

Electronic Supplementary Information

Solar denitrification coupled with *in situ* water splitting

Shinbi Lee,[†] Suhyeon Kim,[‡] Cheolwoo Park,^{§,||} Wooyul Kim,[§] Sunmin Ryu,[‡] and Wonyong Choi^{,†}*

[†]Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 37673, Korea

[‡]Department of Chemistry, Pohang University of Science and Technology (POSTECH), Pohang 37673, Korea

[§]Department of Chemical and Biological Engineering, College of Engineering, Sookmyung Women's University, Seoul 04310, Korea

^{||} Department of Energy Science, Sungkyunkwan University, Suwon 16419, Korea

*Corresponding author. E-mail: wchoi@postech.edu ; phone: +82-54-279-2283 (W.C.)

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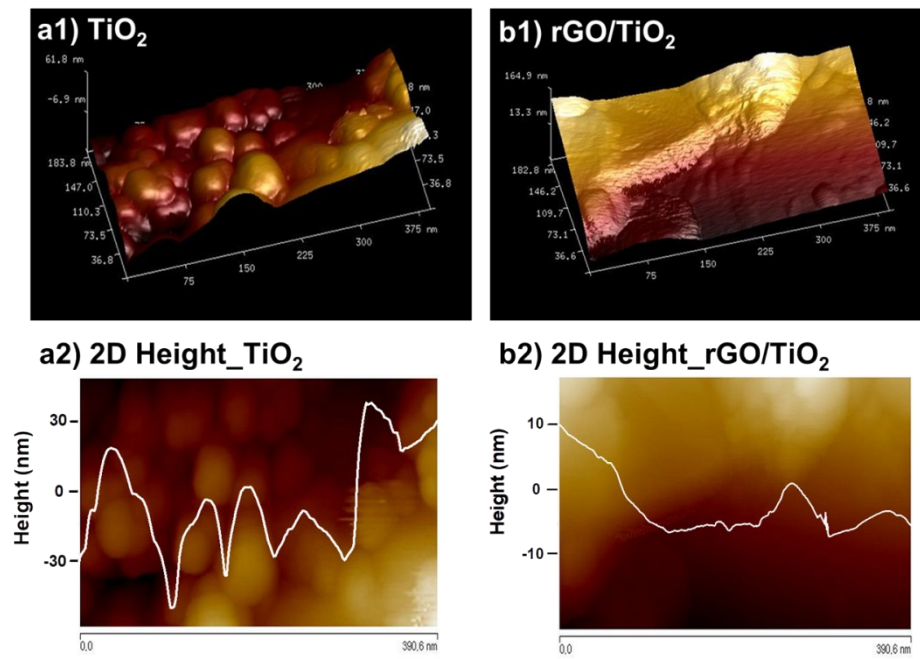


Fig. S1 Tapping-mode AFM 3D-images (left) and the height cross-sectional profiles (right) of (a1-2) bare TiO_2 and (b1-2) rGO/TiO_2 .

