

Electronic Supporting Information

A stable dual-functional system of visible-light-driven Ni(II) reduction to a nickel nanoparticle catalyst and robust *in situ* hydrogen production

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Formation of FI-TEOA-Ni²⁺ hydrogen production systems and hydrogen measurement

In a typical reaction, a quartz tube containing an aqueous solution of NiCl₂ (1.0×10^{-5} M) and TEOA (5%, v/v) was adjusted to pH 11.35 with 0.1 M NaOH under atmospheric conditions. FI (10 mg, 1.0 mM) was added to the solution with vigorous stirring. The solution was deoxygenated with N₂ for 30 min and then the tube was sealed with a rubber cap. Ten samples were subjected to an irradiation apparatus composed of an LED light source (30×3 W, $\lambda > 420$ nm) and magnetic stirrer at room temperature. The hydrogen generated by the systems was measured at different time intervals by a GC (GC-14C, Shimadzu) equipped with a 5 Å molecular sieve column (3 m \times 2 mm), thermal conductivity detector and N₂ carrier gas. The amount of hydrogen was quantified by an external standard method.

Cyclic hydrogen production reactions with *in situ* generated Ni nanoparticles

The nickel nanoparticles used for cyclic hydrogen reactions were precipitated after 5 to 8 hours of irradiation in our photoreduction system with nickel chloride as catalyst precursor. The nanoparticles were collected and washed several times with degassed ethanol and protected under a nitrogen atmosphere and characterized to be nickel by XRD and TEM and other methods. For the cyclic hydrogen production reactions, 5 mg of these nanoparticles were incorporated into a quartz tube containing 2 mM FI, 1.5 mL TEOA and 28.5 mL deoxygenized water, then the system was degassed for 30 min and subjected to light irradiation with LED light source (30×3 W, $\lambda > 420$ nm), the hydrogen produced was measured by GC every few of hours for 20 hours when the

inner pressure of the tube becomes high. Then the tube was opened and re-degassed and again subjected to light irradiation, without further adding of any component. Eleven of these cyclic procedures were done and continual hydrogen production was observed during that time (221 h).

Characterization of Ni nanoparticles

The Ni nanoparticles precipitated after irradiation were washed several times with deoxygenated ethanol, centrifuged and dried under a nitrogen atmosphere. The dried nanoparticles were used directly for XRD measurement. For TEM measurement, the nanoparticles were dispersed in deoxygenated ethanol solution. HRTEM and EDS measurements were performed on a TEM (JEM 2100F) that was operated at an accelerating voltage of 200 kV. XRD spectra were collected on a diffractometer (Bruker D8 Focus) using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$).

Photocurrent measurement

Photocurrent experiments were performed using a three electrode system. For the *in situ* hydrogen-generating aqueous systems, ITO glass as a working electrode was immersed in 0.1 M KCl electrolyte (immersed surfaced area about $1 \times 1 \text{ cm}^2$, double face), a saturated calomel electrode (SCE) was used as a reference electrode and a Pt coil as the counter electrode. Intervals of visible light irradiation and darkness were both 40 s. The photocurrent was small at the beginning of irradiation, and gradually increased with irradiation time. It was accompanied by a black precipitation forming in the solution, implying the gradual accumulation of Ni nanoparticles. In the photocurrent measurement experiment, the ITO surface was initially in ample contact with the colloidal Ni(OH) $_2$ precursor. Upon light irradiation, Ni(OH) $_2$ was *in situ* photoreduced to nickel nanoparticles which self-deposited on the electrode surface and caused the photocurrent. This self-deposition method is convincing to provide proof that Ni(0) nanoparticles are the real catalyst in the photocatalytic system and Ni(OH) $_2$ is only pre-catalyst to be reduced to the real catalyst, as the photocurrent is initially low and gradually increases over irradiation time. If Ni(OH) $_2$ is catalyst and Ni(0) is not, the photocurrent would be initially high and gradually decreases as Ni(OH) $_2$ is reduced to Ni, however, the situation is vice versa. For photocurrent measurement of the RGO/Ni composite, a working electrode was prepared by drop-coating the RGO/Ni composite onto a precleaned ITO-coated glass surface with a heat lamp to speed drying. The surface immersed in 0.1 M KCl electrolyte was about $2 \times 1 \text{ cm}^2$. A SCE was used as a reference electrode and Pt coil as the counter electrode, with 1 mM F1 and 5% TEA in 30 mL 0.1 M KCl aqueous solution. A visible LED light source was used for irradiation.

