Supporting Information

Converting Cellulose Nanocrystals into Photocatalysts by Functionalisation with Titanium Dioxide Nanorods and Gold Nanocrystals

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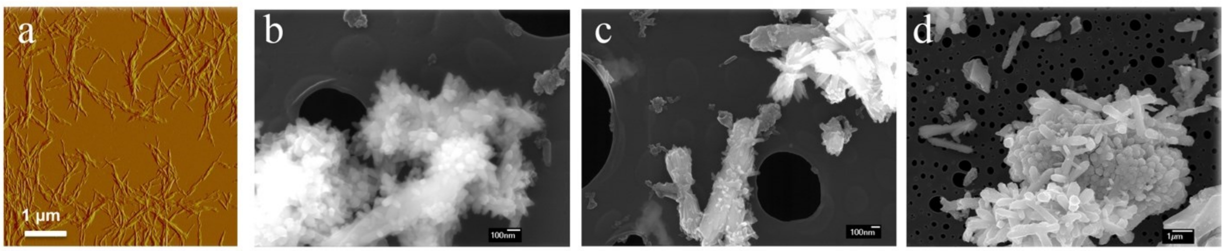

Figure S1. a) AFM images of typical CNCs produced by sulphuric acid hydrolysis and (b-d)CNC/TiO2-NRs hybrids based on sulphonyl, carboxyl and phosphoryl functionalized CNC nanocrystals.

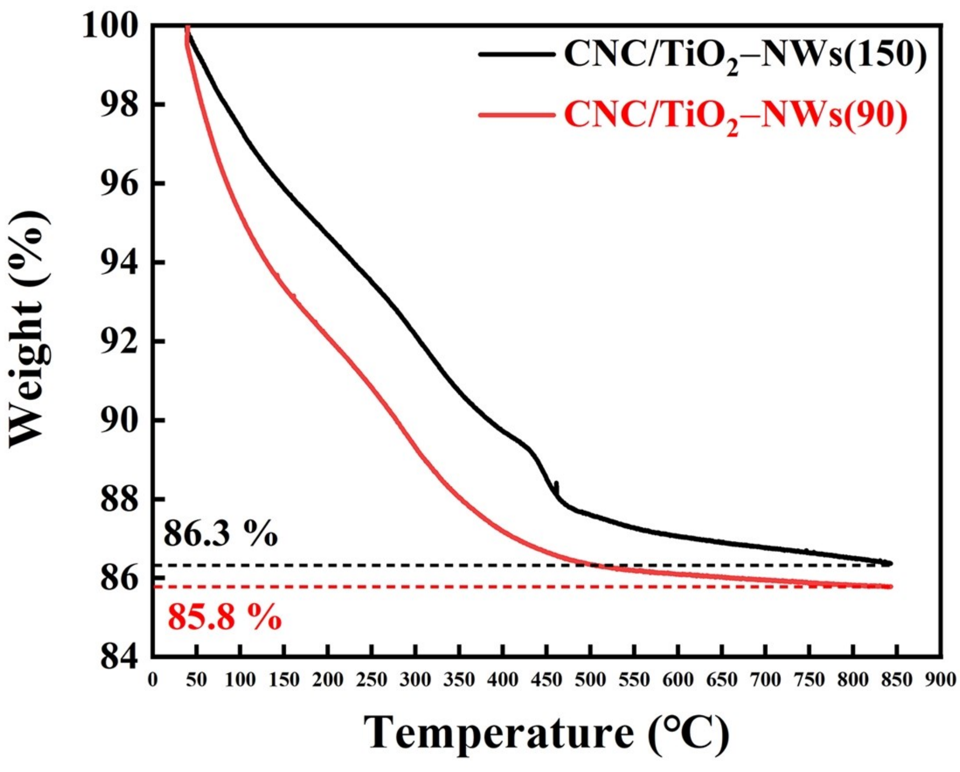

Figure S2. TGA curves of the CNC/TiO_2-NRs (90), CNC/TiO_2-NRs(150) (ramp 10 ºC/min, 35–850 ºC, in air)

