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Solar photochemical-thermal water splitting at 140 °C with Cu-loaded TiO_2

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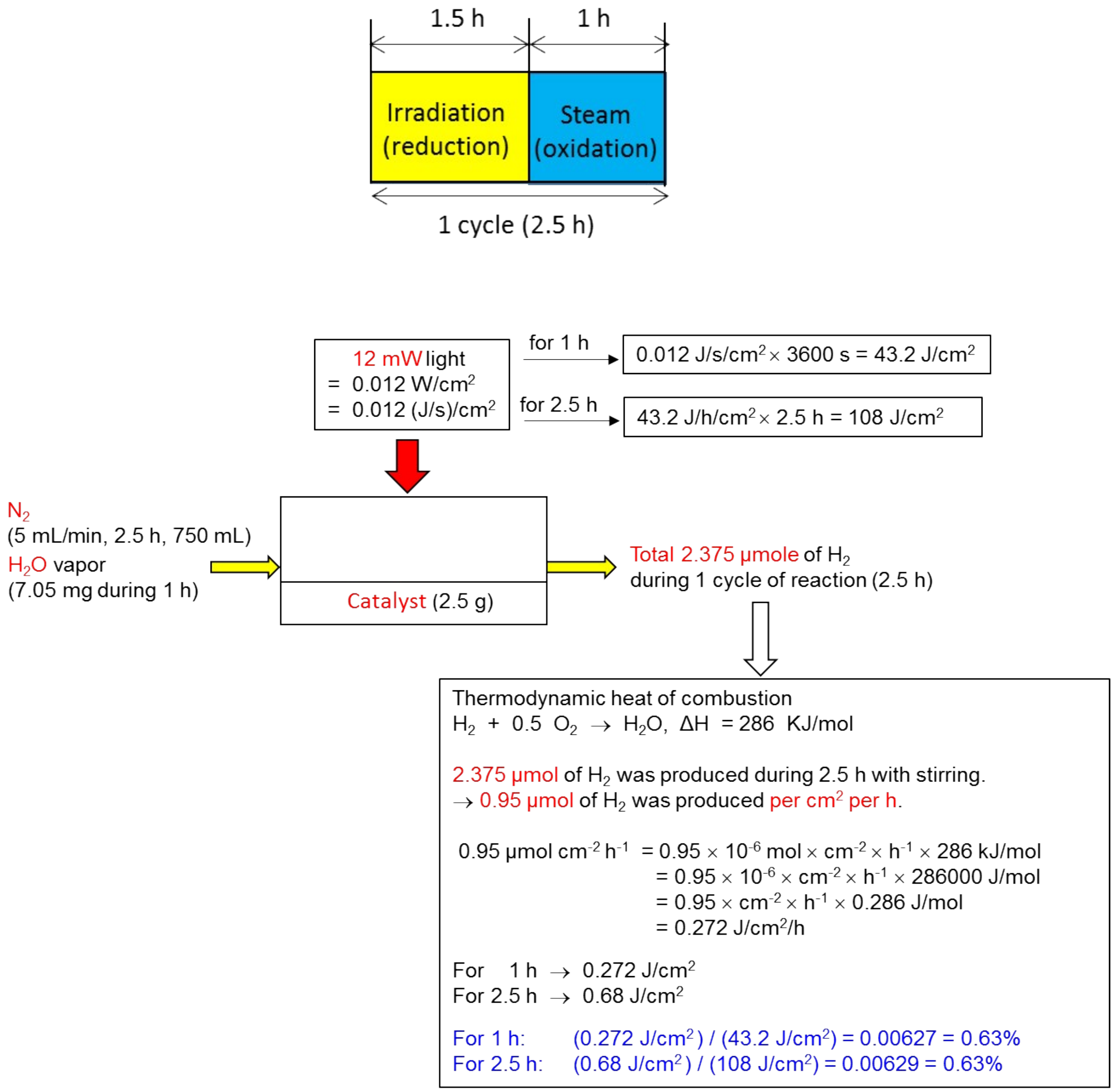

Figure S1. Illustration and bases for calculation of solar-to-H_2 conversion efficiency.

