



Supporting Information

for

Hierarchical Bi₂WO₆/TiO₂-nanotube composites derived from natural cellulose for visible-light photocatalytic treatment of pollutants

Zehao Lin, Zhan Yang and Jianguo Huang

Beilstein J. Nanotechnol. **2022**, *13*, 745–762. [doi:10.3762/bjnano.13.66](https://doi.org/10.3762/bjnano.13.66)

Additional figures

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

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

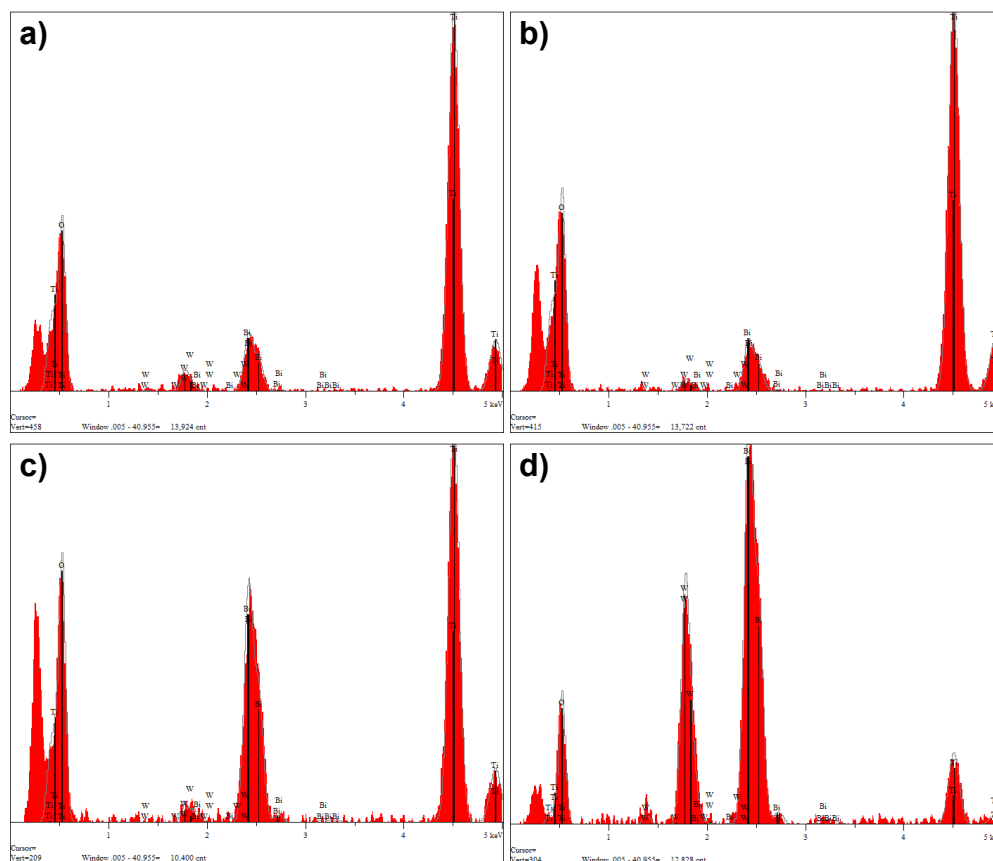


Figure S1: EDX spectra of the hierarchical (a) 30%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, (b) 50%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, (c) 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, and (d) 90%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$ nanocomposites.

Table S2: Practical mass contents of Ti and Bi elements, as well as the Bi₂WO₆ component in the hierarchical Bi₂WO₆/TiO₂-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