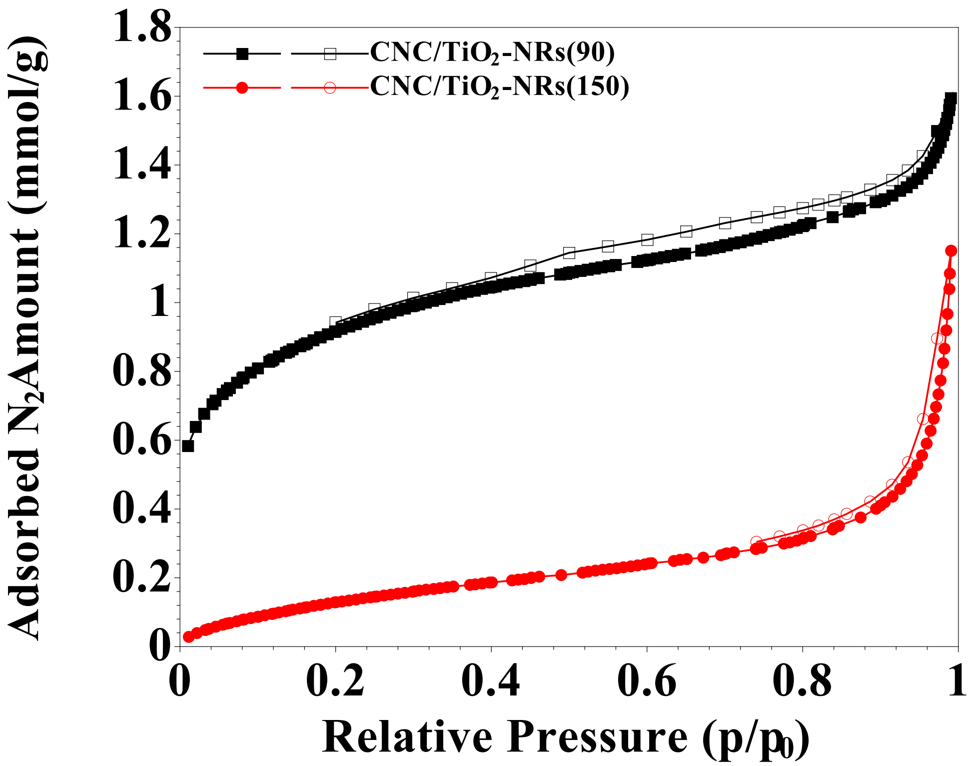

Figure S3. Nitrogen adsorption-desorption BET isotherms of CNC/TiO_2-NRs (90) and CNC/TiO_2-NRs(150)