Physical measurement

Electronic absorption spectra were recorded on a spectrophotometer (Hitachi U-3010). Fluorescence spectral measurements were carried out with a fluorescence spectrophotometer (Hitachi F-4500) adapted to a right angle configuration at room temperature. Photocurrent experiments were recorded on a computer-controlled CHI660C electrochemical workstation with a three electrode system composed of a platinum counter electrode, mercury-coated glassy carbon

working electrode and SCE reference. pH values were adjusted with a pH meter (S-3C, Mettler Toledo FE20). DLS measurements were performed with a Dyanpro NanoStar instrument (Wyatt Technology). The DLS instrument used in this study can detect particle sizes ranging from 0.5 to 2000 nm. The light source for the scattering experiments is a He-Ne gas laser (100 mW, $\lambda = 658$ nm). Data were obtained using a scattering angle of 90° at 25°C .

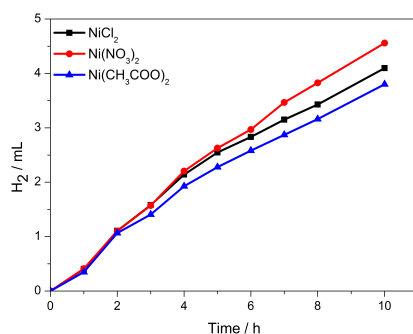


Fig. S1 Hydrogen production over time with nickel salts (NiCl₂, Ni(NO₃)₂ and Ni(CH₃COOH)₂) of different anions. Ni²⁺ (1.0 × 10⁻⁴ M), TEOA (1.5 mL) and FI (1.0 × 10⁻³ M) in H₂O (28.5 mL) in a 60 mL volume quartz tube

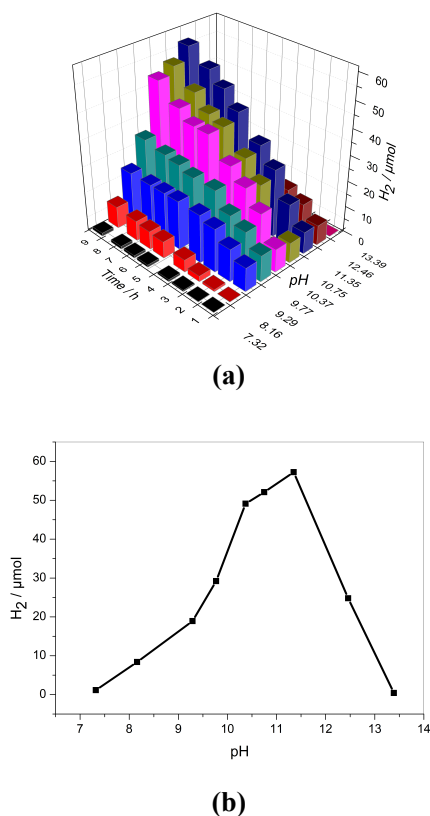


Fig. S2 (a) and **(b)**: Relationship between hydrogen production at various pH values and irradiation time from system containing NiCl₂ (1.0 × 10⁻⁴ M), TEOA (1.5 mL) and FI (1.0 × 10⁻³ M) in H₂O (28.5 mL) in a 60 mL volume quartz tube. The light source for irradiation is LED with λ > 420 nm.