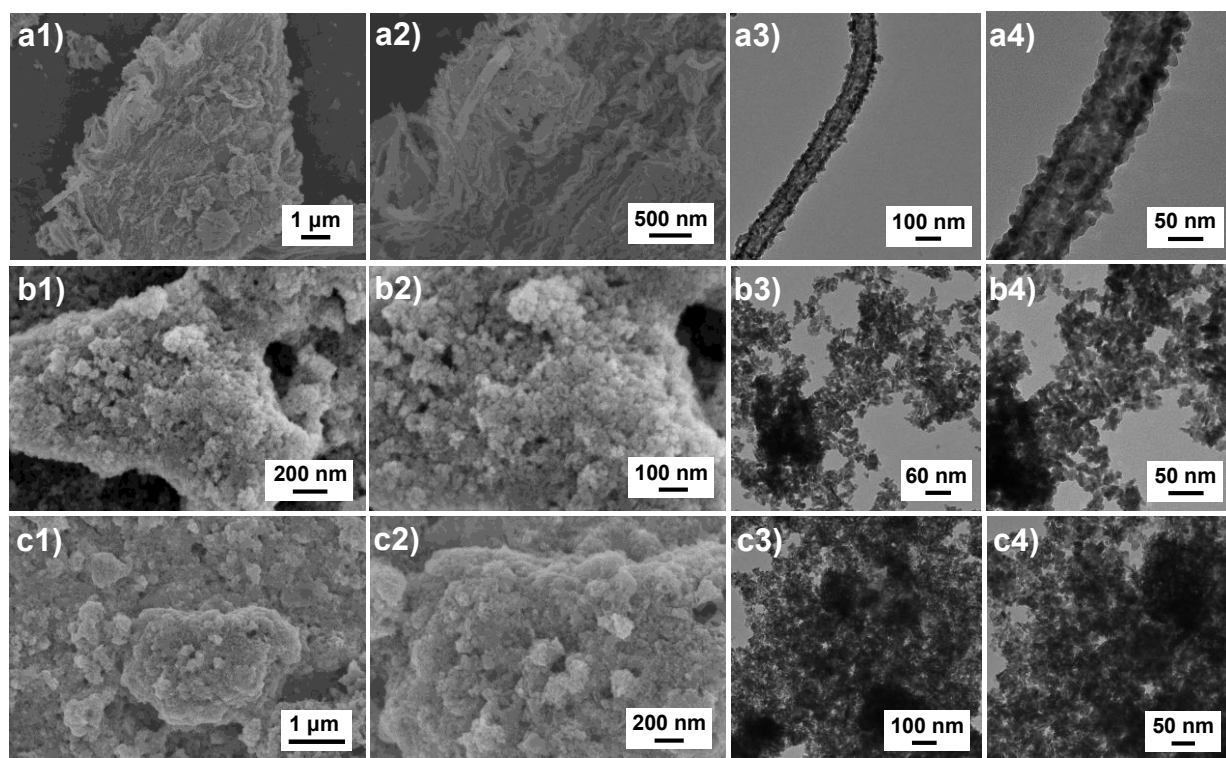


Figure S2: Electron micrographs of the (a1–a4) pure TiO₂-NT sample, (b1–b4) pure Bi₂WO₆ powder sample, and (c1–c4) the Bi₂WO₆/TiO₂ sample prepared without the cellulose template. The first two columns represent the FE-SEM images, and the last two columns exhibit the TEM images of the corresponding samples.

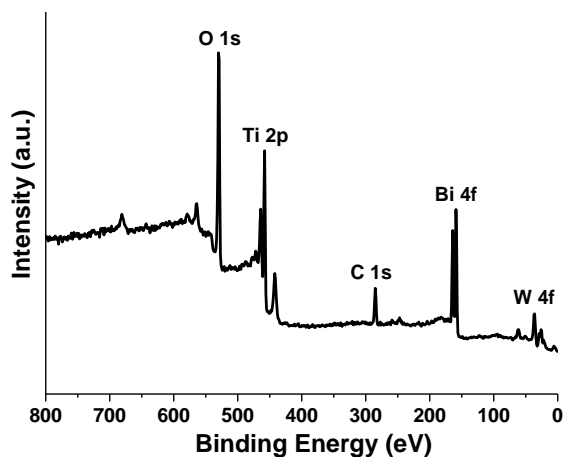


Figure S3: XPS survey spectrum of the hierarchical 70%-Bi₂WO₆/TiO₂-NT nanocomposite.

