Electronic Supplementary Information

Photocatalytic hydrogen evolution from carbon-neutral oxalate with 2-phenyl-4-(1-naphthyl)quinolinium Ion and metal nanoparticles

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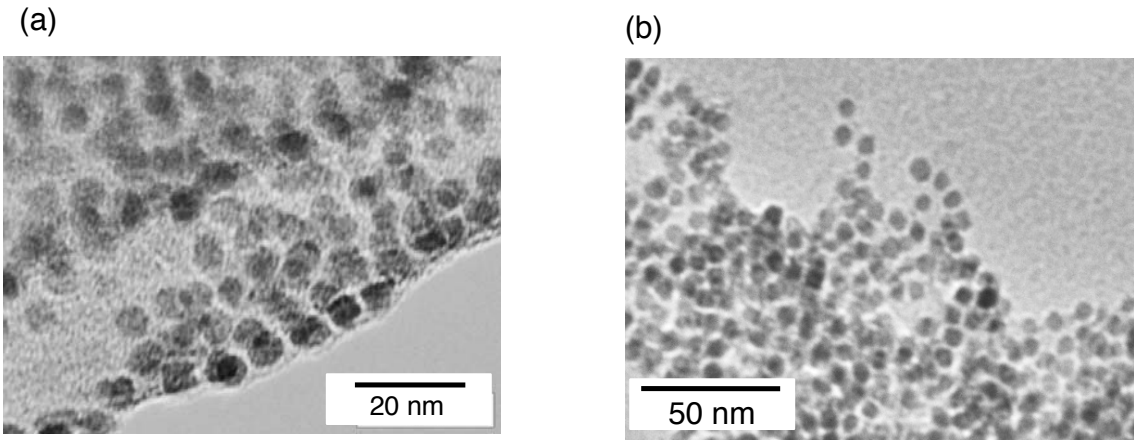

Fig. S1 TEM images of (a) Ru nanoparticles and (b) Ni nanoparticles.

