



Article

# Mesoporous Tungsten Trioxide Photoanodes Modified with Nitrogen-Doped Carbon Quantum Dots for Enhanced Oxygen Evolution Photo-Reaction

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## Supporting Information

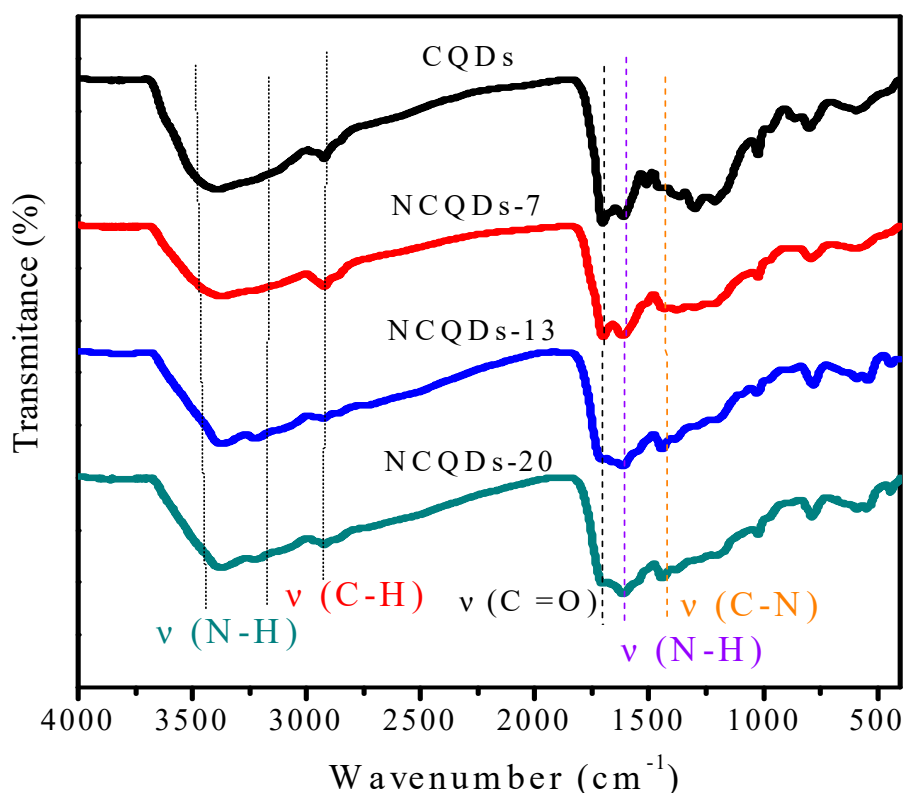
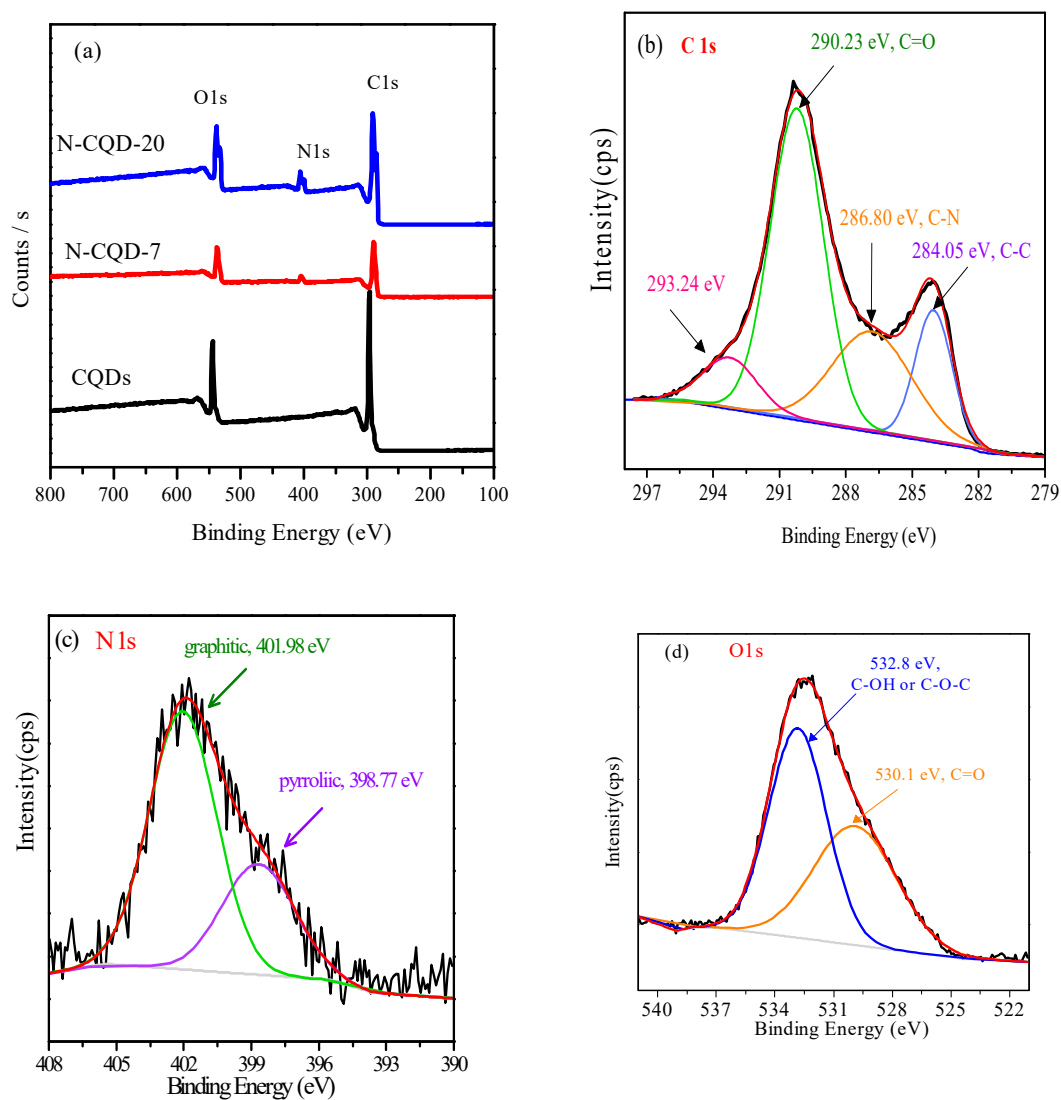
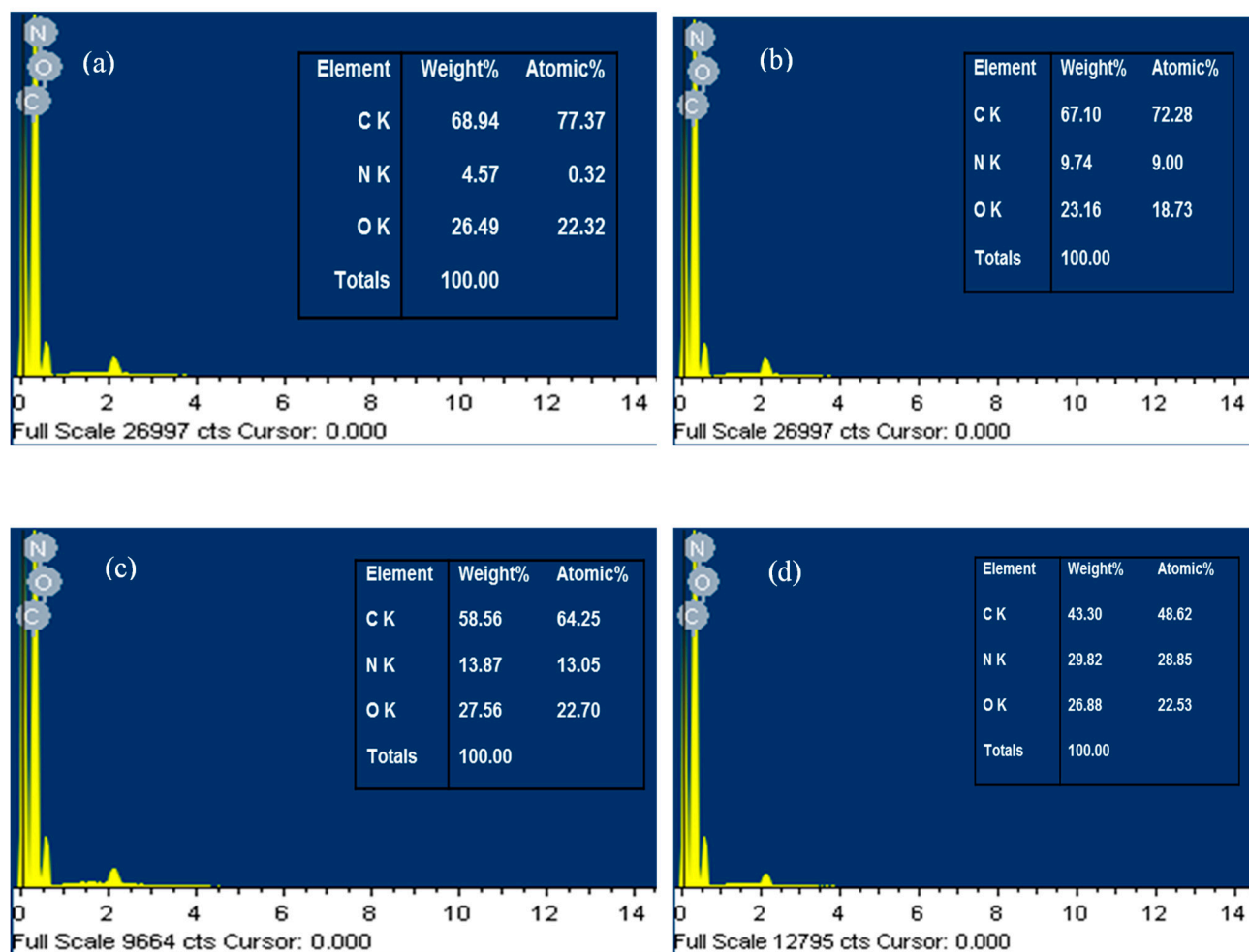