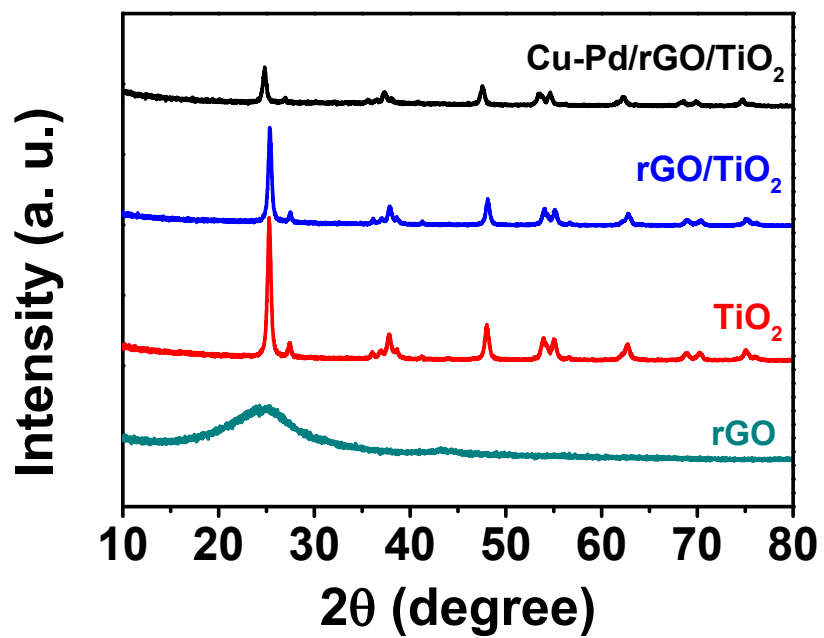


Fig. S2 X-ray diffraction patterns (XRD) of rGO, bare TiO₂, rGO/TiO₂ and Cu-Pd/rGO/TiO₂.

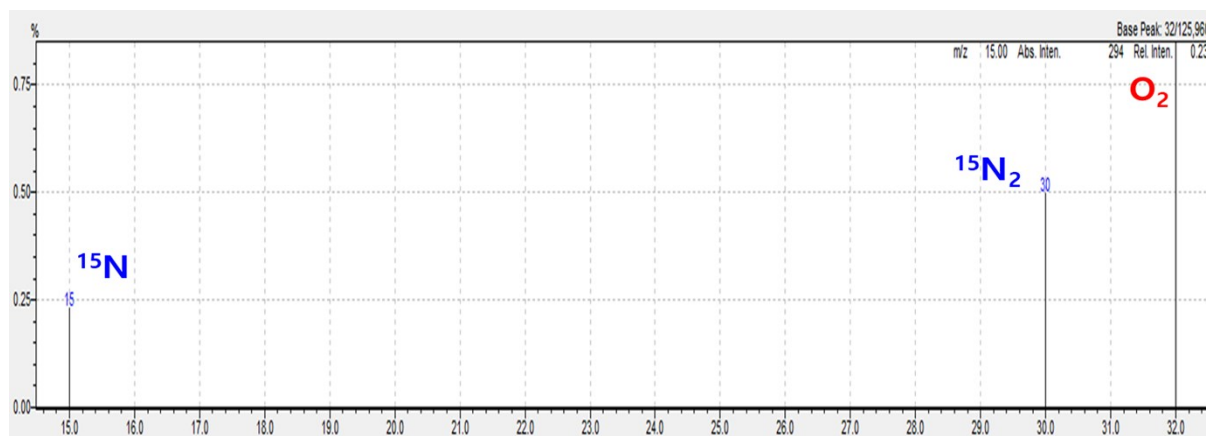


Fig. S3 The gas chromatography-mass spectrometry (GC-MS) spectrum of the gas product generated from $^{15}\text{NO}_3^-$ photoreduction on Cu-Pd/rGO/TiO₂. Experimental conditions: [catalyst] = 1.5 g/L, $[\text{NO}_3^-]_0 = 100 \mu\text{M}$, the content of rGO, Cu, and Pd: 1 wt% each, pH = 5.3 (not adjusted), initially Ar-purged (de-aerated suspension) and $\lambda > 320 \text{ nm}$ irradiation.

$^{15}\text{N}_2$ and O_2 were generated as final gas products of the photoreaction and ^{15}N was detected as a result of ionization of $^{15}\text{N}_2$.

