

Supplementary Information

Photocatalytic H₂O₂ Production Over Photocatalysts Prepared By Phosphine-protected Au₁₀₁ Nanoclusters on WO₃

Imran Hakim Abd Rahim,¹ Xuan Yin Lee,¹ Abdulrahman S. Alotabi,^{2,3} D. J. Osborn,⁴ Sunita Gautam Adhikari,² Gunther G. Andersson,² Gregory F. Metha,⁴ Rohul H. Adnan^{1}*

1. Nanoscience Lab, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
2. Flinders Institute for NanoScale Science and Technology, Flinders University, Adelaide, SA 5042, Australia
3. Department of Physics, Faculty of Science and Arts in Baljurashi, Albaha University, Baljurashi 65655, Saudi Arabia
4. Department of Chemistry, University of Adelaide, Adelaide, SA 5005, Australia

*Corresponding author: rohuladnan@gmail.com

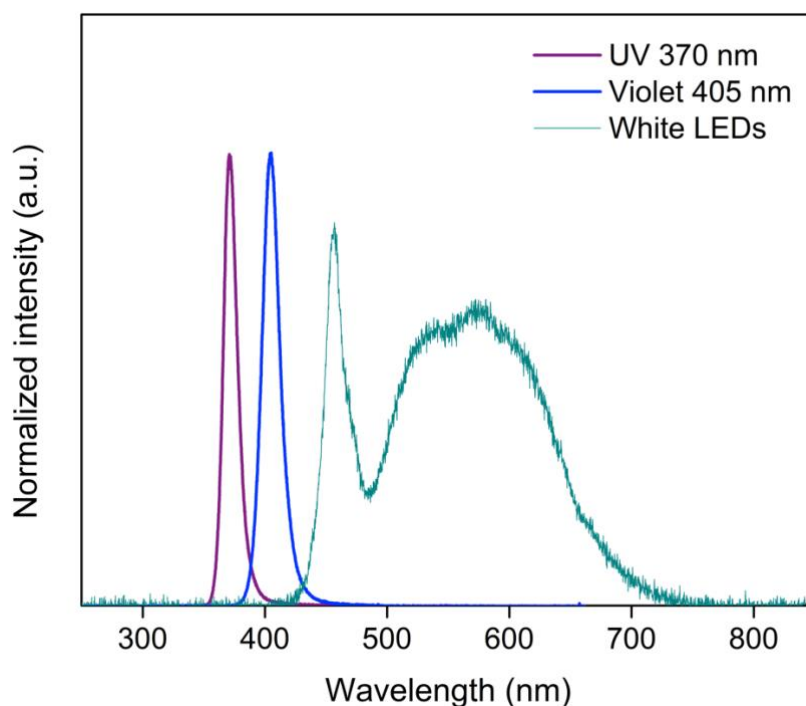


Fig. S1. Emission profile of 370 nm and 405 nm LED lamps used in this work

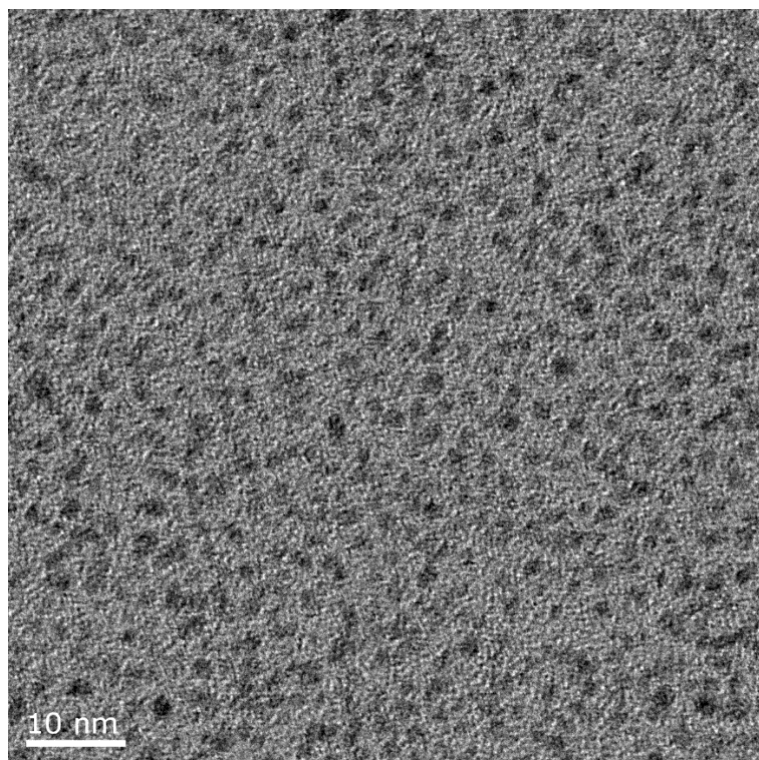


Fig. S2. HRTEM image of pristine Au₁₀₁ clusters dissolved in DCM.

