Electronic Supplementary Information

for

Synergistic effects of Ni and Cu nanoparticles supported on TiO_2 and SiO_2 on photocatalytic H_2 evolution with an electron donor-acceptor linked molecule

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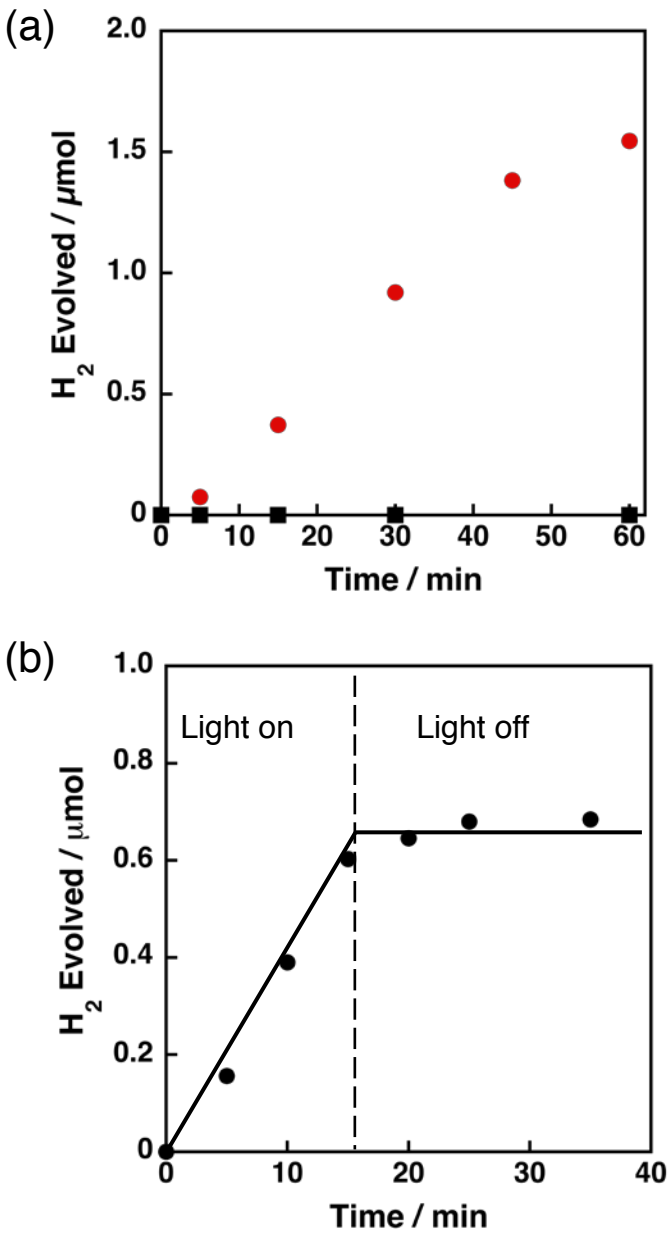

Fig. S1 (a) Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/TiO_2 (100 mg L^{-1}) in the presence (red circle) and absence (black square) of $QuPh^+$–NA (8.8×10^{-4} M). (b) Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/TiO_2 (100 mg L^{-1}) for 15 min. No H_2 evolution was observed in the dark (after 15 min).

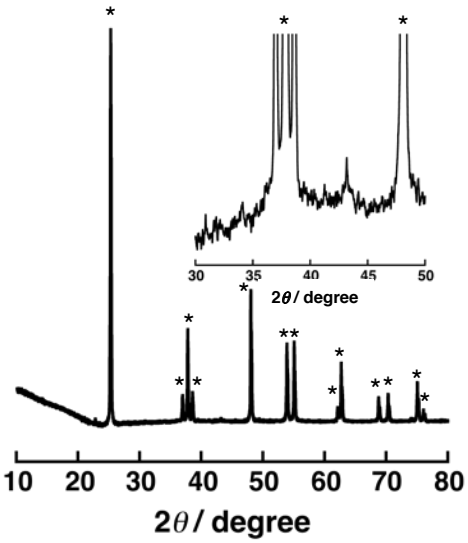

Fig. S2 Powder X-ray diffraction patterns of 3 wt% Ni-Cu/TiO_2 [Ni/Cu = 1:1 (w/w)] after the photocatalytic H_2 evolution. The peaks with * originate from TiO_2 (anatase).