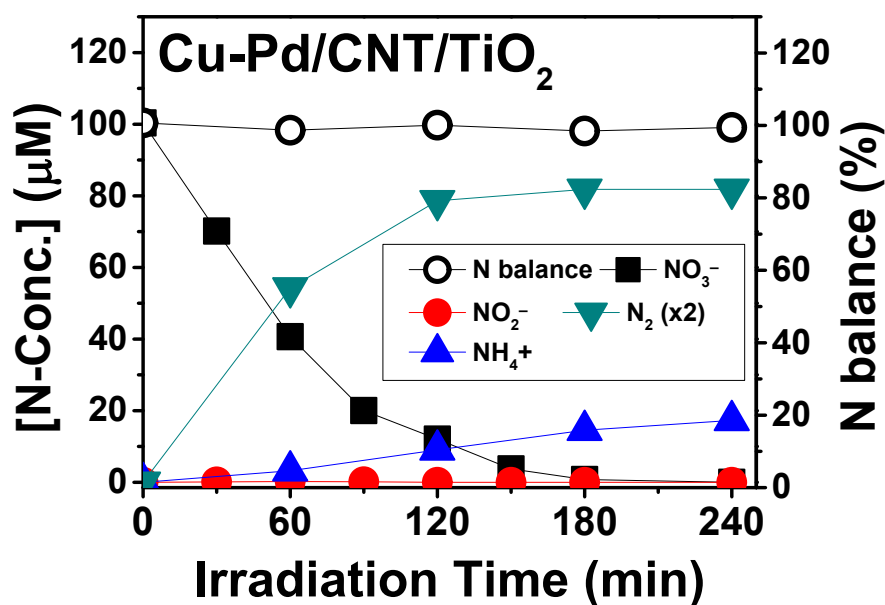


Fig. S4 The time profiles of nitrate removal and N balance (%) along with the accompanying production of NO_2^- , NH_4^+ , and N_2 gas in the headspace in the suspension of Cu-Pd/CNT/TiO₂. The concentration of N_2 dissolved in the solution should be negligibly small (< 2% of the N_2 gas in the headspace, smaller than the experimental uncertainty of N_2 gas amount) according to the Henry's law constant of N_2 and was neglected in the N balance calculation. Experimental conditions: [catalyst] = 1.5 g/L, the content of CNT, Cu, and Pd: 1 wt% each, $[\text{NO}_3^-]_0 = 100 \mu\text{M}$, pH = 5.3-6.0 (not adjusted), initially Ar-purged (de-aerated suspension), and $\lambda > 320 \text{ nm}$ irradiation.

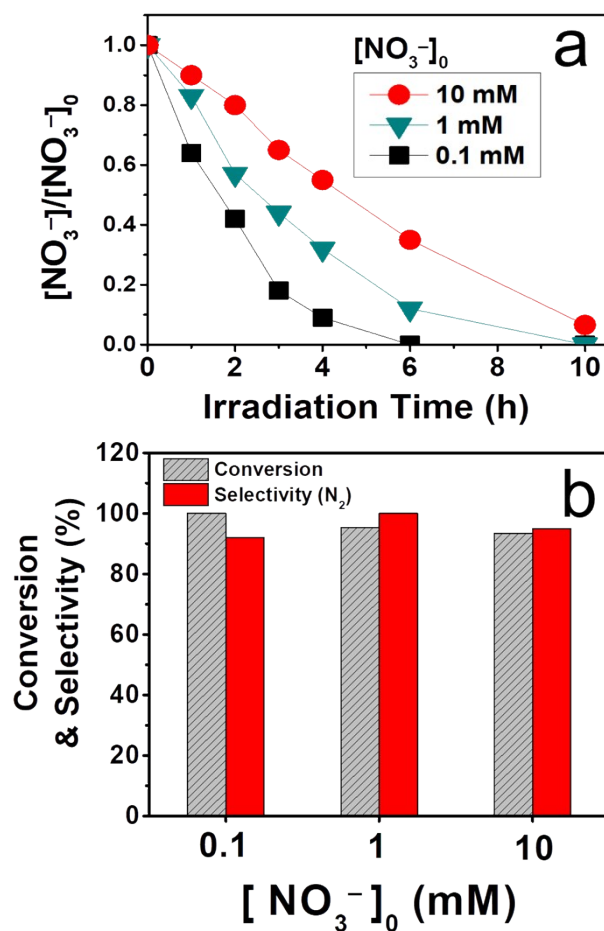


Fig. S5 (a) The time profiles of photocatalytic removal of nitrate in the suspension of Cu-Pd/rGO/TiO₂ with different initial concentrations of nitrate. (b) The nitrate conversion and the selectivity to N₂ after 10 h photoreaction in Cu-Pd/rGO/TiO₂ suspension with different initial concentrations of nitrate. Experimental conditions were [catalyst] = 1.5 g/L, rGO content: 1 wt%, Cu content: 1 wt%, Pd content: 1 wt%, initially Ar-purged and $\lambda > 320$ nm irradiation.