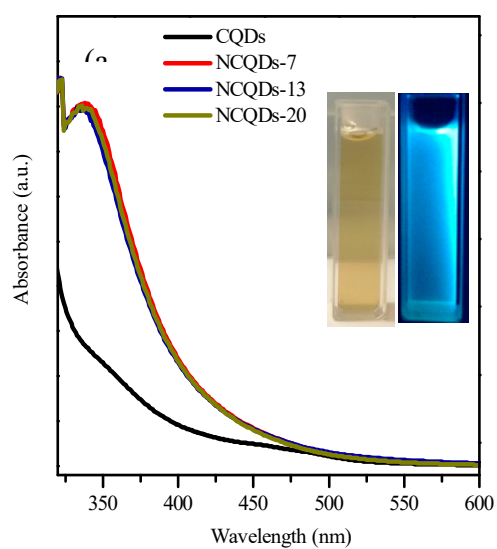
Figure 1. FTIR spectra of CQDs and N-CQDs samples.

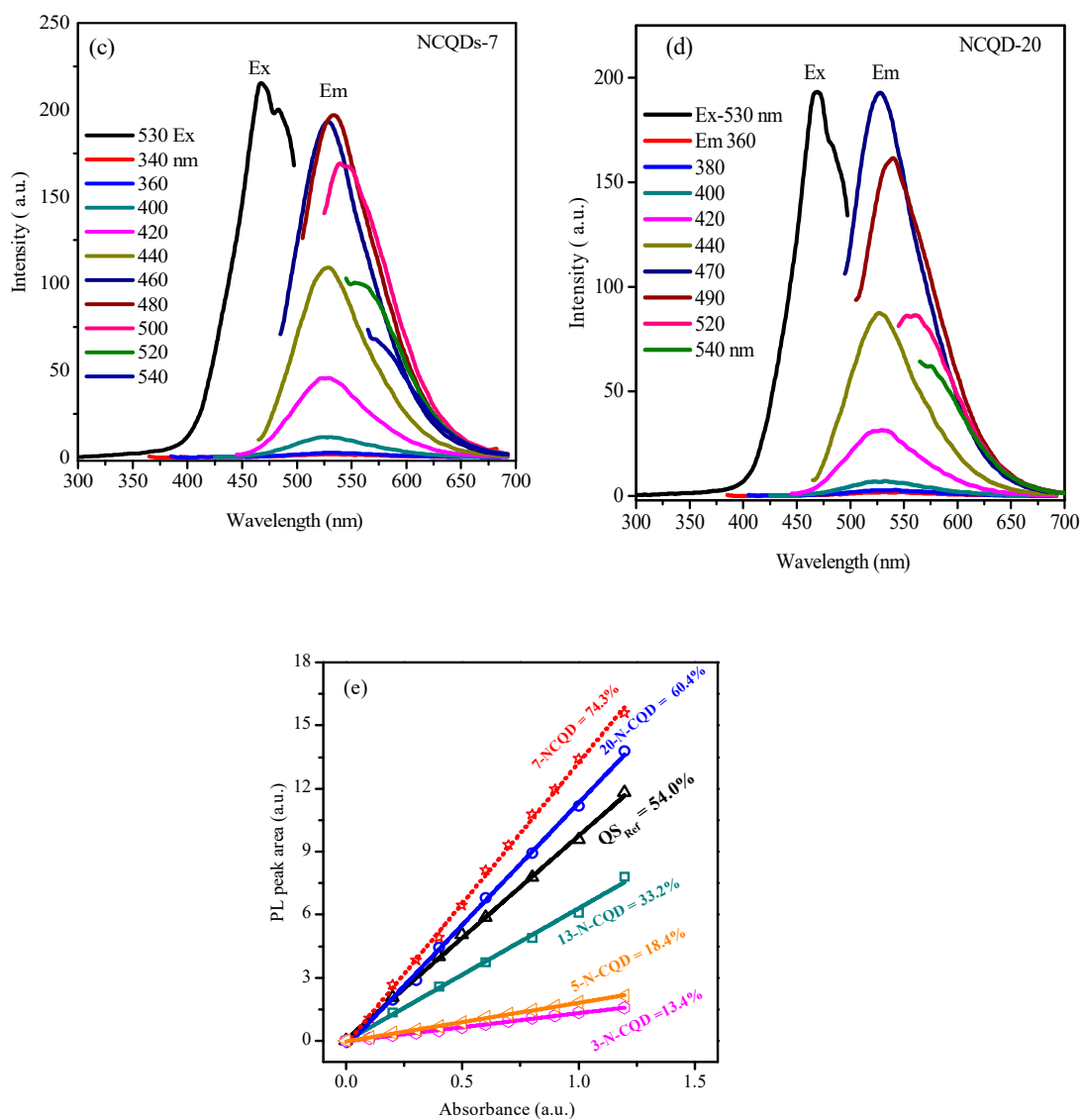


**Figure 2.** (a) XPS survey spectra for the CQDs, N-CQD-7 and N-CQD-20 samples. The only elements identified were carbon, nitrogen and oxygen. (c) C 1s, (d) N 1s and (E) O 1s high resolution XPS spectra for N-CQD-7 sample.



**Figure S3.** EDX spectra of N-CQDs samples, (a) N-CQD-3, (b) N-CQD-5, (c) N-CQD-7, and (d) N-CQD-20.





**Figure S4.