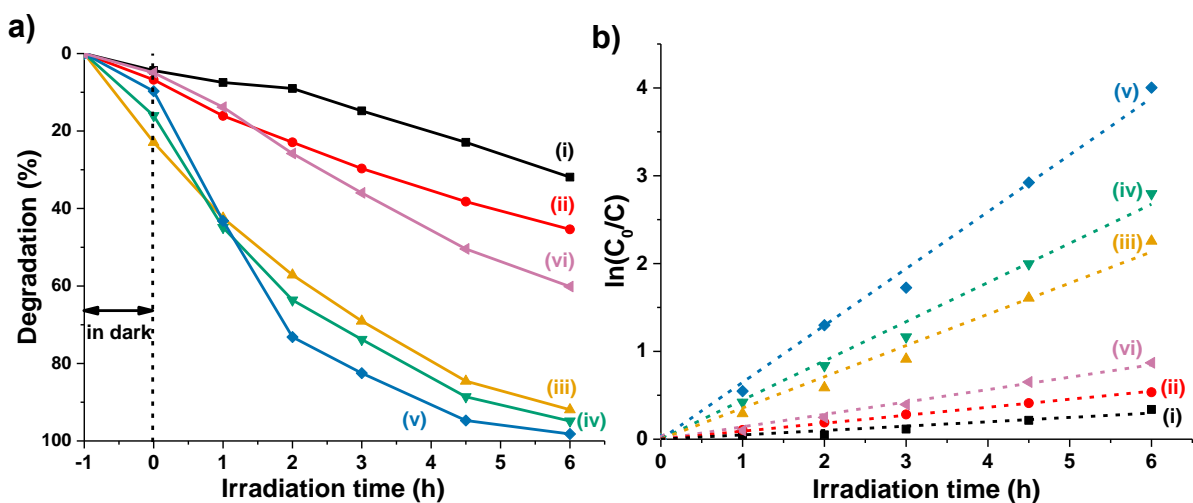


Figure S4: (a) The visible-light ($\lambda > 420$ nm) induced photocatalytic degradation profiles and (b) the corresponding linear fitting curves based on the pseudo-first-order kinetic model towards the photodegradation of RhB pollutant solution ($10 \text{ mg}\cdot\text{L}^{-1}$) by the (i) pure TiO₂-NT,

(ii) pure Bi_2WO_6 powder, as well as the hierarchical (iii) 30%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, (iv) 50%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, (v) 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$, and (vi) 90%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$ nanocomposites.