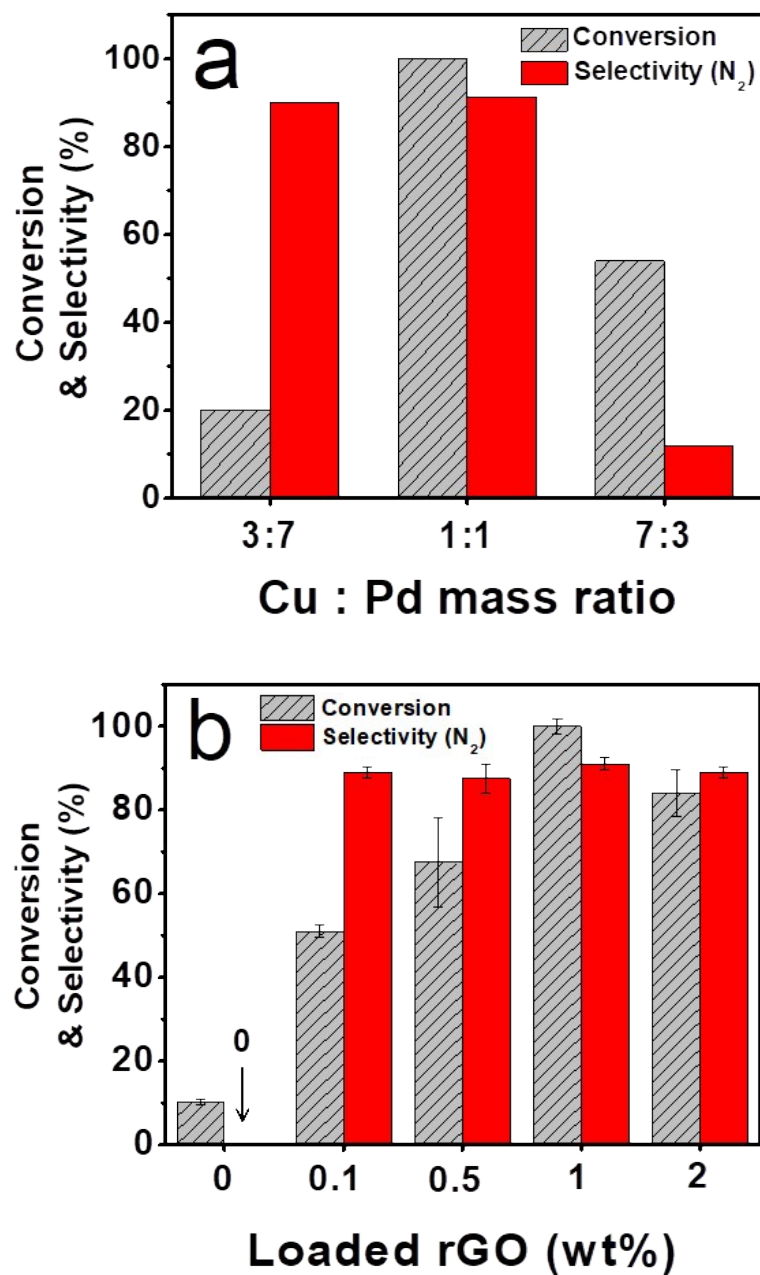


Fig. S6 Photocatalytic nitrate conversion efficiency and the selectivity to N₂ with varying (a) the bimetal ratio and (b) the content of rGO. Experimental conditions: [catalyst] = 1.5 g/L, rGO content: 1 wt% for (a), Cu and Pd content: 1 wt% each for (b), [NO₃⁻]₀ = 100 μM, pH = 5.3-6.4 (not adjusted), initially Ar-purged (de-aerated suspension), and λ > 320 nm irradiation. The total weight percent of the loaded metals (Cu+Pd) was maintained at 2 wt% for (a).