** (a) UV-Vis absorption spectra for the CQDs and N-CQDs samples. Inserts show digital photos of aqueous N-CQD-7 (left) and their bright blue PL (right) under UV, (b,c,d) PL spectra for the N-CQD-7, N-CQD-13 and N-CQD-20. The excitation wavelength was increased from 340 to 540 nm in 20 nm increments. (e) External quantum yields for the N-CQDs samples under 360 nm excitation, calibrated against quinine sulfate.

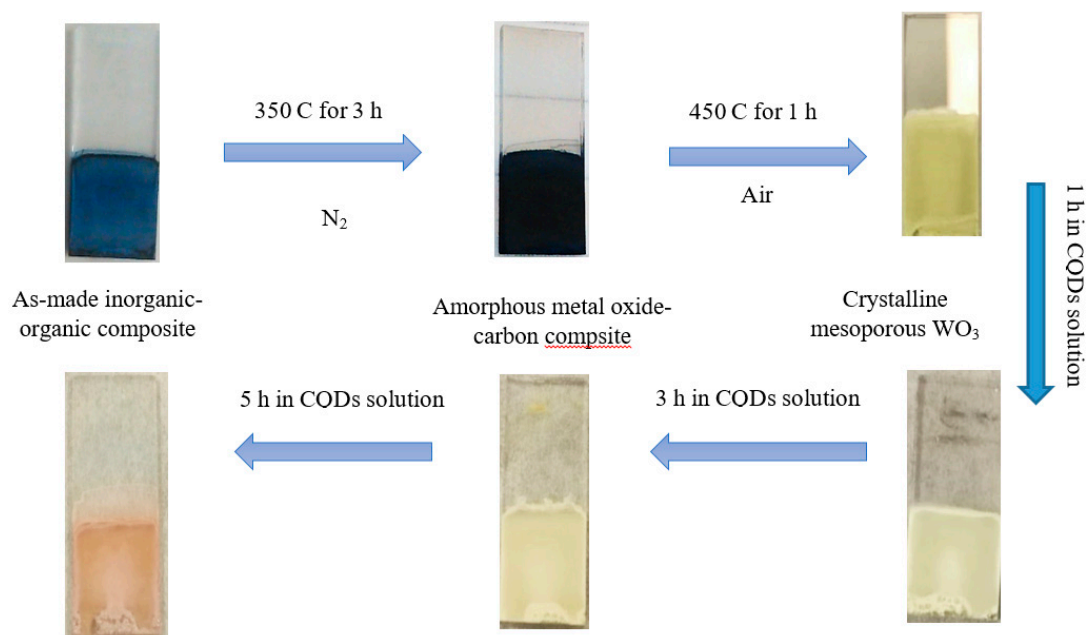


Figure 5. steps for the synthesis of *meso*-WO<sub>3</sub> and modification with CQDs.

