Electronic Supplementary Information

Visible-light sensitive Cu(II)-TiO₂ with sustained anti-viral activity for efficient indoor environment remediation

Min Liu,^b Kayano Sunada, ^b Kazuhito Hashimoto, *, ^{b,c} Masahiro Miyauchi, *, ^{a,d}

^aDepartment of Metallurgy and Ceramics Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan.

^bResearch Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan.

^cGraduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

^dJapan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan.

Samples	Cu(II)-TiO ₂ (950-HCl)						
Grafting pH value	2	4	7	10	12	14	
Initial amount of Cu(II) (wt%)	0.1	0.1	0.1	0.1	0.1	0.1	
Measured Cu(II) (wt%)	0.002	0.006	0.011	0.018	0.089	0.101	

Table S1. ICP measurement of Cu(II)-TiO₂ (950-HCl) with different pH value.

Table S2. ICP measurement of Cu(II)-TiO₂ (950-HCl-12) with different initial amount of Cu(II).

Samples	Cu(II)-TiO ₂ (with acid treatment)						
Initial amount of Cu(II) (wt%)	0.05	0.1	0.25	0.5			
Measured Cu(II) (wt%)	0.037	0.089	0.203	0.476			



Figure S1. TG-DTA curves of TiO₂ powders.



Figure S2. SEM images of TiO_2 samples obtained at different temperature.



Figure S3. Images of TiO_2 samples obtained at different temperatures.



Figure S4. XPS spectra of bare and Cu(II) nanoclusters grafted TiO₂, which was annealed at 950 °C for 3h.



Figure S5. UV-Vis spectra of bare TiO₂ and Cu(II)-TiO₂, which was annealed at 950 °C for 3h.



Figure S6. The CO₂ generation curve over Cu(II)-TiO₂ (950) sample under visible light irradiation. The CO₂ generation rate (R_{CO2}) was obtained from the slope of the CO₂ generation curve between the irradiation time of ca. 0 to 60 h.

The calculation of quantum efficiency (QE) was conducted using the same procedure reported in literature (1).

Take Cu(II)-TiO₂ (950) sample for example. Under the visible light irradiation, the wavelength of visible light is from 420 to 530 nm, and the light intensity is 1 mW/cm². The irradiating area is 5.5 cm². Therefore, the absorption rate of incident photons (R_p^a) was determined to be 9.78×10^{14} quanta · sec⁻¹ using the following equation: $R_p^a = \int_{400}^{530} S \times \alpha \times I$ (*S* is the area of the sample, α is the light absorption and *I* is the light intensity at each wavelength). As for CO₂ generation, assuming that the reaction from IPA to CO₂ is proceeded: $C_3H_8O+5H_2O+18h^+\rightarrow 3CO_2+18H^+$, that is, six photons are required to produce one CO₂ molecule. The CO₂ generation rate (R_{CO2}) was obtained from the slope of the CO₂ generation curve in Figure S6. As shown in Figure S10, R_{CO2} was determined to be 0.13 µmol·h⁻¹. Thus the QE for CO₂ generations were calculated using the following equation:

 $QE = 6 \times CO_2$ generation rate/absorption rate of incident photon

 $=6 \times (1.3 \times 10^{-1} \times 10^{-6}/3.6 \times 10^{3})$ mol·sec-1×

 6.0×10^{23} quanta · mol⁻¹/9.78 × 10¹⁴ quanta · sec⁻¹

 $= 13.2 \times 10^{-1} (13.2\%).$



Figure S7. a) Na 1s and b) Ca 2p core-level spectra of raw TiO₂, 950 °C annealed TiO₂ and HCl treated TiO₂ (950) samples.



Figure S8. SEM images of TiO₂ (950) samples before and after acid treatment.



Figure S9. Cu 2p core-level spectra of Cu(II)-TiO₂ (950-HCl) samples obtained from different pH values.



Figure S10. Comparative studies of CO_2 generation over Cu(II)-Ti O_2 (950-HCl) with different initial amount of Cu(II) under the same conditions.



Figure S11. Photos for CuCl₂ hydrolyzed products at different pH value.



Figure S12. XRD pattern of CuCl₂ hydrolyzed products obtained at pH 14. The result shows that the products are crystallized CuO.



Figure S13. a) Ti 2p and b) Cu 2p core-level spectra of Cu(II)-TiO₂ (950-HCl-12).



Figure S14. Inactivation of $Q\beta$ bacteriophage by Cu(II)-TiO₂ (950-HCl-12) under dark after black light and visible-light irradiation.

References

1 H. G. Yu, H. Irie, Y. Shimodaira, Y. Hosogi, Y. Kuroda, M. Miyauchi, K. Hashimoto, J. *Phys. Chem. C* 2010, **114**, 16481–16487.