Total solar energy input

0.12 Sun = 12 mW/cm^2; (1 mW = 1 mJ/s = 3.6 J/h)

12 mW = 43.2 J/h

- Total area of irradiation = 6 cm^2

During 1 h period of steam treatment all the energy can be converted to heat energy

$\Rightarrow$ Total energy input per h = 43.2 $J/h/cm^2 \times 1\ h \times 6\ cm^2$ = 259.2 J

- During irradiation for 1.5 h, 22.2% of energy is absorbed by Cu/TiO_2 (See Figure 6C)

$\rightarrow$ 77.8% of energy can be converted to heat energy

$\rightarrow$ 259.2 J x $h^{-1} \times 1.5\ h \times 0.778$ = 302.5 J

Total energy which can be converted to heat energy (during 2.5 h)

= 259.2 + 302.5 = **561.7 J**

Materials and Heat capacity

Cu/TiO_2 = 2.5 g, Heat Capacity = 0.711 J/(g.K)

N_2 = 750 mL, Heat capacity = 1.041 J/(g.K)

H_2O vapor = 7.05 mg, Heat capacity = ~1.88 J/(g.K)

Total Energy consumption for Heating to 140 ^{o}C

Cu/TiO_2 = 2.5 g $\rightarrow$ 2.5 g x 0.711 J/(g.K) x 115 K = 204.4 (J)

N_2 = 750 mL $\rightarrow$ 0.9375 g x 1.041 J/(gK) x 115 K = 112.3 (J)

H_2O vapor = 7.05 mg $\rightarrow$ 0.007 g x 1.88 J/(gK) x 115 K = 1.5 (J)

Total amount of energy consumption = 318.2 (J)

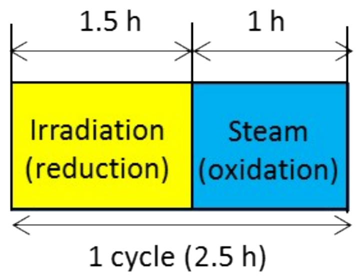

Figure S2. Illustration and bases for calculation of total solar energy input and total energy consumption.