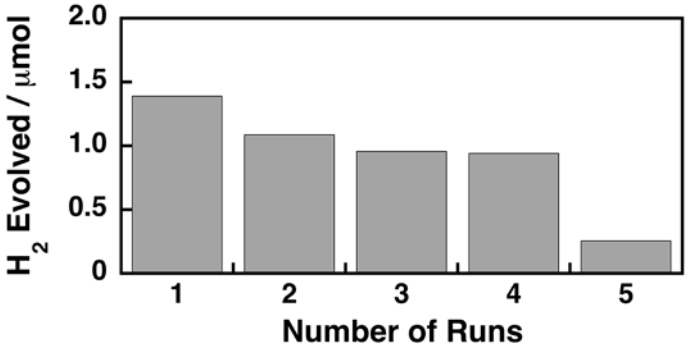

Fig. S3 Volume of evolved H_2 in the repetitive experiments at each run. H_2 evolution was carried out by photoirradiation ($\lambda > 340$ nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (1.1×10^{-4} M), 3 wt% Ni-Cu/TiO_2 (100 mg L^{-1}) and NADH (1.0×10^{-3} M). A small potion of an aqueous solution of concentrated NADH was added to the reaction after ceasing H_2 evolution. The concentration of NADH was 1.0×10^{-3} M in a starting solution at each run.

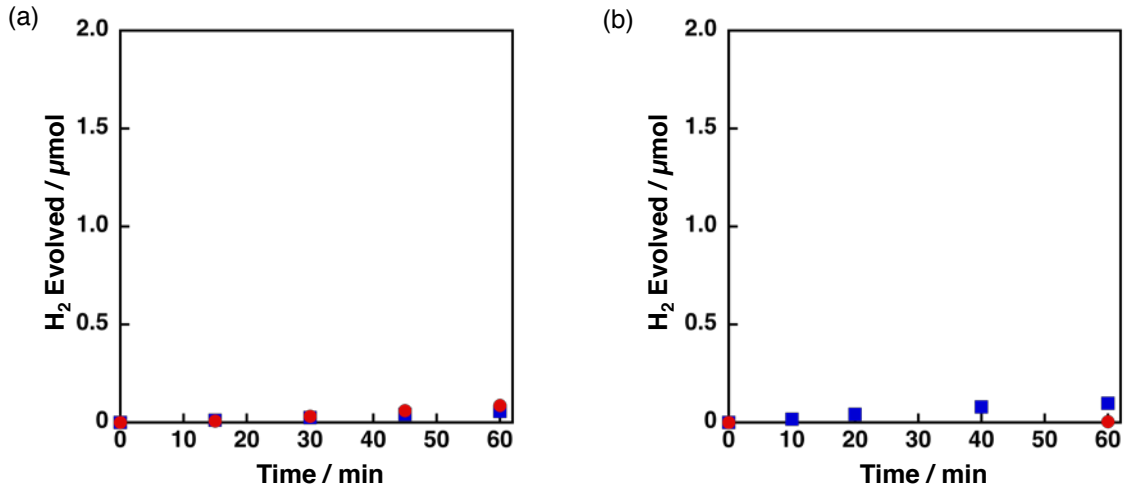

Fig. S4 Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and (a) 3 wt% Ni/TiO_2 (red circle) and Cu/TiO_2 (blue square) and (b) 3 wt% Ni/SiO_2 (red circle) and Cu/SiO_2 (blue square) (100 mg L^{-1}).