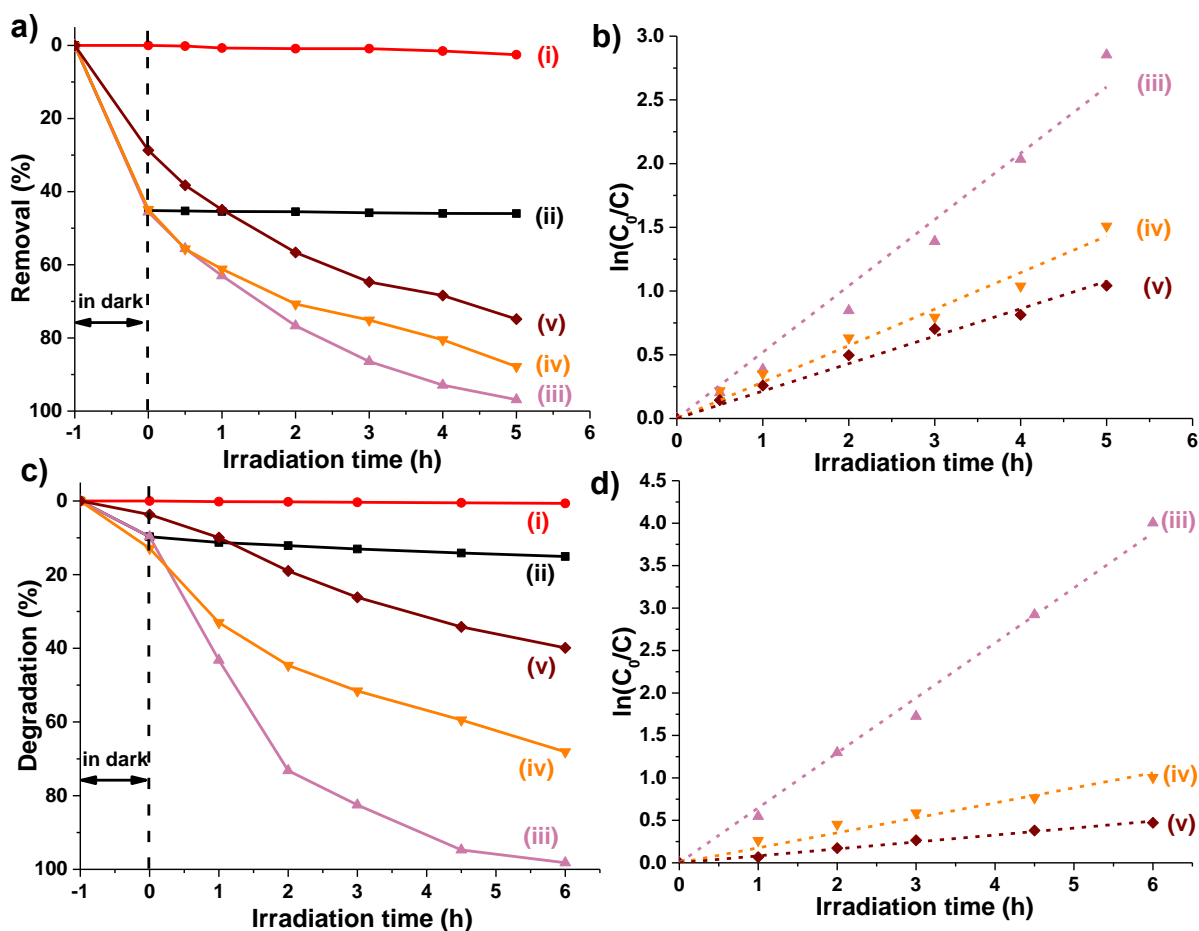


Figure S5: (a) The reduction profiles towards Cr(VI) pollutant solution ($10 \text{ mg}\cdot\text{L}^{-1}$, pH 4) and (c) the degradation profiles towards RhB pollutant solution ($10 \text{ mg}\cdot\text{L}^{-1}$) as well as (b,d) the corresponding linear fitting curves based on the pseudo-first-order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

nanocomposite, (iv) the $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ sample prepared without the cellulose template, and (v) the $\text{Bi}_2\text{WO}_6\text{-TiO}_2$ sample prepared by physical blend as the photocatalysts.

