. Periodic boundary conditions were employed in all DFT calculations. All atoms were fully relaxed until the Helmann–Feynman forces were less than 0.001 eV/Å.

<table>
<thead>
<tr>
<th>Model</th>
<th>1P atom</th>
<th>2P atom-1</th>
<th>2P atom-2</th>
<th>3P atom-1</th>
<th>3P atom-2</th>
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<tr>
<td>Concentration (x)</td>
<td>0.0625</td>
<td>0.125</td>
<td>0.125</td>
<td>0.1875</td>
<td>0.1875</td>
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<tr>
<td>$E_{\text{form}}$ (eV)</td>
<td>-3.236</td>
<td>-2.922</td>
<td>-2.878</td>
<td>-2.326</td>
<td>-2.609</td>
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</table>

In order to investigate the P doped Cr$_2$O$_3$, we created a supercell including 80 atoms (32 Cr atom and 48 O atom) of 16 unit cells. We then introduced 1, 2 or 3 P
atoms to replace the O atoms randomly distributed. Five models involve different numbers of P atoms are shown in Figure S10b. The formation energy ($E_{\text{form}}$) of impurity P in Cr$_2$O$_3$ was computed by formula shown as following:

$$E_{\text{form}} = (E_{\text{Cr}_2\text{O}_3\cdot P_x} + E_{\text{O}}) - (E_{\text{Cr}_2\text{O}_3} + E_{P})$$

(1)

Here, $E_{\text{Cr}_2\text{O}_3}$ is the energy per unit cell for pure Cr$_2$O$_3$; $E_{\text{Cr}_2\text{O}_3\cdot P_x}$ is the energy per unit cell for P doped Cr$_2$O$_3$; $x$ represents the concentration of P defects in one unit cell of Cr$_2$O$_3$ (to form Cr$_2$O$_{3-x}$P$_x$). $E_{\text{O}}$ and $E_{P}$ denote the energy of single O atom and single P atom for their ground states, respectively. This equation describes the formation energy of P atoms doped in Cr$_2$O$_3$ to replace O atoms. The calculated formation energies are in between -2.33 per unit and -3.24 eV per unit as shown in Table S2. Although they are obviously dependent on the concentration and geometrical configuration of P impurities, the negative values suggest that P atoms are feasible to dope into the Cr$_2$O$_3$.

Figure S10a shows that doping one P into Cr$_2$O$_3$ supercell will lead to the defective bands within the bandgap due to the hybrid of Cr 3p3d4s, O 2p and P 3p. The curves of band structure presented in Figure S10b demonstrate that the P impurities contribute the “defective bands” (plotted as red lines) within the band gap. Compared with different models shown in Figure S10b (1 to 5), the DOS curves reveals that the defect levels are highly dependent on the concentration and geometrical configurations of doped P atoms. With the increase of the doping content, the defective bands with different energy level form within the band gap. It guarantees the light absorption extending to NIR region.
**Figure S10** (a) The calculated density of partial state (PDOS) of Cr$_2$O$_3$\:P using the PBE+U method; (b) The structure details (Color represents: red, O; grey Cr, blue P.), calculated electronic band structure and density of state (DOS) using the PBE+U method at different concentration P doing Cr$_2$O$_3$. (1): one P atom randomly substitution for O sites; (2) and (3): two P atom randomly substitution for O sites; (4) and (5): three P atom randomly substitution for O sites, respectively.
3. Heterojunction band alignment

The conductive band (CB) and valence band (VB) positions of Cr$_2$O$_3$:P can be estimated by Mulliken electronegativity theory,$^{13}$ which values at the point of zero charge can be calculated by following formula:

$$E_{CB} = \chi - E + 0.5E_g$$
$$E_{VB} = E_{CB} + E_g$$

(2)

Where $E_{CB}$ and $E_{VB}$ are the potential of conduction band and valence band, respectively. $\chi$ is the geometric mean of electronegativity of the component atoms, $E_c$ (4.5 eV) is the scaling factor between the hydrogen electrode scale (NHE) and absolute vacuum scale (AVS). Here, by using $\chi = 5.68$ and $E_g = 2.9$ eV, the $E_{CB}$ and $E_{VB}$ were calculated to be -0.27 V and 2.63 V (vs. NHE, pH = 0), respectively. Here the obtained band gap ($E_g$) of Cr$_2$O$_3$:P is 2.9 eV (Figure 3). And the CB potential of fibrous is -0.9 V vs. NHE (pH = 0) according to literature. According to the above values, we draw the schematic diagram of band structures for Cr$_2$O$_3$:P and fibrous P before contact, as shown in Figure S11. As we have known from the calculated band structures, the valence band is close to its Fermi level for p-type semiconductor.$^{14}$ Thus, the Fermi level of Cr$_2$O$_3$:P is more positive than fibrous P. After Cr$_2$O$_3$:P and f-P contact, the band position of Cr$_2$O$_3$:P will shift upward along with its Fermi level while those of fibrous P will shift downward along until established the equilibrium of Fermi level between two semiconductors. Finally, there will be a built-in potential between the core-shell contact interfaces, which can dramatically enhance the
separation of photogenerated electron and holes and then improve photocatalytic performance.

Figure S11 Schematic diagram of band structures for Cr$_2$O$_3$:P and fibrous P before contact.

4. Reference