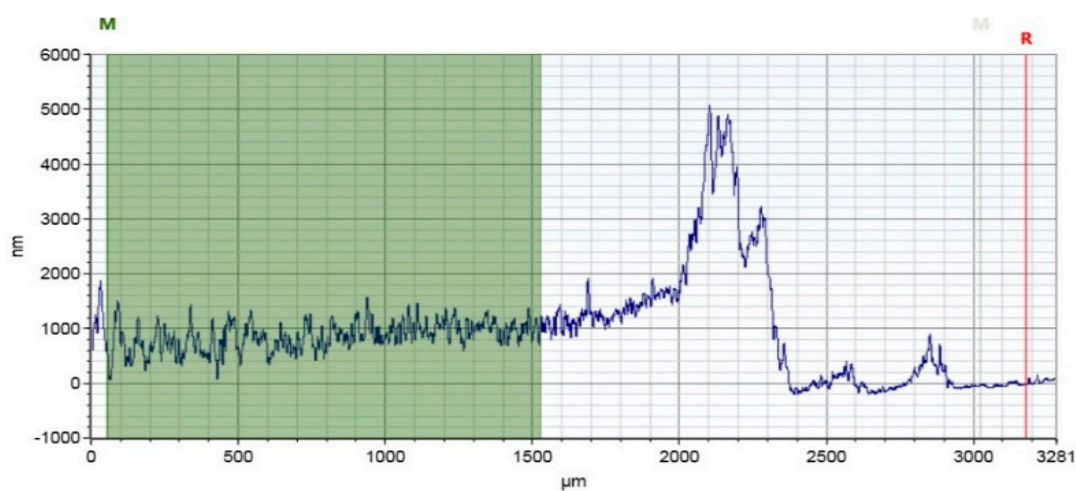


Figure 6. Thickness of of *meso*-WO<sub>3</sub> and modification with CQDs as measured by profilometer.

Table 1. Comparison the photocurrent density of WO<sub>3</sub> based composite materials.

Photoelectrodes	Synthesis method	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (nm)	Photocurrent Density	Light Source	Electrolyte	Ref.
NCQDs/ <i>meso</i> -WO <sub>3</sub>	Impregnation/surfactant self-assembly	105	0.27	5.0	1.45 mA cm <sup>-2</sup> , 1.23 V vs RHE	AM 1.5G, 100 mW cm <sup>-2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	This Work
NCQDs/ <i>meso</i> -WO <sub>3</sub> (450 °C)	Impregnation/surfactant self-assembly	28	0.071	7.5	0.40 mA cm <sup>-2</sup> , 1.23 V vs RHE	AM 1.5G, 100 mW cm <sup>-2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	This Work
<i>Bulk</i> -WO <sub>3</sub>	Impregnation/no surfactant	18	0.038	--	0.25 mA cm <sup>-2</sup> , 1.23 V vs	AM 1.5G, 100 mW cm <sup>-2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	This Work