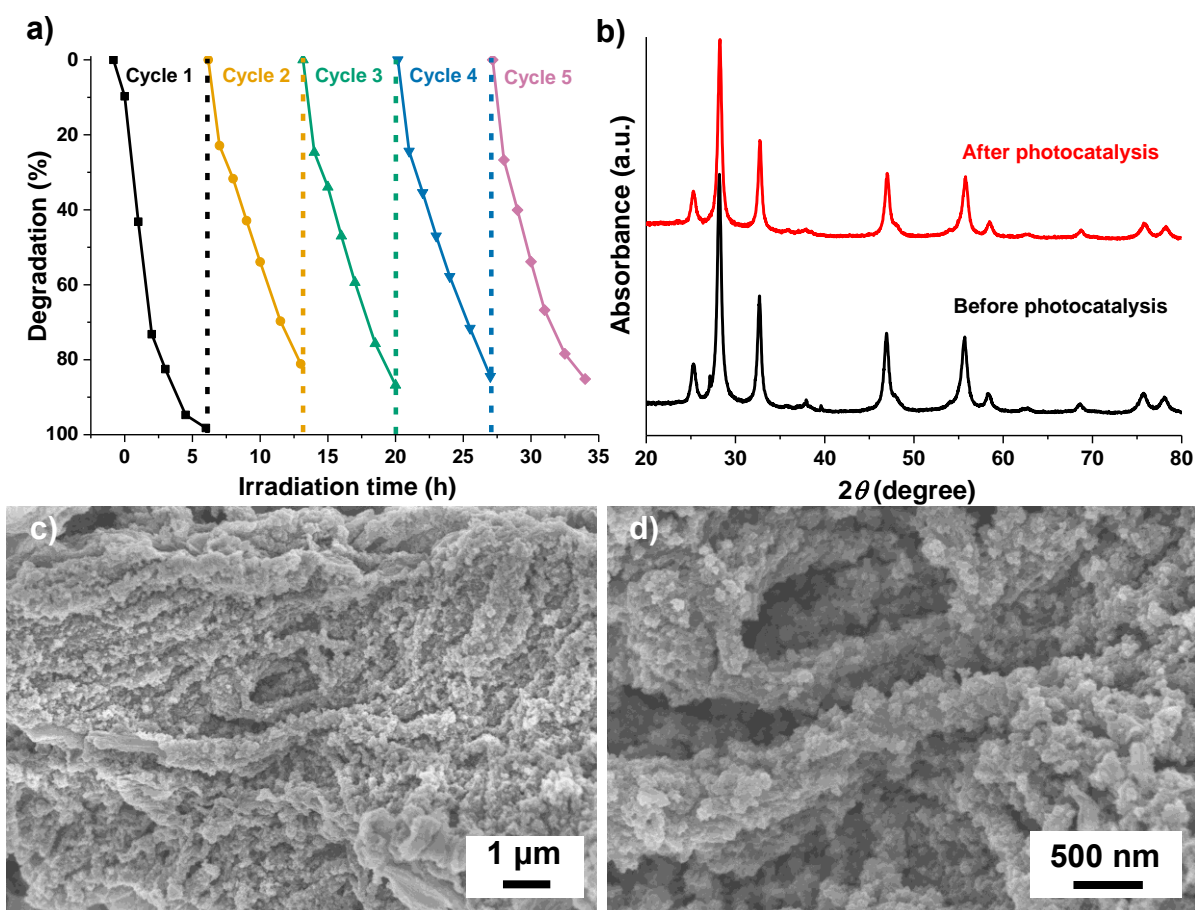


Figure S6: (a) The visible-light ($\lambda > 420$ nm) induced photocatalytic degradation profiles towards the photodegradation of RhB pollutant solution ($10 \text{ mg}\cdot\text{L}^{-1}$) for five cycles by the hierarchical 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$ nanocomposite. (b) The XRD patterns of the 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$ nanocomposites before and after 5-cycle photocatalysis. (c,d) The FE-SEM images of the 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2\text{-NT}$ nanocomposite after 5-cycle photocatalysis.

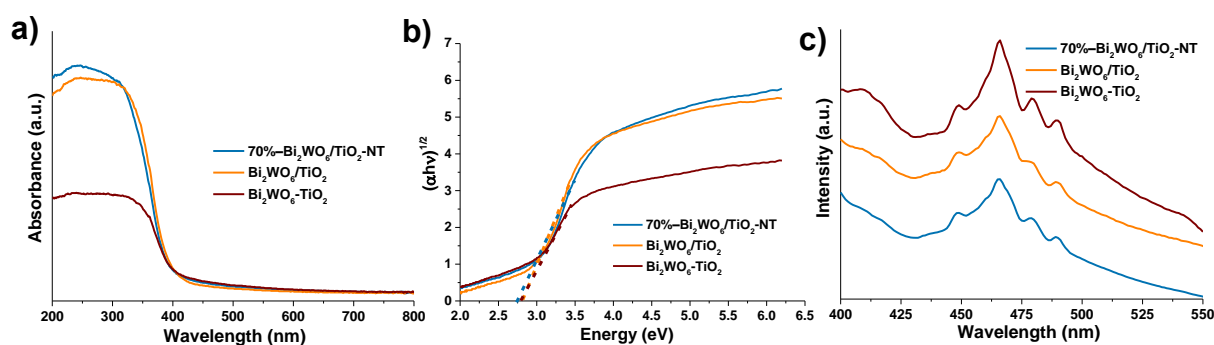


Figure S7: (a) The UV-vis DRS, (b) the band gaps determined by the intercept on the x-axis of the respective Tauc plots, and the PL emission spectra under the excitation of 360 nm of the hierarchical 70%-Bi₂WO₆/TiO₂-NT nanocomposite, the Bi₂WO₆/TiO₂ sample prepared without the cellulose template, and the Bi₂WO₆-TiO₂ sample prepared by physical blend.

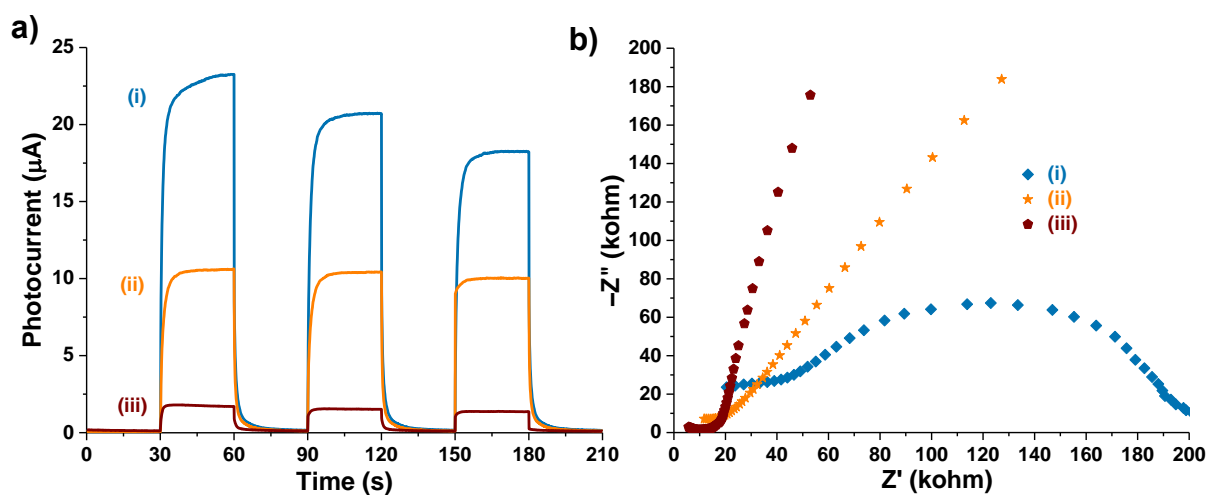


Figure S8: (a) The transient photocurrent responses and (b) EIS Nyquist plots of (i) the hierarchical 70%-Bi₂WO₆/TiO₂-NT nanocomposite, (ii) the Bi₂WO₆/TiO₂ sample prepared without the cellulose template, and (iii) the Bi₂WO₆-TiO₂ sample prepared by physical blend.