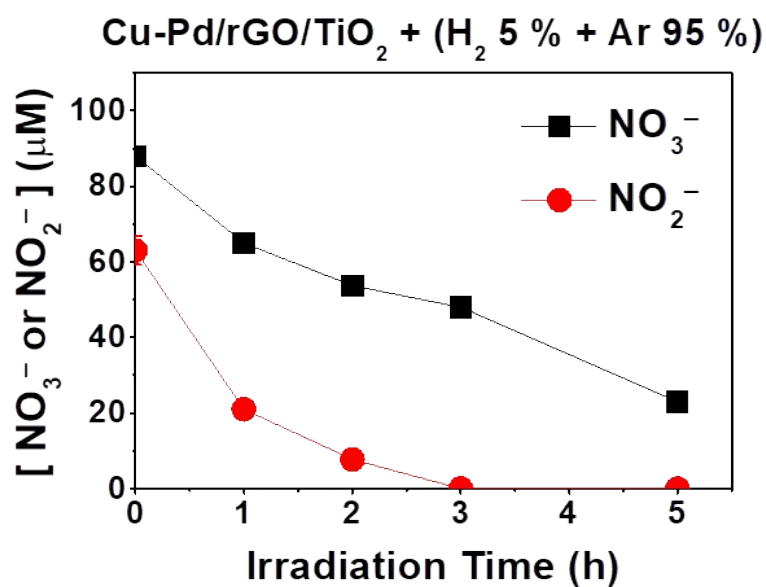


Fig. S7 Time profiles of the removal of nitrate and nitrite on Cu-Pd/rGO/TiO₂ under dark condition. Experimental conditions: [catalyst] = 1.5 g/L, the content of rGO, Cu, and Pd: 1 wt% each, [NO₃⁻]₀ = [NO₂⁻]₀ = 100 μM, pH = 5.3-5.8 (not adjusted), continuously gas-purged.

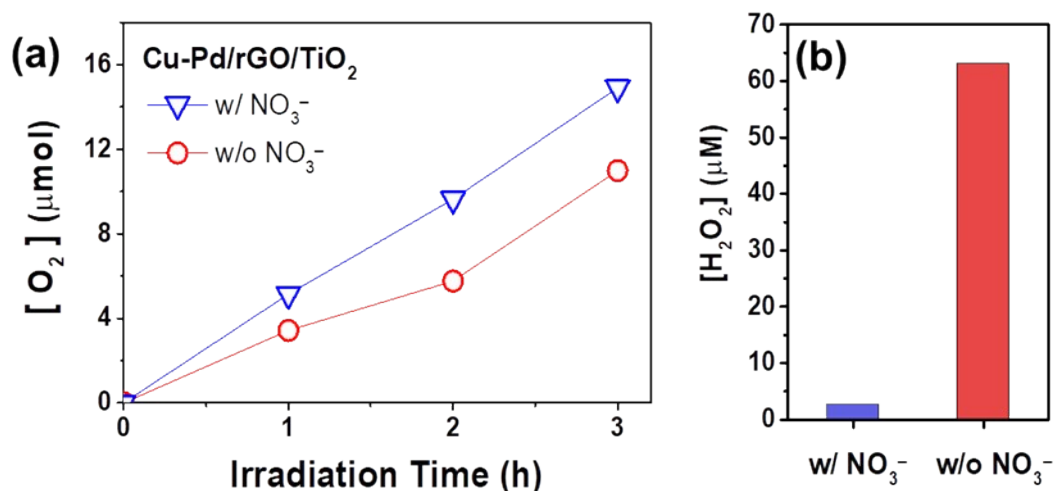


Fig. S8 Photogeneration of (a) O_2 and (b) H_2O_2 on Cu-Pd/rGO/TiO₂ in the presence or absence of nitrate. Experimental conditions: [catalyst] = 1.5 g/L, the content of rGO, Cu, and Pd: 1 wt% each, $[NO_3^-]_0 = 100 \mu\text{M}$, pH = 5.3-6.0 (not adjusted), initially Ar-purged, $\lambda > 320$ nm irradiation. The concentration of H_2O_2 was estimated using DPD method.