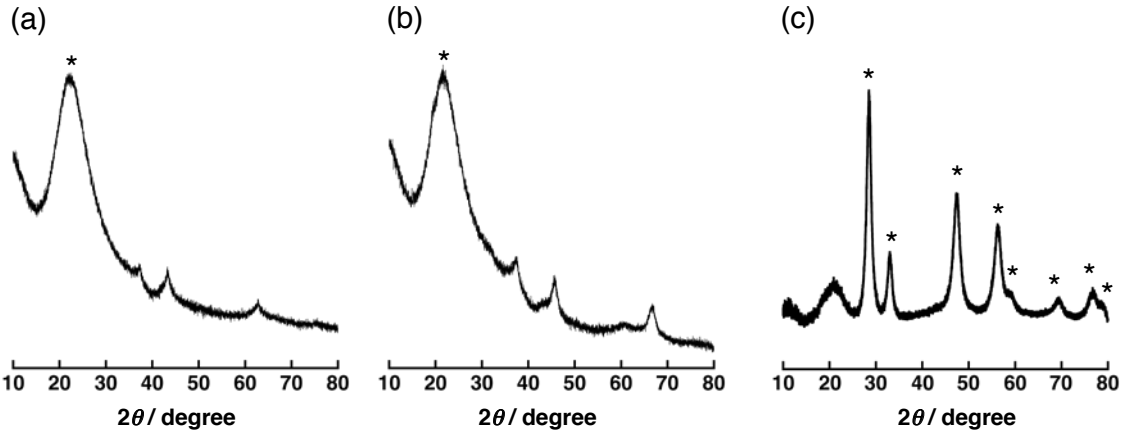

Fig. S5 Powder X-ray diffraction patterns of 3 wt% Ni-Cu/MO_x. [MO_x = (a) SiO_2, (b) SiO_2-Al_2O_3 and (c) CeO_2]. The peaks with * originate from MOx.

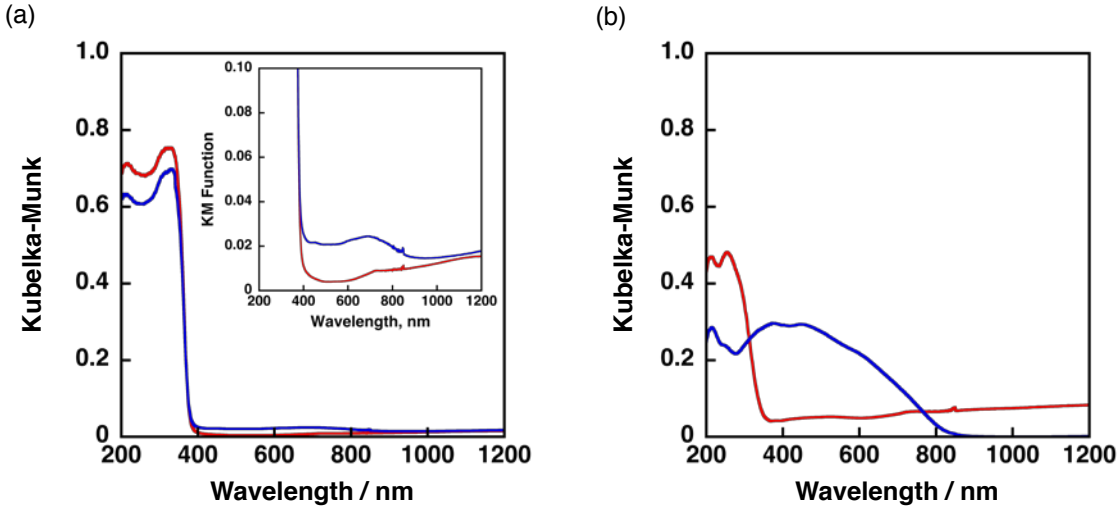

Fig. S6 Diffuse reflectance UV-vis spectra of (a) 3 wt% Ni/TiO_2 (red) and 3 wt% Cu/TiO_2 (blue) and (b) 3 wt% Ni/SiO_2 (red) and 3 wt% Cu/SiO_2 (blue) prepared by co-impregnation.

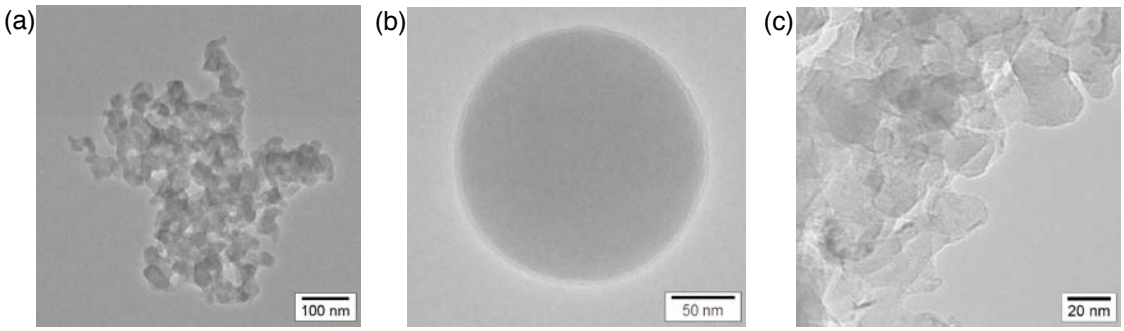

Fig. S7 TEM images of 3 wt% $Ni\text{-}Cu/SiO_2$ with different morphologies and surface areas. (a) unshaped (low surface area), (b) spherical and (c) unshaped (high surface area).