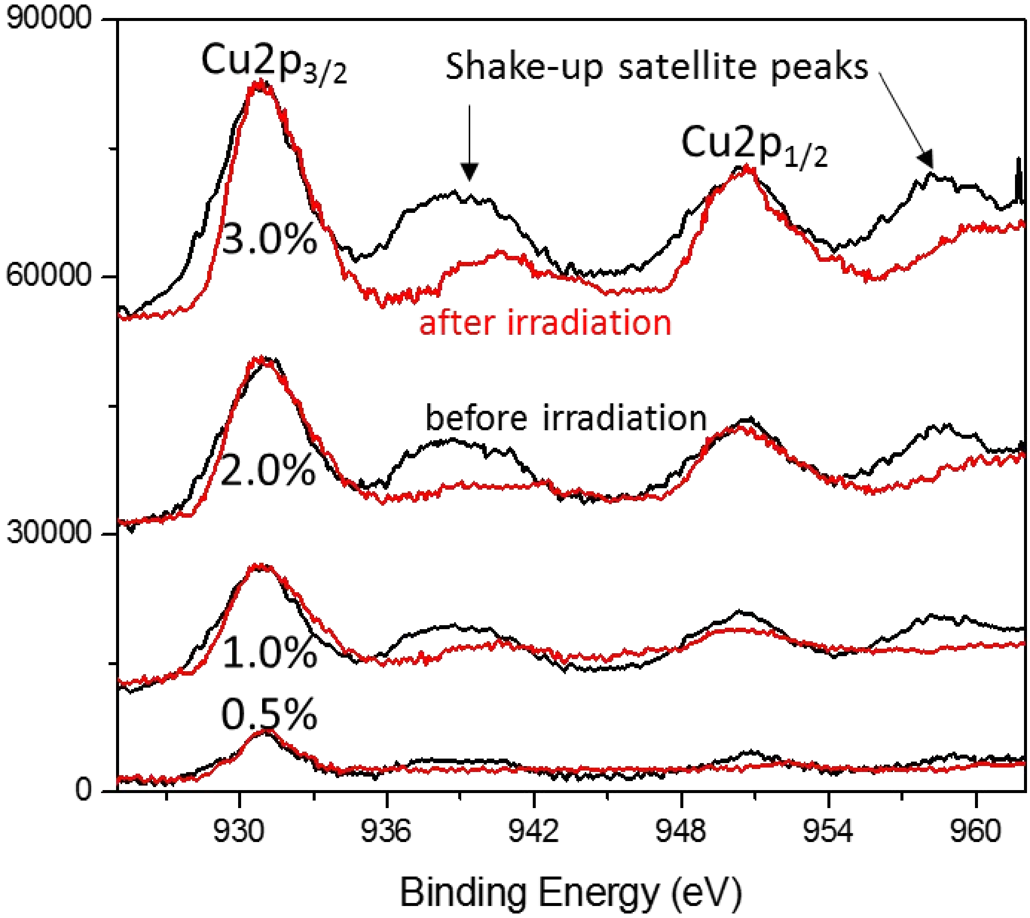

Figure S3. XPS spectra of Cu(n)/TiO_2 with n = 0.5, 1.0, 2.0, and 3.0 in the region for $Cu2p_{3/2}$ and $Cu2p_{1/2}$ before (black) and after (red) irradiation with solar simulated light. The appearance of shake-up satellite peaks due to the ligand (O^{2-}) to metal (a partially filled d orbital of Cu^{2+}) at ~938 and ~958.5 eV shows that the initial oxidation state of Cu species in Cu(n)/TiO_2 is +2 and the decrease of the satellite peaks upon irradiation shows the solar light induced reduction of Cu^{2+} to Cu^{+} or Cu^{0}.

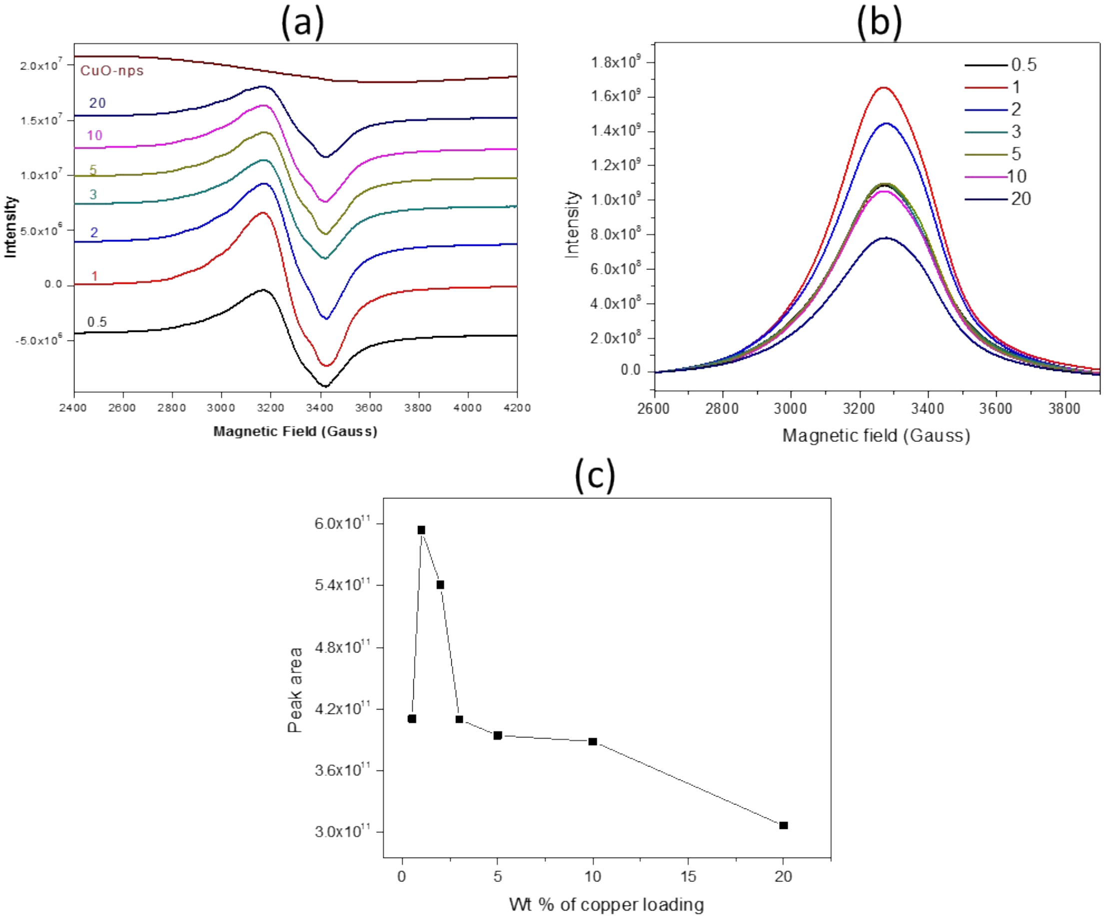

Figure S4. ESR spectra of Cu(n)/TiO2 with n = 0.5, 1.0, 2.0, 3.0, 5.0, 10.0, and 20.0 in the first derivative (a) and normal (b) forms. (c) Plot of the ESR intensity with respect to loading n.