CQDs/WO <sub>3</sub> nanoplates	immersing /hydrothermal	--	--	--	1.18 mA cm <sup>-2</sup> , 1.23 V vs RHE	simulate d solar light	0.5 M Na <sub>2</sub> SO <sub>4</sub>	S1
CQDs/WO <sub>3</sub> nanoflakes	Seed-mediated solvothermal	--	--	--	1.46 mA cm <sup>-2</sup> , 1.0 V vs. Ag/AgCl	AM 1.5G, 100 mW cm <sup>-2</sup>	1 M H <sub>2</sub> SO <sub>4</sub>	S2
NCDs/WO <sub>3</sub> nanoflakes	Seed-mediated hydrothermal	--	--	--	1.42 mA cm <sup>-2</sup> , 1.0 V vs. SCE	AM 1.5G, 100 mW cm <sup>-2</sup>	1 M H <sub>2</sub> SO <sub>4</sub>	S3
CDots/WO <sub>3</sub> nanorods	Reflux/hydrotherma l	--	--	--	11.5 μA cm <sup>-2</sup>	150 W Xe lamp, (780> λ> 420 nm)	0.1 M Na <sub>2</sub> SO <sub>4</sub>	S4
Z-scheme WO <sub>3</sub> /C <sub>3</sub> N <sub>4</sub>	Electrophoretic deposition	--	--	--	0.82 mA cm <sup>-2</sup> , 1.23 V vs RHE	AM 1.5G, 100 mW cm <sup>-2</sup>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	S5
Nanoporous carbon / WO <sub>3</sub>	Wet chemistry	--	--	--	~ 8 μA cm <sup>-2</sup> , 0.6 V vs. Ag/AgCl	blue LED, 371 nm	0.5 M Na <sub>2</sub> SO <sub>4</sub>	S6
rGO/WO <sub>3</sub>	Thermal treatment	31.7	--	--	~1.1 mA cm <sup>-2</sup> , 1 V vs Ag/AgCl	AM 1.5 G, 100 mW cm <sup>-2</sup>	0.5 M H <sub>2</sub> SO <sub>4</sub>	S7
rGO/Nano-plate-WO <sub>3</sub>	Wet chemistry / thermal decomposition	175.6	--	--	30 μA cm <sup>-2</sup> , 0.6V vs. Ag/AgCl	AM 1.5G, 100 mW cm <sup>-2</sup>	0.1 M Na <sub>2</sub> SO <sub>4</sub>	S8

## References

- Zhao, Z.; Butburee, T.; Peerakiathajohn, P.; Lyu, M.; Wang, S.; Wang, L.; Zheng, H. Carbon Quantum Dots sensitized Vertical WO<sub>3</sub> Nanoplates with Enhanced Photoelectrochemical Properties. *ChemistrySelect* **2016**, *1*, 2772–2777.
- Shi, W.; Zhang, X.; Brillet, J.; Huang, D.; Li, M.; Wang, M.; Shen, Y. Significant enhancement of the photoelectrochemical activity of WO<sub>3</sub> nanoflakes by carbon quantum dots decoration. *Carbon N. Y.* **2016**, *105*, 387–393.
- Kong, W.; Zhang, X.; Liu, S.; Zhou, Y.; Chang, B.; Zhang, S.; Fan, H.; Yang, B. N Doped Carbon Dot Modified WO<sub>3</sub> Nanoflakes for Efficient Photoelectrochemical Water Oxidation. *Adv. Mater. Interfaces* **2019**, *6*, 1–8.
- Zhang, J.; Ma, Y.; Du, Y.; Jiang, H.; Zhou, D.; Dong, S. Carbon nanodots/WO<sub>3</sub> nanorods Z-scheme composites: Remarkably enhanced photocatalytic performance under broad spectrum. *Appl. Catal. B Environ.* **2017**, *209*, 253–264.
- Wang, C.H.; Qin, D.D.; Shan, D.L.; Gu, J.; Yan, Y.; Chen, J.; Wang, Q.H.; He, C.H.; Li, Y.; Quan, J.J.; et al. Assembly of g-C<sub>3</sub>N<sub>4</sub>-based type II and Z-scheme heterojunction anodes with improved charge separation for photoelectrojunction water oxidation. *Phys. Chem. Chem. Phys.* **2017**, *19*, 4507–4515.
- Gomis-Berenguer, A.; Celorrio, V.; Iniesta, J.; Fermin, D.J.; Ania, C.O. Nanoporous carbon/WO<sub>3</sub> anodes for an enhanced water photooxidation. *Carbon N. Y.* **2016**, *108*, 471–479.
- Lin, J.; Hu, P.; Zhang, Y.; Fan, M.; He, Z.; Ngaw, C.K.; Loo, J.S.C.; Liao, D.; Tan, T.T.Y. Understanding the photoelectrochemical properties of a reduced graphene oxide-WO<sub>3</sub> heterojunction photoanode for efficient solar-light-driven overall water splitting. *RSC Adv.* **2013**, *3*, 9330–9336.
- Prabhu, S.; Manikumar, S.; Cindrella, L.; Kwon, O.J. Charge transfer and intrinsic electronic properties of rGO-WO<sub>3</sub> nanostructures for efficient photoelectrochemical and photocatalytic applications. *Mater. Sci. Semicond. Process.* **2018**, *74*, 136–146.



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