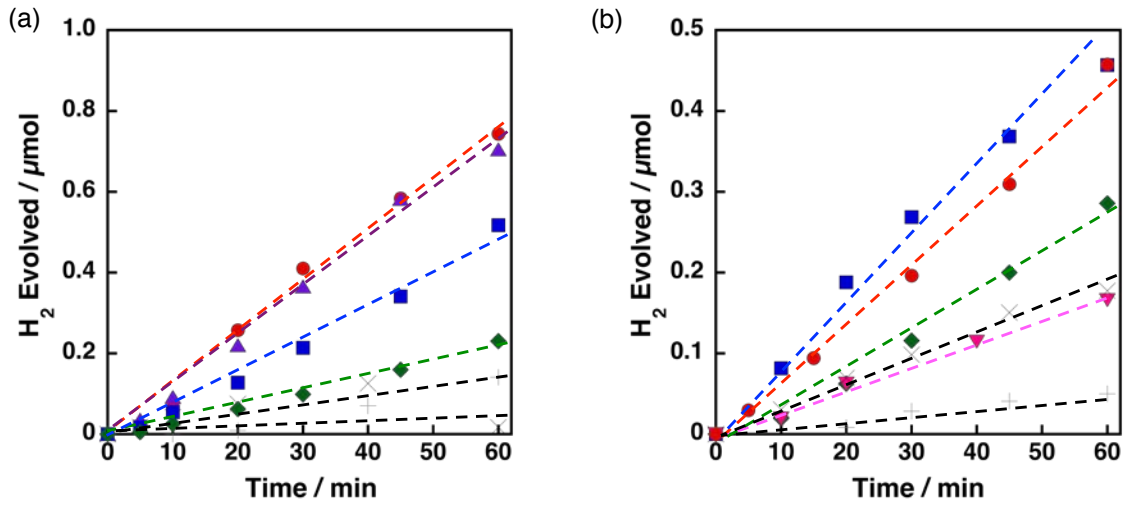

Fig. S8 Time course of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/SiO_2 (100 mg L^{-1}) with various Ni/(Ni+Cu) ratio prepared by a co-impregnation method. [(a) SiO_2 (spherical) and (b) SiO_2 (unshaped, HS) with Ni/(Ni+Cu) = 0% (plus), 25% (green diamond), 33% (blue square), 50% (red circle), 67% (purple triangle), 75% (pink inverse triangle) and 100% (cross)].

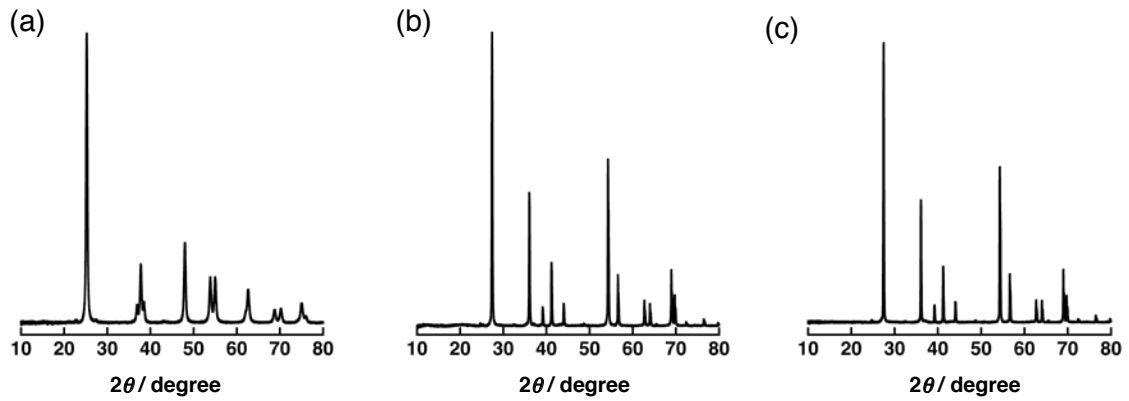

Figure S9. Powder X-ray diffraction patterns of TiO_2 (a) anatase with high surface area, (b) rutile high surface area and (c) rutile low surface area.