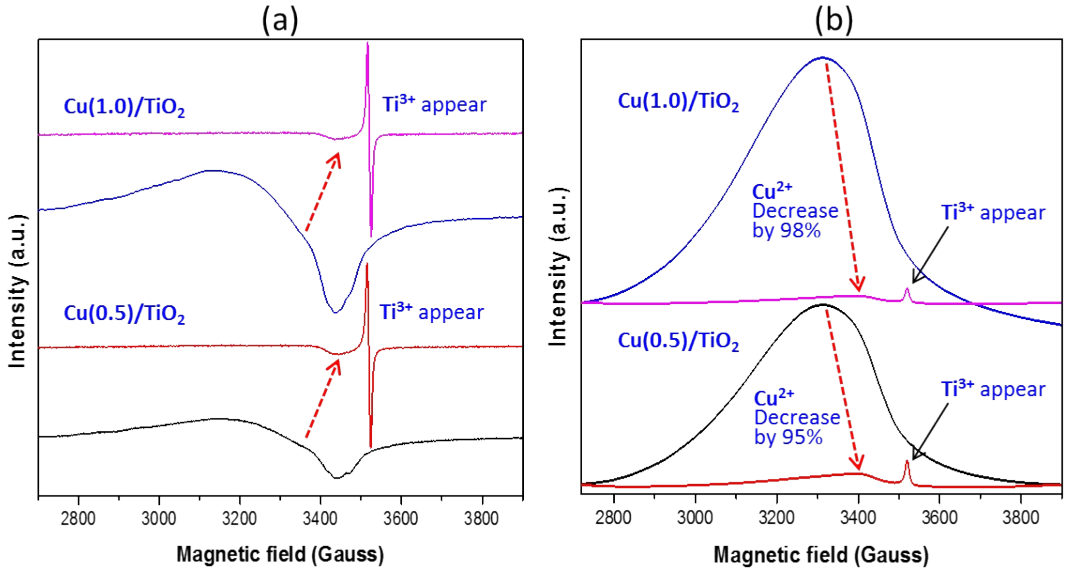

Figure S5. ESR spectra of Cu(0.5)/TiO_2 and Cu(1.0)/TiO_2 before and after irradiation with solar simulated light showing the decrease of the Cu^{2+} signal and appearance of Ti^{3+} signal. A: First derivative spectra, B: Original spectra.