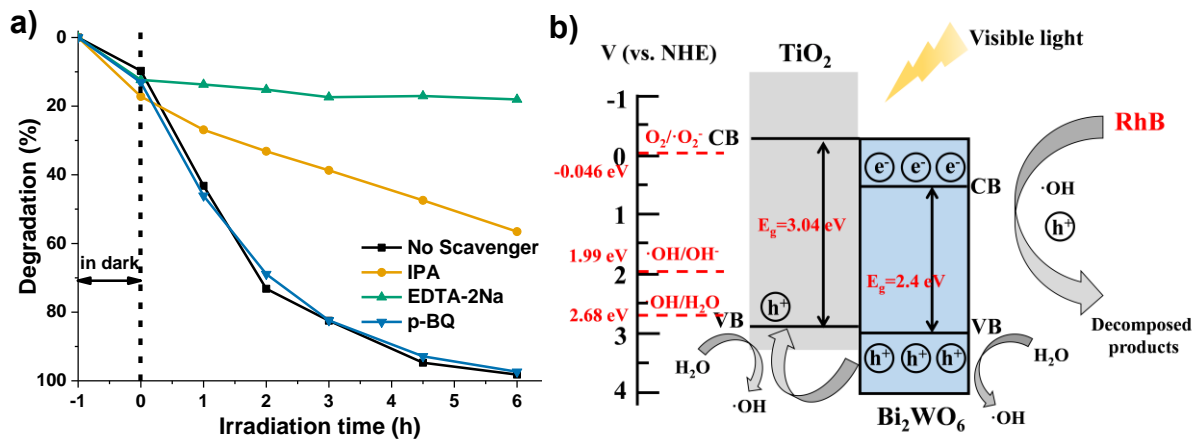


Figure S9: (a) The visible-light ($\lambda > 420$ nm) induced photocatalytic degradation profiles towards the RhB pollutant solution ($10 \text{ mg}\cdot\text{L}^{-1}$) added with IPA, EDTA-2Na, and p-BQ by the hierarchical 70%– $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ -NT nanocomposite. (b) The schematic illustration of the photocatalytic degradation mechanism towards the RhB pollutant by the hierarchical $\text{Bi}_2\text{WO}_6/\text{TiO}_2$ -NT nanocomposite under the irradiation of visible light ($\lambda > 420$ nm).

Table S3: Comparison of the hierarchical Bi₂WO₆/TiO₂-nanotube composite with the natural cellulose substance derived Ag₂O-nanoparticle/TiO₂-nanotube composite, g-C₃N₄/TiO₂-nanotube composite, and H₃PW₁₂O₄₀/TiO₂ nanocomposite reported by our group.

composites	Light source	morphology	pollutants	K_{app}	Ref.
Bi ₂ WO ₆ /TiO ₂ -NT	350 W Xe $\lambda > 420$ nm	Bi ₂ WO ₆ nanoparticles coated on the TiO ₂ nanotubes	RhB Cr(VI)	0.65 h ⁻¹ 0.52 h ⁻¹	This work
Ag ₂ O-NP/TiO ₂ -NT	300 W, Hg	Ag ₂ O nanoparticles coated on the TiO ₂ nanotubes	MB RhB NFCX	0.62 min ⁻¹ 0.37 min ⁻¹ 0.29 min ⁻¹	[1]
g-C ₃ N ₄ /TiO ₂ -NT	350 W Xe $\lambda > 420$ nm	g-C ₃ N ₄ layer anchored on the TiO ₂ nanotube surfaces	MB	0.21 h ⁻¹	[2]
H ₃ PW ₁₂ O ₄₀ /TiO ₂ -NT	300 W, Hg	H ₃ PW ₁₂ O ₄₀ nanoparticles coated on the TiO ₂ nanotubes or on the TiO ₂ /cellulose composite sheet	MB	0.54 min ⁻¹	[3]

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.