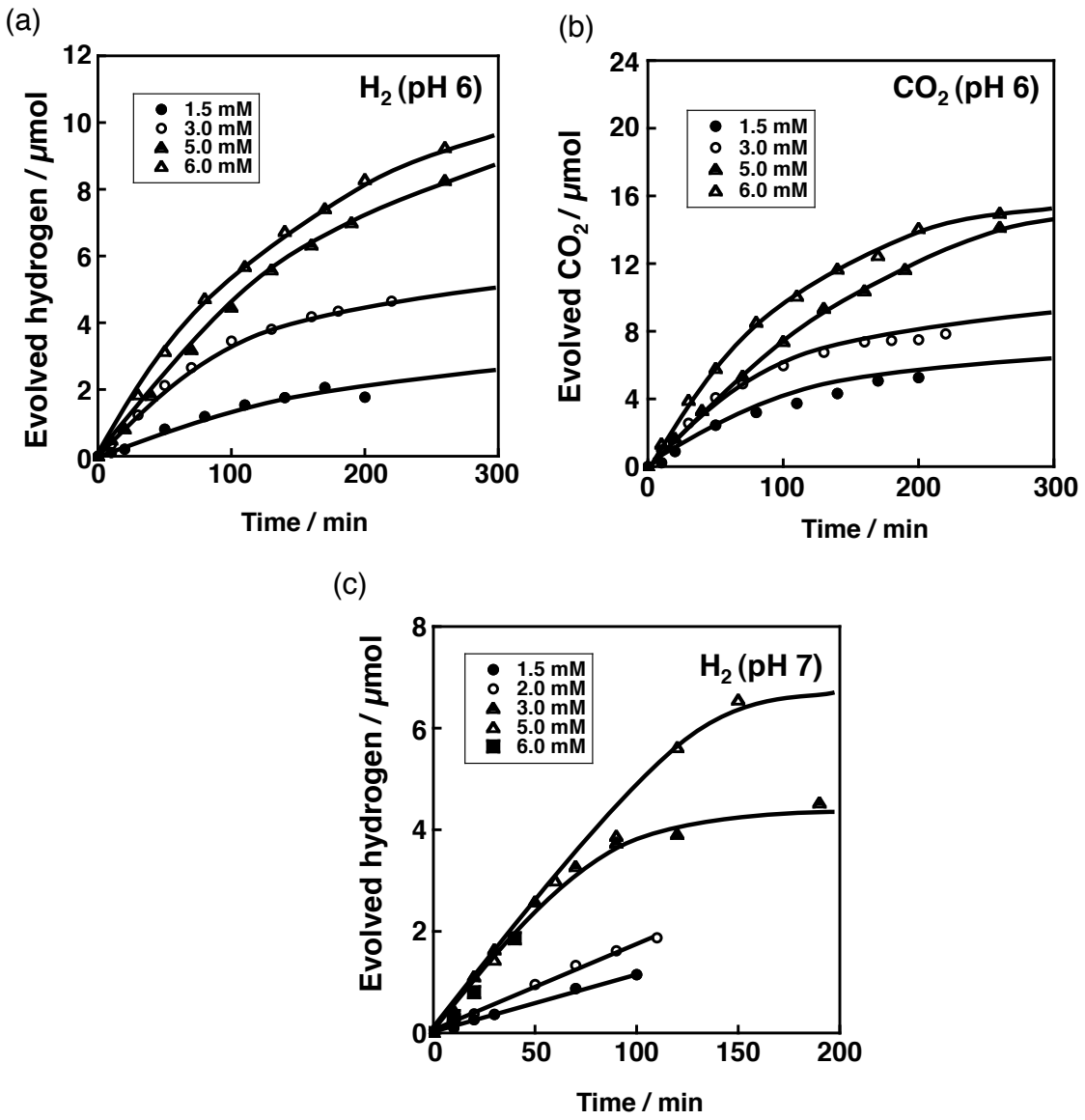

Fig. S2 Time courses of evolution of (a) hydrogen and (b) CO_2 under photoirradiation (λ > 340 nm) of a deaerated mixed solution (2.0 mL) of a phosphate buffer (pH 6.0) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (0.22 mM), Pt NPs (12.5 mg L^{-1}) and oxalate ions (1.5 mM, closed circle; 3.0 mM, open circle; 5.0 mM, closed triangle; 6.0 mM, open triangle). (c) Time courses of hydrogen evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution (2.0 mL) of an aqueous buffer (pH 7.0) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (0.22 mM), Pt NPs (12.5 mg L^{-1}) and oxalate ions (1.5 mM, closed circle; 3.0 mM, open circle; 5.0 mM, closed triangle; 6.0 mM, open triangle).