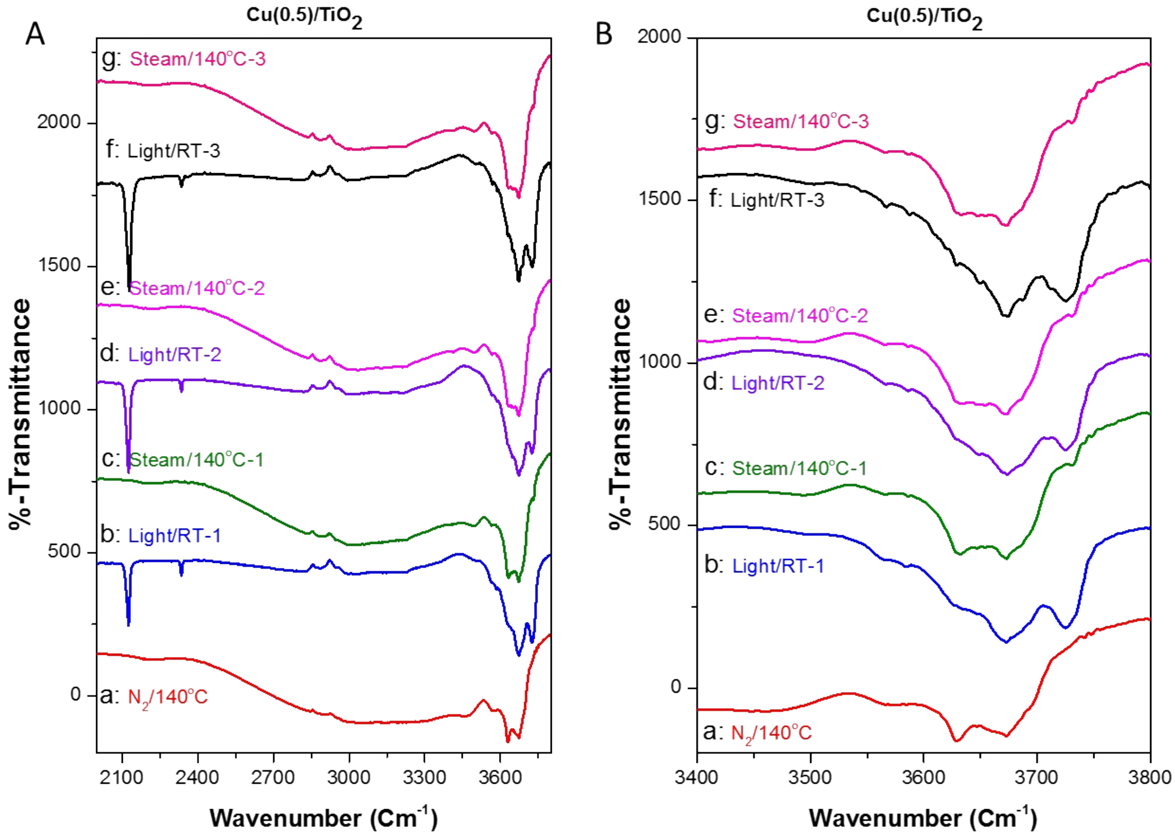

Figure S6. FT-IR spectra of the partially dried Cu(0.5)/TiO_2 obtained by dehydrating the pristine Cu(0.5)/TiO_2 by passing high purity N_2 into the environmental chamber at 140 °C for 5 h (a), the partially dried Cu(0.5)/TiO_2 after irradiation with a solar simulated light (b), the irradiated Cu(0.5)/TiO_2 after steam treatment at 140 °C in the dark (c), the steam treated partially dried Cu(0.5)/TiO_2 after the second time irradiation with a solar simulated light (d), after second steam treatment (e), after the their time irradiation (f), and after third steam treatment in the 2000-3800 (A) and 3400-3800 cm^{-1} (B) regions.

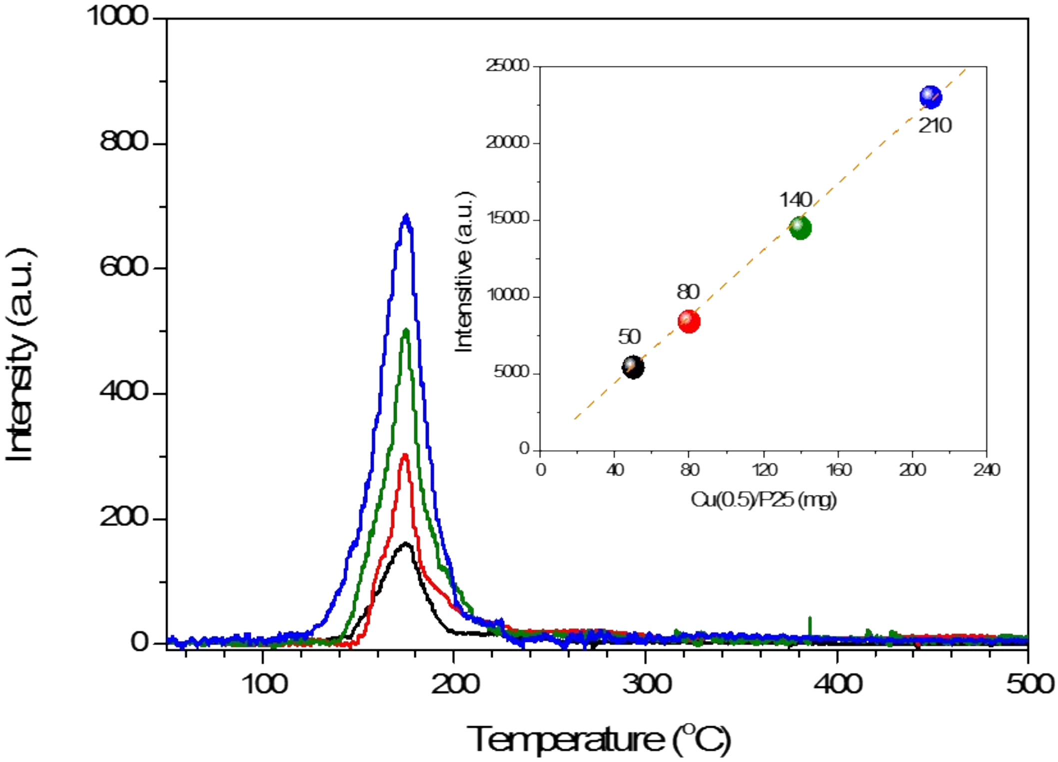

Figure S7. The linear relationship between the total area of H_2 uptake by Cu^{2+} ions and the loaded amount of rigorously dried $Cu(0.5)/TiO_2$ in the sample holder.