Solar photochemical-thermal water splitting at 140 °C with Cu-loaded TiO₂

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Figure S1. Illustration and bases for calculation of solar-to-H₂ conversion efficiency.
**Total solar energy input**

- Total area of irradiation = 6 cm²
  - During 1 h period of steam treatment all the energy can be converted to heat energy
  \[ \Rightarrow \text{Total energy input per h} = 43.2 \text{ J/h/cm}^2 \times 1 \text{ h} \times 6 \text{ cm}^2 = 259.2 \text{ J} \]

- During irradiation for 1.5 h, 22.2% of energy is absorbed by Cu/TiO₂ (See Figure 6C)
  \[ \Rightarrow 77.8\% \text{ of energy can be converted to heat energy} \]
  \[ \Rightarrow 259.2 \text{ J/h} \times 1.5 \text{ h} \times 0.778 = 302.5 \text{ J} \]

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

\[ = 259.2 + 302.5 = 561.7 \text{ J} \]

**Materials and Heat capacity**

- Cu/TiO₂ = 2.5 g, Heat Capacity = 0.711 J/(g.K)
- N₂ = 750 mL, Heat capacity = 1.041 J/(g.K)
- H₂O vapor = 7.05 mg, Heat capacity = ~1.88 J/(g.K)

**Total Energy consumption for Heating to 140 °C**

- Cu/TiO₂ = 2.5 g → 2.5 g \times 0.711 J/(g.K) \times 115 K = 204.4 (J)
- N₂ = 750 mL → 0.9375 g \times 1.041 J/(g.K) \times 115 K = 112.3 (J)
- H₂O vapor = 7.05 mg → 0.007 g \times 1.88 J/(g.K) \times 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 Cu\(2p_{3/2}\) and Cu\(2p_{1/2}\) 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.