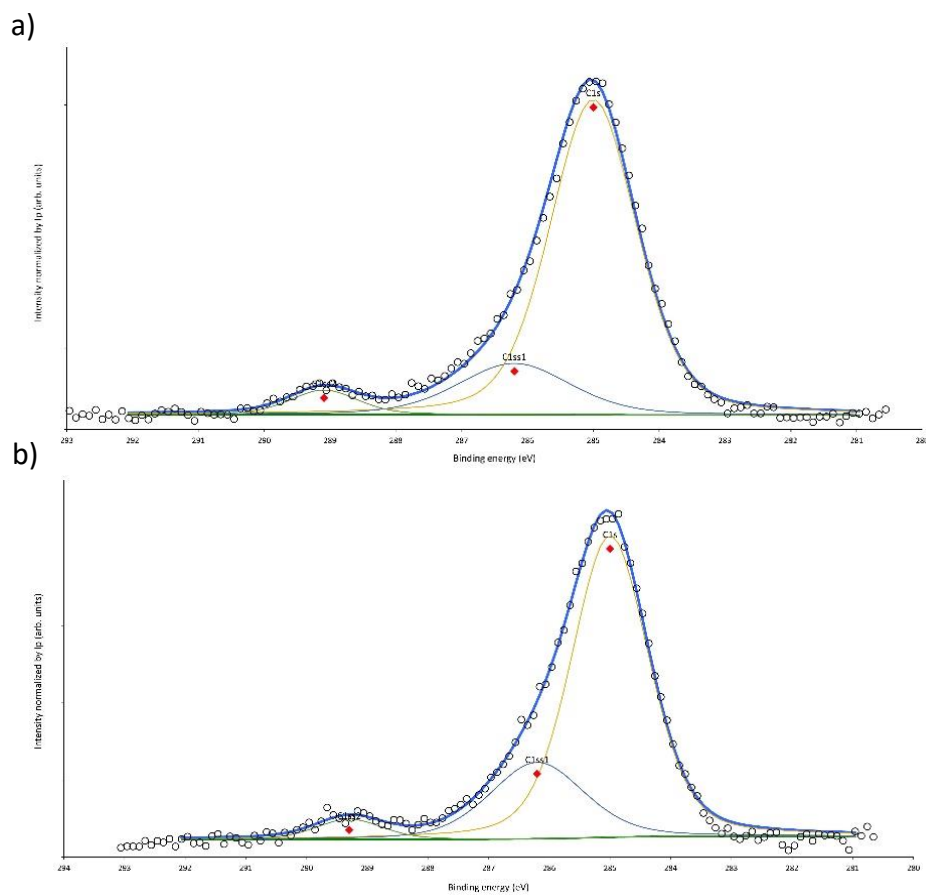


Fig. S3. C1s spectra of a) uncalcined, and b) calcined Au₁₀₁/WO₃ photocatalysts.

Table S1. Peak element and percentage composition of WO₃-based photocatalysts

	Element	Peak position (± 0.2eV)	WO ₃	Au ₁₀₁ /WO ₃	Au ₁₀₁ /WO ₃ calcined
Before photocatalytic reaction	C 1s	P1 - (285)	13.9	20.2	14.3
		P2 - (286.2)	5.5	5.4	6.0
		P3 - (289.2)	1.1	1.3	0.9
	O 1s	P1 - (530.5)	52.5	49.5	56.3
		P2 - (531.5)	11.0	7.2	7.3
	Au 4f _{7/2}	P1 - (84.2)	-	0.36	0.24
	P 2p _{3/2}	P1 - 131.8 (Au-PPh ₃)	-	0.22	-
		P2 - 132.7 (O= PPh ₃)	-	-	0.14
W 4f _{7/2}	P1 (35.7-35.9)	16.0	14.9	14.9	
			Au₁₀₁/WO₃ 1h	Au₁₀₁/WO₃ calc. 1h	Au₁₀₁/WO₃ calc. 3h
After photocatalytic reaction	C 1s	P1 - (285)	9.7	14.1	10.2
		P2 - (286.2)	14.4	6.3	6.9
		P3 - (289.2)	1.4	1.2	1.4
	O 1s	P1 - (530.5)	47.0	51.5	56.6
		P2 - (531.5)	13.9	11.8	10.1
	Au 4f _{7/2}	P1 - (84.2)	0.26	0.17	0.16
	P 2p _{3/2}	P1 - 131.8 (PPh ₃)	0	0	0
		P2 - 132.7 (O= PPh ₃)	0	0	0
W 4f _{7/2}	P1 (35.7-35.9)	13.4	15.0	14.6	