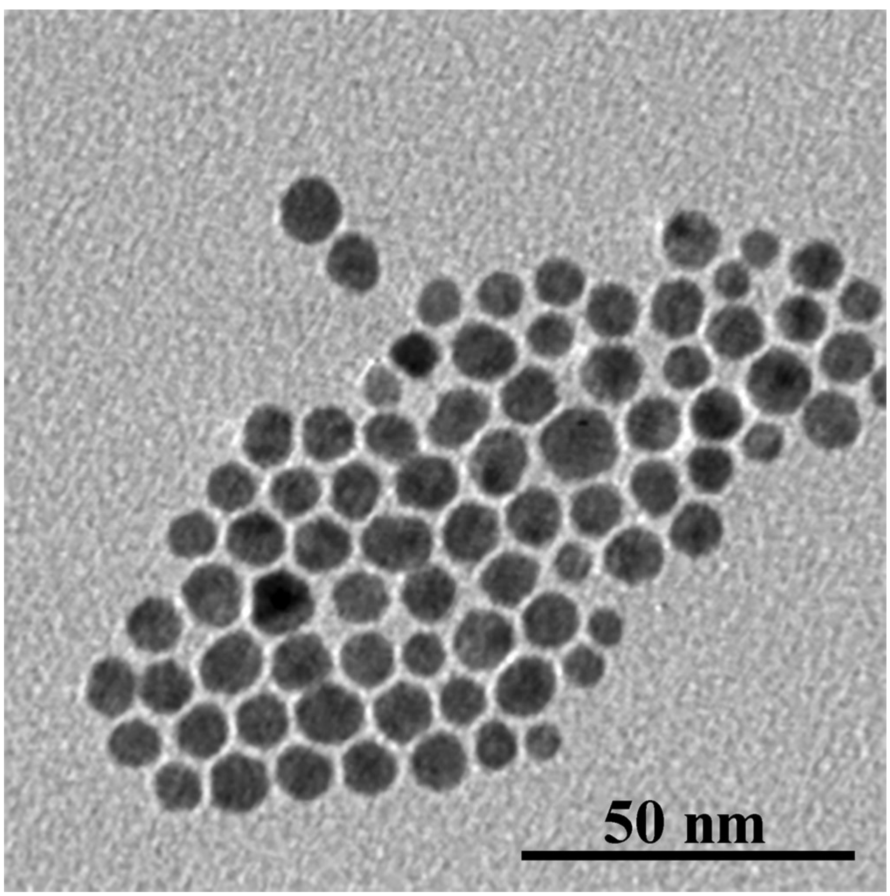

Figure S4. TEM image of Au NCs before decoration

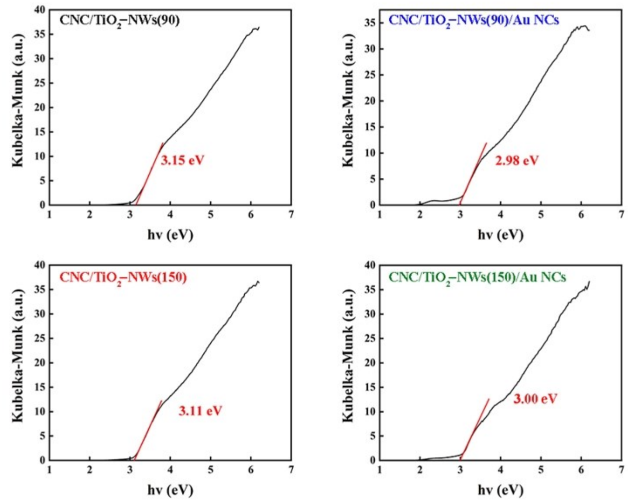

Figure S5. Tauc plot images of CNC/TiO_2-NRs(90), CNC/TiO_2-NRs(150), CNC/TiO_2-NRs(90)/Au NCs and CNC/TiO_2-NRs(150)/Au NCs

Degradation mechanism

During the solar simulator illumination, LSPR-induced hot electrons in Au NCs on the surface of TiO_2 NRs with energies higher than the Schottky barrier energy can be injected into the conductive band (CB) of TiO_2.[1] This process can significantly promote the separation of electron-hole pairs. The injected electrons in CB are trapped by absorbed O_2 molecules and then participated in the photoreduction reaction to get $\cdot O_2^-$. However, $\cdot O_2^-$ is quite unstable in aqueous solution, so that it would readily decompose into hydroxyl radicals.[2, 3]

$O_2 + e^- \rightarrow \cdot O_2^-$

$\cdot O_2^- + 2H^+ + 2e^- \rightarrow \cdot OH + OH^-$

After the transfer of hot electrons, the holes on Au NCs are supposed to participate in photo-oxidation reaction with superoxide anion radicals $\cdot O_2^-$, yielding singlet oxygen ($^1O_2$).[4]

$\cdot O_2^- + h^+ \rightarrow {}^1O_2$

The photolysis of hydrogen peroxide in aqueous to hydroxyl radicals happened simultaneously, following the reaction:

$H_2O_2 + hv \rightarrow 2\cdot OH$

Finally, the reactive oxygen species including $\cdot OH$, $\cdot O_2^-$ and $\cdot O_2^-$ can easily degrade RhB into CO_2 and H_2O.[5, 6]

1. Furube, A.; Du, L.; Hara, K.; Katoh, R.; Tachiya, M. Ultrafast plasmon-induced electron transfer from gold nanodots into TiO2 nanoparticles. *J. Am. Chem. Soc.* **2007,** *129*, 14852-14853.
2. Shi, H.; Wang, X.; Zheng, M.; Wu, X.; Chen, Y.; Yang, Z.; Zhang, G.; Duan, H. Hot-Electrons Mediated Efficient Visible-Light Photocatalysis of Hierarchical Black Au-TiO2 Nanorod Arrays on Flexible Substrate. *Adv. Mater. Interfaces* **2016,** *3*, 1600588.
3. Sułek, A.; Pucelik, B.; Kuncewicz, J.; Dubin, G.; Dąbrowski, J. M. Sensitization of TiO2 by halogenated porphyrin derivatives for visible light biomedical and environmental photocatalysis. *Catal. Today* **2019,** *335*, 538-549.
4. Li, B.; Hao, Y.; Shao, X.; Tang, H.; Wang, T.; Zhu, J.; Yan, S. Synthesis of hierarchically porous metal oxides and Au/TiO2 nanohybrids for photodegradation of organic dye and catalytic reduction of 4-nitrophenol. *J. Catal.* **2015,** *329*, 368-378.
5. Ansari, S. A.; Khan, M. M.; Ansari, M. O.; Cho, M. H. Gold nanoparticles-sensitized wide and narrow band gap TiO2 for visible light applications: a comparative study. *New J. Chem.* **2015,** *39*, 4708-4715.
6. Yin, M.; Li, Z.; Kou, J.; Zou, Z. Mechanism investigation of visible light-induced degradation in a heterogeneous TiO2/Eosin Y/Rhodamine B system. *Environ. Sci. Technol.* **2009,** *43*, 8361-8366.