Supplementary Information

Photoreduction Route for Cu_2O/TiO_2 Nanotubes Junction for Enhanced Photocatalytic Activity

Van Viet Pham, [a] * *Dai Phat Bui,* [a] *Hong Huy Tran,* [a] *Minh Thi Cao,* [b] *Tri Khoa Nguyen,* [c] *Yong Soo Kim,* [c] * *and Van Hieu Le* [a]

[a]Nanomaterials for Environmental Applications Laboratory, Faculty of Materials Science and Technology, University of Science, VNU-HCMC, Ho Chi Minh City, 700000, Vietnam

[b]CM Thi Laboratory, Ho Chi Minh City University of Technology (HUTECH), Ho Chi Minh City, 700000, Vietnam

[c]Department of Physics and Energy Harvest-Storage Research Center, University of Ulsan, Ulsan 44610, South Korea

*Corresponding authors: pvviet@hcmus.edu.vn (V. V. Pham), yskim2@ulsan.ac.kr (Y. S. Kim)

Summary: There are 08 pages including 04 figures and 01 table

Table Captions

Table S1. The evaluated oxygen contents of materials

Figure Captions

Figure S1. Phenol photodegradation ability of the TNTs and Cu_2O/TNTs under visible light

Figure S2. Photocatalytic stability of Cu_2O/TNTs

Figure S3. Color of TNTs (a), Cu_2O/TNTs under ambient condition (b), and Cu_2O/TNTs at 150 ^oC (c) and 300 ^oC (d) under hydrogen gas environment

Figure S4. Cu 2*p* HRXPS of Cu_2O/TNTs at different annealing temperature under hydrogen gas environment

Experimental

The photocatalytic activity of Cu_2O/TNTs for the phenol photodegradation under visible light can be described as follows:

Initially, 120 mL of phenol solution with an initial concentration of 6.25×10^{-5} (mol.L^{-1}) and 0.04 g of catalyst were stirred magnetically for 60 min to reach the adsorption/desorption equilibrium in the dark. Secondly, the mixture was then irradiated to a simulated Xenon lamp (ABET 230 V, 150 W). The visible light was separated by an UV-cut optical filter ($\lambda > 420$ nm). The absorption spectra of phenol was recorded at regular intervals (30 min) of irradiation. The photocatalytic efficiency (η) was calculated by using the following formula, $\eta[\%] = \frac{C_0 - C_t}{C_0} \times 100$, where C_0 and C_t is the absorption intensity of the phenol solution at 270 nm of wavelength after the adsorption/desorption reached on the equilibrium and at time t, respectively. The stability of the photocatalytic activity of Cu_2O/TNTs was tested by the measurement of the recycle for 5 times.

Table S1. The evaluated oxygen contents of materials

Sample	Binding energy (eV)		The atomic number ratio of O_L, Ti and Cu	Percentage of O_L (%)	Percentage of O_{-OH} (%)	Evaluated percentage of oxygen vacancies (%)
	O 1s (O_L)	O 1s (O_{-OH})				
TNTs	530.16	532.56	100:55.66:0	55.95	44.05	11.32
Cu_2O/TNTs	530.15	532.66	100:56.56:2.56	39.50	60.50	14.40

The evaluated oxygen contents of TNTs and Cu_2O/TNTs were determined based on the XPS results of O 1*s*, Ti 2*p*, and Cu 2*p* respectively. The estimated results tabulated in **Table S1** show that the percentage of oxygen vacancies increased after the formation of the heterojunction structure of Cu_2O and TNTs leading to the increase of the surface hydroxyl oxygen.[1]

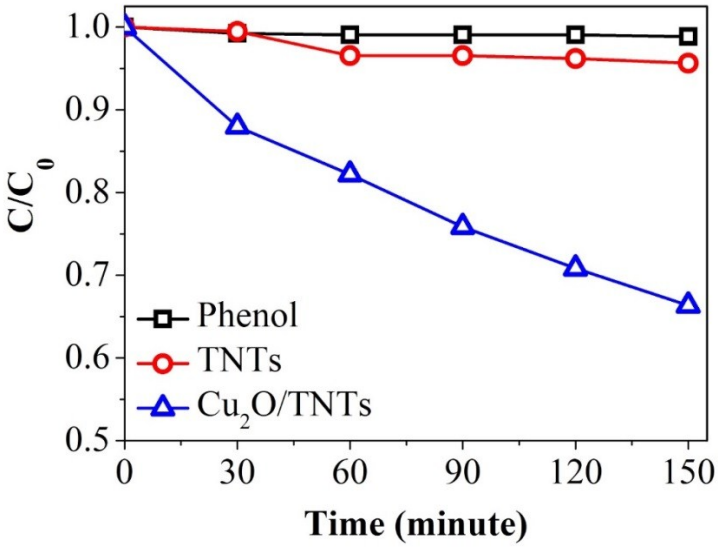

Figure S1. Phenol photodegradation ability of the TNTs and Cu_2O/TNTs under visible light

Moreover, phenol solution is well known as a hard remediation and no self-sensitization by visible light.[2] Therefore, phenol is widely used as an organic pollutant indicator. **Figure S1** shows the phenol photodegradation over TNTs and Cu_2O/TNTs for 150 min under visible

light. The result shows that the TNTs have low photocatalytic performance in this case due to its large band gap and poor photoactive ability in visible light. Meanwhile, it is clear that, the Cu_2O/TNTs heterojunction is much more active, which confirms that the formation of heterojunction can strongly enhance the visible-light activity of the TNT. Generally, the stability Cu_2O semiconductor is poor; however, the Cu_2O/TNTs heterojunction exhibits good stability after 5 times of recycling test, as shown in **Figure S2.**