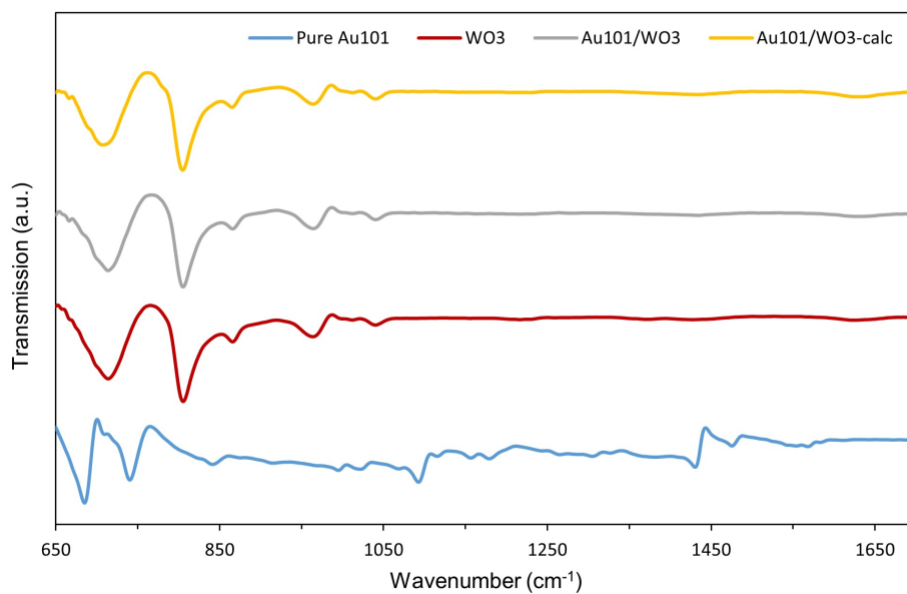


Fig. S4. FTIR spectra of pure Au₁₀₁ clusters, WO₃, uncalcined and calcined Au₁₀₁/WO₃.

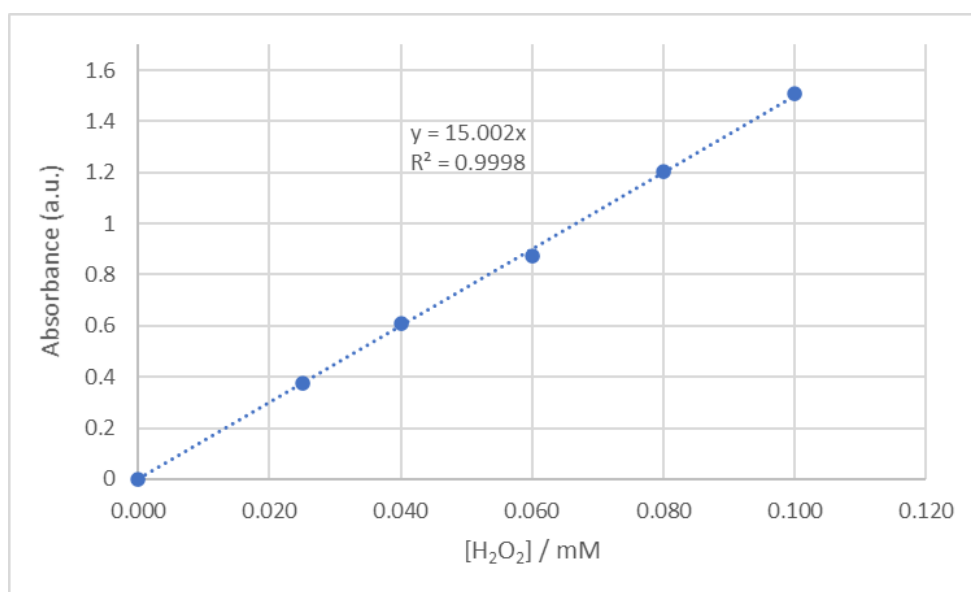


Fig. S5. Calibration curve of standard H₂O₂ solutions monitored at 454 nm by UV-vis spectroscopy.

