Supporting Information

for

Hierarchical Bi$_2$WO$_6$/TiO$_2$-nanotube composites derived from natural cellulose for visible-light photocatalytic treatment of pollutants

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Additional figures
Table S1: The dosages of Bi(NO$_3$)$_3$·5H$_2$O and Na$_2$WO$_4$·2H$_2$O reagents in the preparation processes of the hierarchical Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites.

| Nanocomposites     | Bi(NO$_3$)$_3$·5H$_2$O/mg | Na$_2$WO$_4$·2H$_2$O/mg |
|--------------------|---------------------------|--------------------------|
| 30%–Bi$_2$WO$_6$/TiO$_2$-NT | 23.8          | 8.1                      |
| 50%–Bi$_2$WO$_6$/TiO$_2$-NT  | 55.6          | 18.9                     |
| 70%–Bi$_2$WO$_6$/TiO$_2$-NT  | 129.7         | 44.1                     |
| 90%–Bi$_2$WO$_6$/TiO$_2$-NT  | 500.3         | 170.2                    |

Figure S1: EDX spectra of the hierarchical (a) 30%–Bi$_2$WO$_6$/TiO$_2$-NT, (b) 50%–Bi$_2$WO$_6$/TiO$_2$-NT, (c) 70%–Bi$_2$WO$_6$/TiO$_2$-NT, and (d) 90%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites.
Table S2: Practical mass contents of Ti and Bi elements, as well as the Bi$_2$WO$_6$ component in the hierarchical Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites.

| Nanocomposites | Practical mass content of Ti/wt % | Practical mass content of Bi/wt % | Practical mass content of Bi$_2$WO$_6$/wt % |
|----------------|----------------------------------|----------------------------------|---------------------------------------------|
| 30%–Bi$_2$WO$_6$/TiO$_2$-NT | 47.04                            | 29.26                           | 38.4                                        |
| 50%–Bi$_2$WO$_6$/TiO$_2$-NT | 37.56                            | 44.52                           | 54.3                                        |
| 70%–Bi$_2$WO$_6$/TiO$_2$-NT | 22.40                            | 60.29                           | 72.9                                        |
| 90%–Bi$_2$WO$_6$/TiO$_2$-NT | 3.79                             | 74.50                           | 95.2                                        |

**Figures:**
- **a1)** and **a2)**: Images a1) and a2) show different views of the nanocomposite samples. The labels indicate the magnification levels: 1 µm, 500 nm, and 100 nm.
- **b1)** and **b2)**: Images b1) and b2) provide additional views with magnifications of 200 nm, 100 nm, and 50 nm.
- **c1)** and **c2)**: Images c1) and c2) offer further perspectives with 1 µm, 200 nm, and 100 nm magnifications.
- **a3)** and **a4)**: Images a3) and a4) show the nanocomposite structures at 50 nm and 100 nm magnifications.
- **b3)** and **b4)**: Images b3) and b4) provide details at 60 nm and 50 nm magnifications.
- **c3)** and **c4)**: Images c3) and c4) offer even more specific views at 100 nm and 50 nm magnifications.
**Figure S2:** Electron micrographs of the (a1−a4) pure TiO$_2$-NT sample, (b1−b4) pure Bi$_2$WO$_6$ powder sample, and (c1−c4) the Bi$_2$WO$_6$/TiO$_2$ sample prepared without the cellulose template. The first two columns represent the FE-SEM images, and the last two columns exhibit the TEM images of the corresponding samples.

**Figure S3:** XPS survey spectrum of the hierarchical 70%−Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite.

**Figure S4:** (a) The visible-light (λ > 420 nm) induced photocatalytic degradation profiles and (b) the corresponding linear fitting curves based on the pseudo-first-order kinetic model towards the photodegradation of RhB pollutant solution (10 mg·L$^{-1}$) by the (i) pure TiO$_2$-NT,
(ii) pure Bi$_2$WO$_6$ powder, as well as the hierarchical (iii) 30%–Bi$_2$WO$_6$/TiO$_2$-NT, (iv) 50%–Bi$_2$WO$_6$/TiO$_2$-NT, (v) 70%–Bi$_2$WO$_6$/TiO$_2$-NT, and (vi) 90%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites.