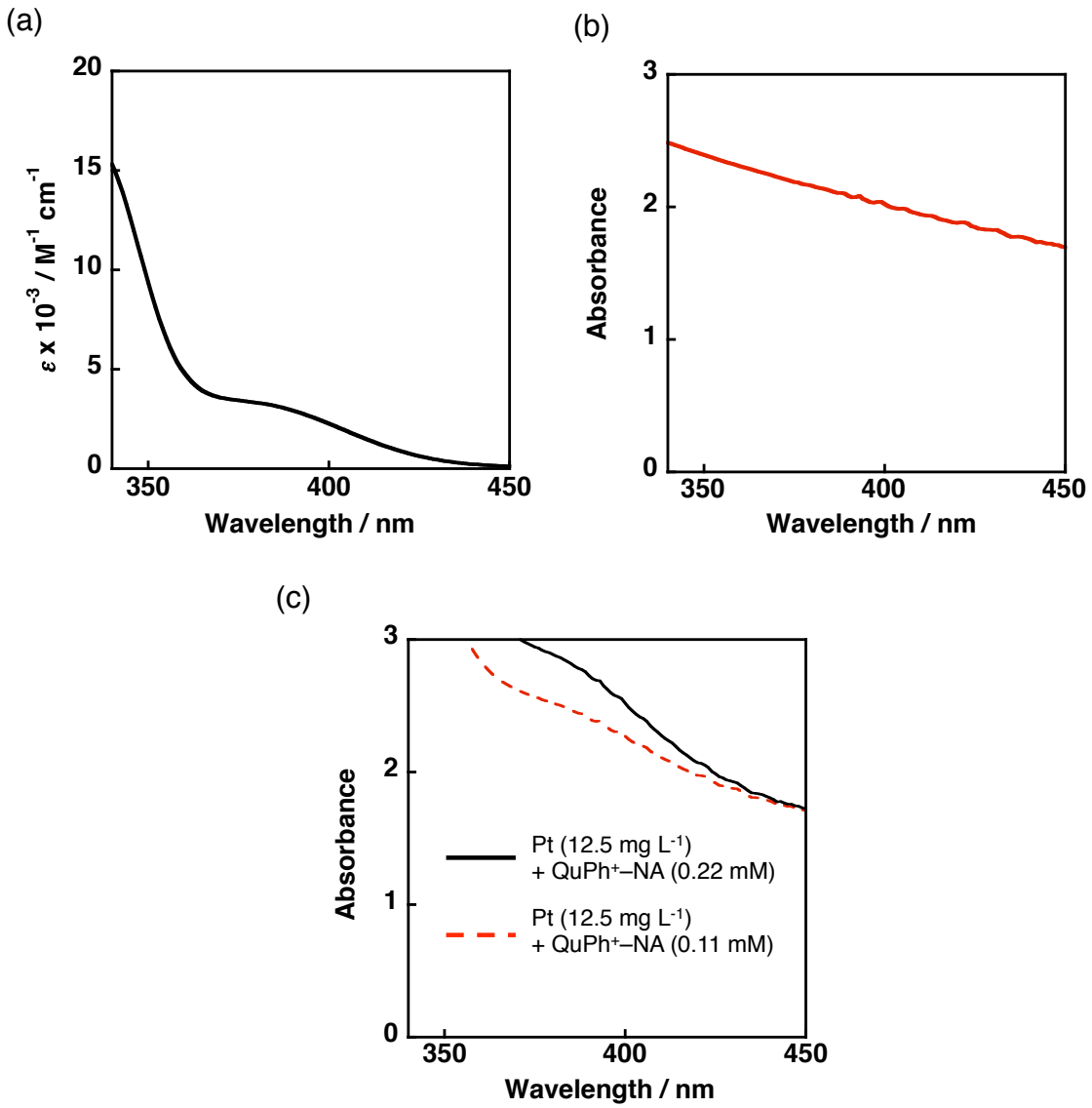

Fig. S3 UV-vis absorption spectra of (a) $(QuPh^{+}–NA)(ClO_4)$, (b) PtNPs (12.5 mg L^{-1}) and (c) PtNPs (12.5 mg L^{-1}) + $(QuPh^{+}–NA)(ClO_4)$ (0.22 mM, black solid line and 0.11 mM, red dashed line) in a mixed solution of phosphate buffer (pH 6.0) and MeCN [1:1 (v/v)].