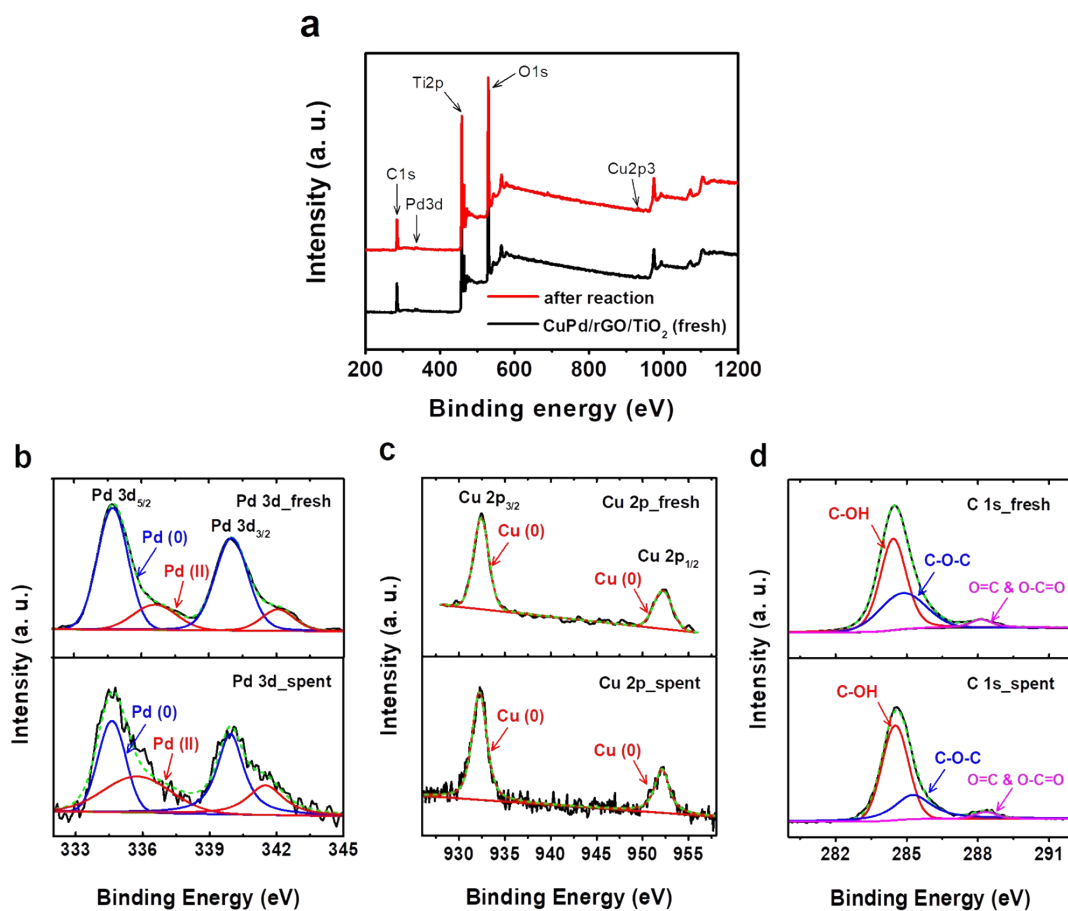


Fig. S9 (a) The survey X-ray photoelectron spectra (XPS) for Cu-Pd/rGO/TiO₂ before and after 20 repeated photoreactions. XPS of (b) Pd 3d bands, (c) Cu 2p bands and (d) C 1s bands for Cu-Pd/rGO/TiO₂ comparing before and after 20 repeated photoreactions. Experimental conditions: [catalyst] = 1.5 g/L, [NO₃⁻]₀ = 10 mM, the content of rGO, Cu, and Pd: 1 wt% each, pH = 5.3-6.0 (not adjusted), initially Ar-purged (de-aerated suspension), and $\lambda > 320$ nm irradiation.