**Figure S5:** (a) The reduction profiles towards Cr(VI) pollutant solution (10 mg·L$^{-1}$, pH 4) and (b) the linear fitting curves based on the pseudo-first-order kinetic model under different conditions. (i) The self-reduction reaction of Cr(VI) or self-degradation reaction of RhB without photocatalysts under visible-light (λ > 420 nm) irradiation. (ii) The self-adsorption by the hierarchical 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite towards Cr(VI) or RhB pollutant solution. And the visible-light (λ > 420 nm) induced photocatalytic reactions towards Cr(VI) or RhB pollutant solution by employing (iii) the hierarchical 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites.
nanocomposite, (iv) the Bi$_2$WO$_6$/TiO$_2$ sample prepared without the cellulose template, and (v) the Bi$_2$WO$_6$-TiO$_2$ sample prepared by physical blend as the photocatalysts.

Figure S6: (a) The visible-light (λ > 420 nm) induced photocatalytic degradation profiles towards the photodegradation of RhB pollutant solution (10 mg·L$^{-1}$) for five cycles by the hierarchical 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite. (b) The XRD patterns of the 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposites before and after 5-cycle photocatalysis. (c,d) The FE-SEM images of the 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite after 5-cycle photocatalysis.
Figure S7: (a) The UV–vis DRS, (b) the band gaps determined by the intercept on the x-axis of the respective Tauc plots, and the PL emission spectra under the excitation of 360 nm of the hierarchical 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite, the Bi$_2$WO$_6$/TiO$_2$ sample prepared without the cellulose template, and the Bi$_2$WO$_6$-TiO$_2$ sample prepared by physical blend.

Figure S8: (a) The transient photocurrent responses and (b) EIS Nyquist plots of (i) the hierarchical 70%–Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite, (ii) the Bi$_2$WO$_6$/TiO$_2$ sample prepared without the cellulose template, and (iii) the Bi$_2$WO$_6$-TiO$_2$ sample prepared by physical blend.
Figure S9: (a) The visible-light ($\lambda > 420$ nm) induced photocatalytic degradation profiles towards the RhB pollutant solution ($10$ mg·L$^{-1}$) added with IPA, EDTA-2Na, and p-BQ by the hierarchical 70%-Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite. (b) The schematic illustration of the photocatalytic degradation mechanism towards the RhB pollutant by the hierarchical Bi$_2$WO$_6$/TiO$_2$-NT nanocomposite under the irradiation of visible light ($\lambda > 420$ nm).
**Table S3:** Comparison of the hierarchical Bi$_2$WO$_6$/TiO$_2$-nanotube composite with the natural cellulose substance derived Ag$_2$O-nanoparticle/TiO$_2$-nanotube composite, g-C$_3$N$_4$/TiO$_2$-nanotube composite, and H$_3$PW$_{12}$O$_{40}$/TiO$_2$ nanocomposite reported by our group.

| composites          | Light source | morphology                          | pollutants | $K_{app}$ | Ref.  |
|---------------------|--------------|-------------------------------------|------------|-----------|-------|
| Bi$_2$WO$_6$/TiO$_2$-NT | 350 W Xe    | Bi$_2$WO$_6$ nanoparticles coated on the TiO$_2$ nanotubes | RhB        | 0.65 h$^{-1}$ | This  |
| TiO$_2$-NT          | $\lambda > 420$ nm |                                      | Cr(VI)     | 0.52 h$^{-1}$ | work  |
| Ag$_2$O-NP/TiO$_2$-NT | 300 W, Hg   | Ag$_2$O nanoparticles coated on the TiO$_2$ nanotubes | MB         | 0.62 min$^{-1}$ |       |
| g-C$_3$N$_4$/TiO$_2$-NT | 350 W Xe    | g-C$_3$N$_4$ layer anchored on the TiO$_2$ nanotube surfaces | MB         | 0.37 min$^{-1}$ | [1]   |
| H$_3$PW$_{12}$O$_{40}$/TiO$_2$-NT | 300 W, Hg | coated on the TiO$_2$ nanotubes or on the TiO2/cellulose composite sheet | MB         | 0.29 min$^{-1}$ | [2]   |

**References**

1. Lin, Z.; Lu, Y.; Huang, J. *Cellulose* **2019**, *26*, 6683–6700.

2. Lin, Z.; Yu, B.; Huang, J. *Langmuir* **2020**, *36*, 5967–5978.

3. Lin, Z.; Huang, J. *Sep. Purif. Technol.* **2021**, *264*, 118427.