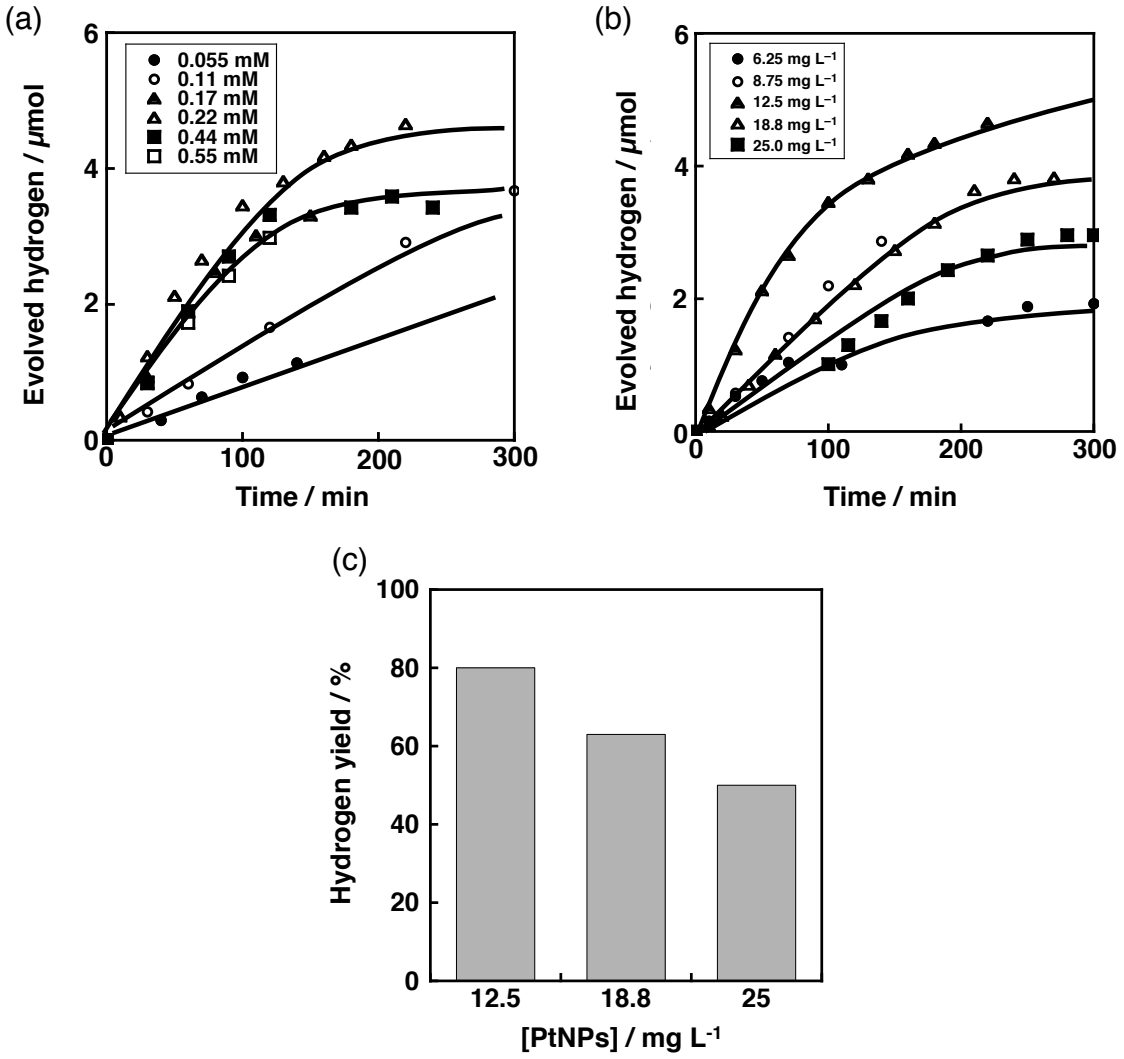

Fig. S4 (a) Time courses of hydrogen evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution (2.0 mL) of an aqueous buffer (pH 6.0) and MeCN [1:1 (v/v)] containing PtNPs (12.5 mg L^{-1}), oxalate ions (3.0 mM) and $QuPh^{+}$–NA with different concentrations (0.055 mM, closed circles; 0.11 mM, open circles; 0.22 mM, closed triangles; 0.44 mM, open triangles). (b) Time courses and (c) hydrogen yield of hydrogen evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution (2.0 mL) of an aqueous buffer (pH 6.0) and MeCN [1:1 (v/v)] containing $QuPh^{+}$–NA (0.22 mM), oxalate ions (3.0 mM) and PtNPs in different concentrations (6.25 mg L^{-1}, closed circle; 8.75 mg L^{-1}, open circle; 12.5 mg L^{-1}, closed triangle; 18.8 mg L^{-1}, open triangle; 25.0 mg L^{-1}, closed square).

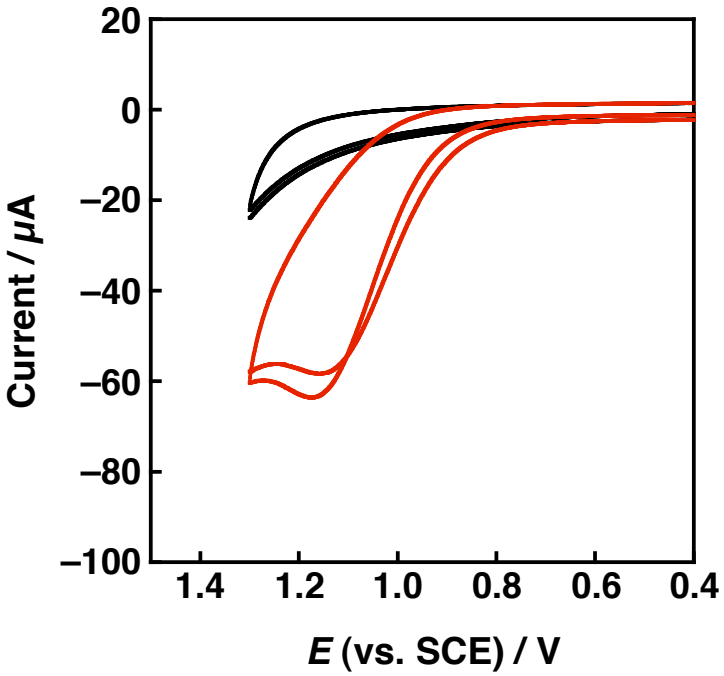

Fig. S5 Cyclic voltammograms of oxalate in a deaerated mixed solution of an aqueous buffer (pH 6.0) and MeCN. The concentration of oxalic acid was 0 mM (black) or 2.5 mM (red) and the scan rate was 100 mV s^{-1}.