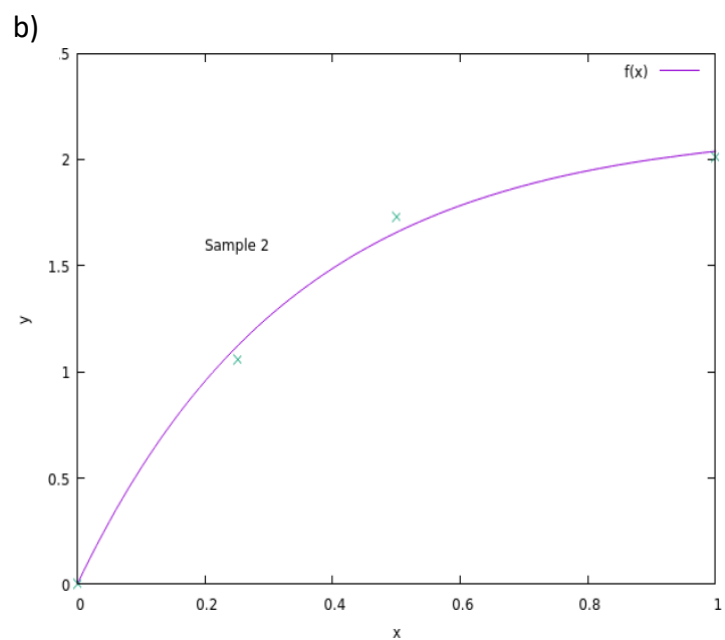
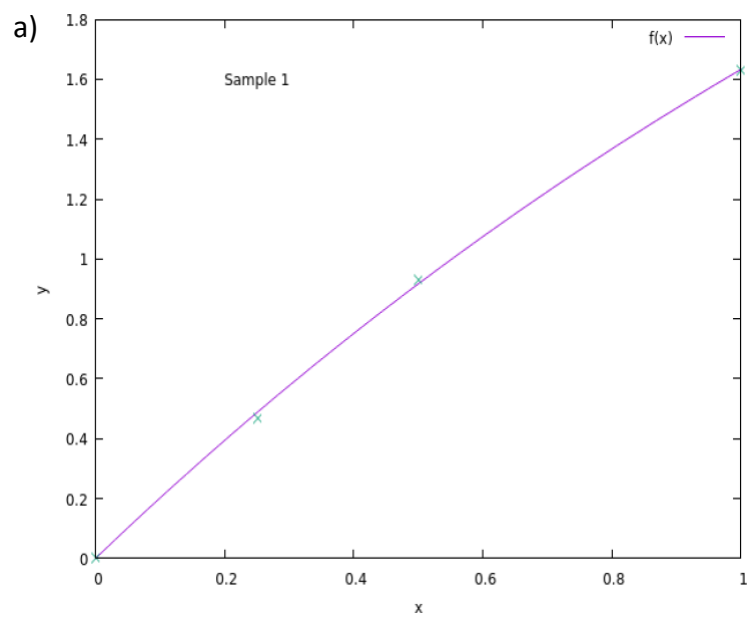


Fig. S6. Curve fitting using GNU Plot software for a) Sample 1 ($\text{Au}_{101}/\text{WO}_3$), and b) Sample 2 ($\text{Au}_{101}/\text{WO}_3$ -calcined)

Table S2. Comparison of photocatalytic activity in H₂O₂ production of Au-based photocatalysts

Photocatalyst	Light source	Reaction mixture	[H ₂ O ₂] (mM)	Time (h)	Ref.
0.25% Au ₁₀₁ /WO ₃ calcined	365 nm	4% EtOH/H ₂ O	2.05	1	This work
		water	0.31	0.5	
0.25% Au/TiO ₂	>300 nm	4% EtOH/H ₂ O	~7	24	1
0.88% Au/TiO ₂ - CO ₃ ²⁻	>430 nm	4% HCOOH/H ₂ O	1 mM	1	2
0.61% Au/TiO ₂	>320 nm	4% MeOH/H ₂ O, pH 9	1.31	10	3
0.34% Au/WO ₃	>420 nm	4% MeOH/H ₂ O	0.54	5	4
		water	0.18	5	

References

1. Teranishi, M.; Naya, S.; Tada, H. In Situ Liquid Phase Synthesis of Hydrogen Peroxide from Molecular Oxygen Using Gold Nanoparticle-Loaded Titanium(IV) Dioxide Photocatalyst. *J. Am. Chem. Soc.* 2010, 132 (23), 7850–7851.
2. Naya, S.; Niwa, T.; Kume, T.; Tada, H. Visible-Light-Induced Electron Transport from Small to Large Nanoparticles in Bimodal Gold Nanoparticle-Loaded Titanium(IV) Oxide. *Angewandte Chemie International Edition* 2014, 53 (28), 7305–7309.
3. Xiong, X.; Zhang, X.; Liu, S.; Zhao, J.; Xu, Y. Sustained Production of H₂O₂ in Alkaline Water Solution Using Borate and Phosphate-Modified Au/TiO₂ Photocatalysts. *Photochemical & Photobiological Sciences* 2018, 17 (8), 1018–1022.
4. Wang, Y.; Wang, Y.; Zhao, J.; Chen, M.; Huang, X.; Xu, Y. Efficient Production of H₂O₂ on Au/WO₃ under Visible Light and the Influencing Factors. *Applied Catalysis B: Environmental* 2021, 284, 119691