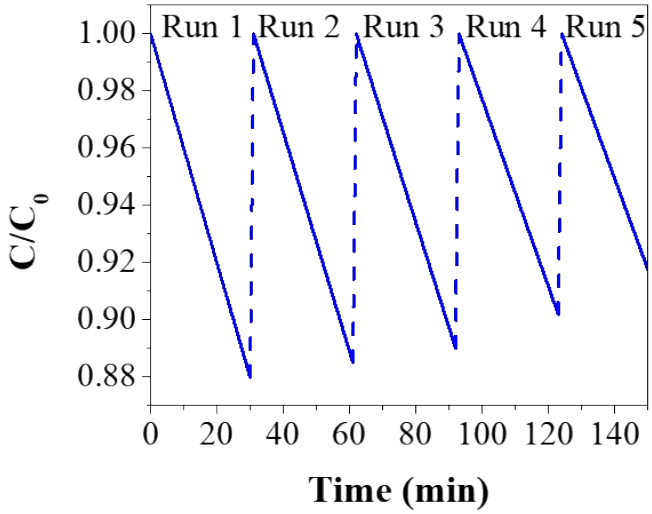

Figure S2. Photocatalytic stability of Cu_2O/TNTs

Additionally, the structural stability of Cu_2O was further tested by annealing it in hydrogen environment in the temperature of 150 ^oC and 300 ^oC. The experiment was conducted in a quartz tube with 5sccm of hydrogen flow rate for 2 hours. Initially, the Cu_2O/TNTs has a light yellow color (**Figure S3 (b)**) which then slightly change upon the reduction by hydrogen at 150 ^oC, as shown in **Figure S3 (c).** The color of the powder was changed to black at 300 ^oC (**Figure S3 (d)**). This result indicates the presence of CuO.[3]

Figure S3. Color of TNTs (a), Cu_2O/TNTs under ambient condition (b), Cu_2O/TNTs at 150 ^oC (c) and 300 ^oC (d) under hydrogen gas environment

Moreover, Figure S4 shows that the BE peaks of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ for the sample annealed at 150 ^oC in hydrogen are similar to those of as-prepared sample. Both position and the separation between the peaks unchanged. However, the same two peaks for the sample annealed at 300 ^oC in hydrogen gas strongly undergo a blue shift. The position of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks for the sample annealed at 300 ^oC appeared at 952.7 eV and 933.2 eV, respectively. This observation indicates the presence of Cu^{2+} state in the sample.[4-6] These HRXPS results are well consistent with the result of the color change of samples in the Figure S3. In conclusion, although hyrogen gas has a high reductive property but the Cu_2O/TNTs still remain the stable ability in this condition. Therefore, it conclusive demonstrates that the stability of Cu_2O/TNTs is good.

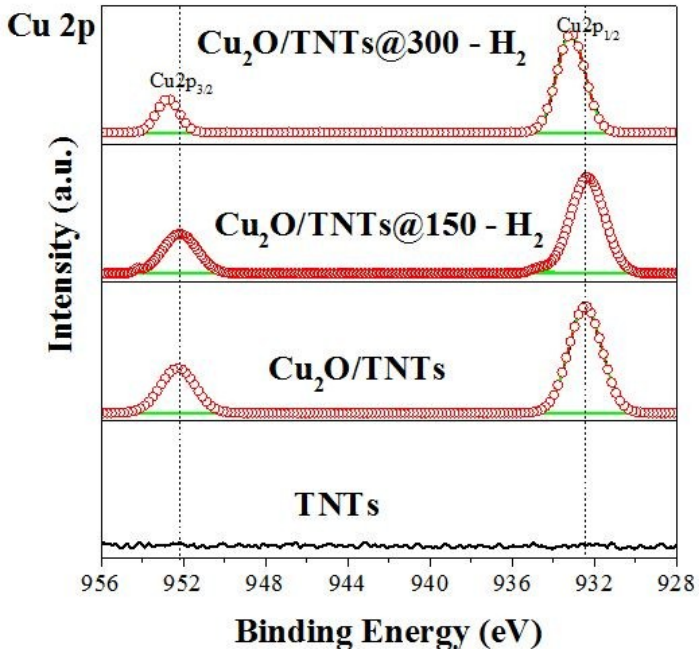

Figure S4. Cu 2*p* HRXPS of Cu_2O/TNTs at different annealing temperature under hydrogen gas environment

References

1. B. Xin, D. Ding, Y. Gao, X. Jin, H. Fu and P. Wang, Applied Surface Science, 2009, **255**, 5896-5901.
2. F.-M. Zhao, L. Pan, S. Wang, Q. Deng, J.-J. Zou, L. Wang and X. Zhang, Applied Surface Science, 2014, **317**, 833-838.
3. W. W. Zhao, Z. Liu, S. Shan, W. W. Zhang, J. Wang, Z. Y. Ma, J. J. Xu and H. Y. Chen, Scientific Reports, 2014, **4**, 4426.
4. H. Tian, X. L. Zhang, J. Scott, C. Ng and R. Amal, Journal of Materials Chemistry A, 2014, **2**, 6432-6438.
5. J. Yu, Y. Hai and M. Jaroniec, Journal of Colloid and Interface Science, 2011, **357**, 223-228.

6. B. Zhu, Q. Guo, X. Huang, S. Wang, S. Zhang, S. Wu and W. Huang, Journal of Molecular Catalysis A: Chemical, 2006, **249**, 211-217.