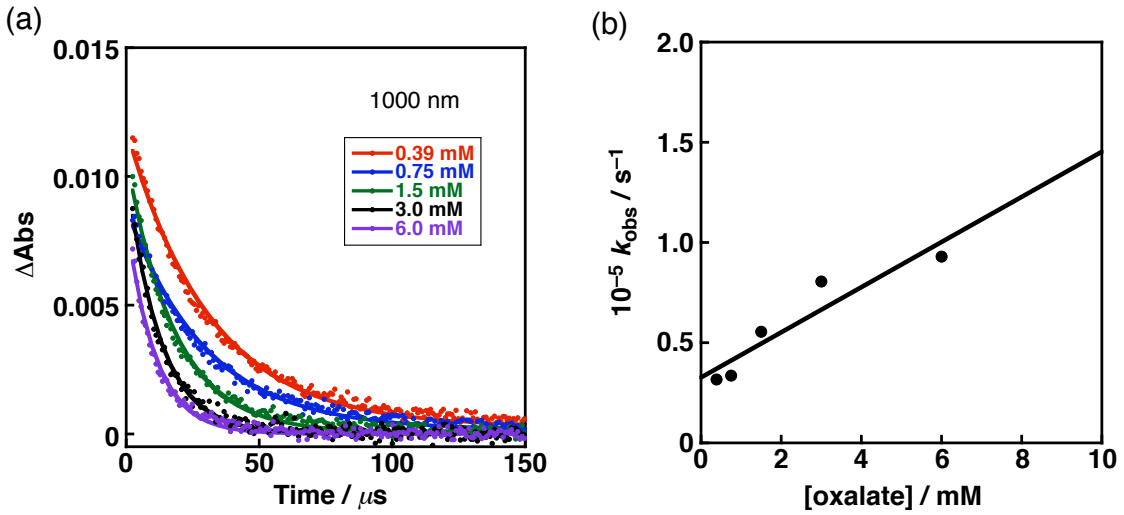

Fig. S6 (a) Decay time profile of absorption at 1,000 nm due to $QuPh^{\bullet}$–$NA^{\bullet+}$ with various concentrations of oxalate (0.39 mM, red; 0.75 mM, blue; 1.5 mM, green; 3.0 mM, black; 6.0 mM, purple) in the presence of $QuPh^{+}$–NA (0.056 mM). $QuPh^{\bullet}$–$NA^{\bullet+}$ was produced by the laser excitation (λ = 355 nm) of a deaerated mixed solution of an aqueous buffer (pH 6.0) and MeCN [1:1(v/v)]. (b) Plot of the pseudo-first-order rate constant (k_{obs}) of electron transfer from oxalate to $QuPh^{\bullet}$–$NA^{\bullet+}$ *vs.* [oxalate].

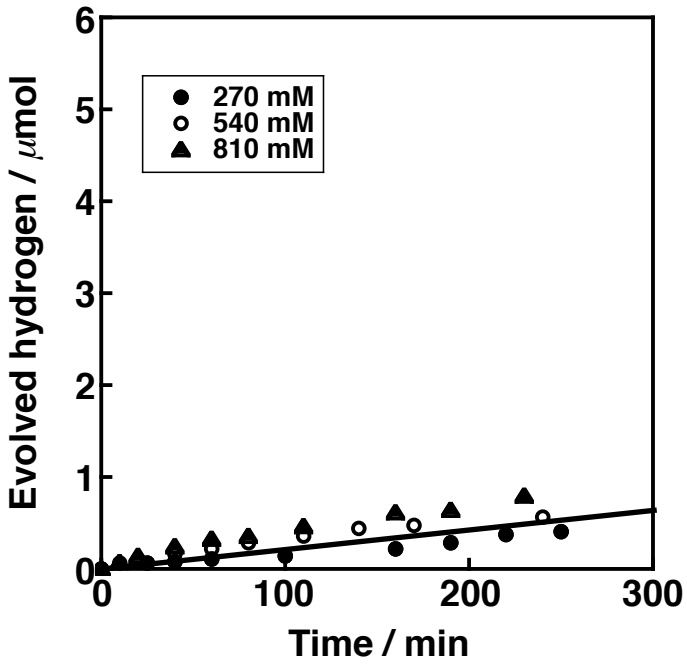

Fig. S7 Time courses of hydrogen evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution of an aqueous buffer (pH 3.0) and MeCN containing formic acid (270 mM, 540 mM and 810 mM), $QuPh^+$–NA (0.22 mM) and PtNPs (12.5 mg L^{-1}).