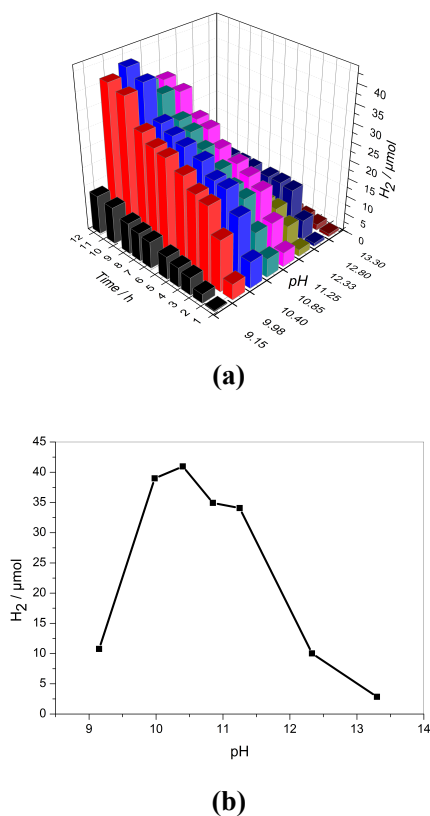


Fig. S3 (a) and (b): Relationship between hydrogen production at various pH values and irradiation time from system containing NiCl_2 (1.0×10^{-5} M), TEA (1.5 mL) and FI (1.0×10^{-3} M) in H_2O (28.5 mL) in a 60 mL volume quartz tube. The light source for irradiation is LED with $\lambda > 420$ nm.

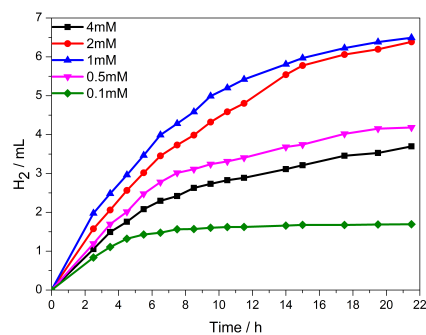


Fig. S4 Hydrogen production from systems containing NiCl_2 (1.0×10^{-4} M) and TEOA (5%, v/v) at pH 11.35 (adjusted with 0.1M NaOH) and various concentrations of FI (0.1, 0.5, 1.0, 2.0 and 4.0 mM) in H_2O under visible light irradiation.

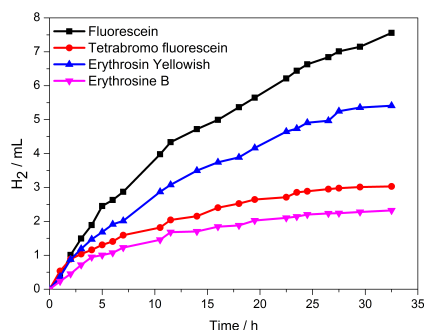


Fig. S5 Photocatalytic hydrogen production with various organic sensitizers (1.0×10^{-3} M) with NiCl_2 (1.0×10^{-4} M) and TEOA (5%, v/v) in H_2O under visible light irradiation.

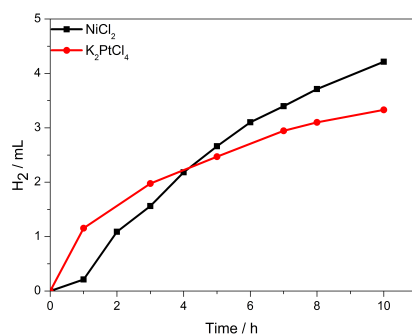


Fig. S6 Photocatalytic hydrogen production with NiCl_2 (1.0×10^{-4} M) and K_2PtCl_4 (1.0×10^{-4} M), Fl (1.0×10^{-3} M) with and TEA (5%, v/v) in H_2O under visible light irradiation under experimental conditions (LED light: $\lambda > 420$ nm, 30×3 W).

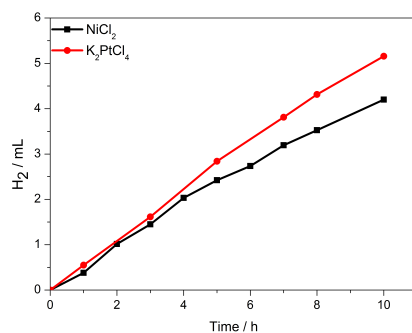


Fig. S7 Photocatalytic hydrogen production with NiCl_2 (1.0×10^{-4} M) and K_2PtCl_4 (1.0×10^{-4} M), Fl (1.0×10^{-3} M) with and TEOA (5%, v/v) in H_2O under visible light irradiation under experimental conditions (LED light: $\lambda > 420$ nm, 30×3 W).

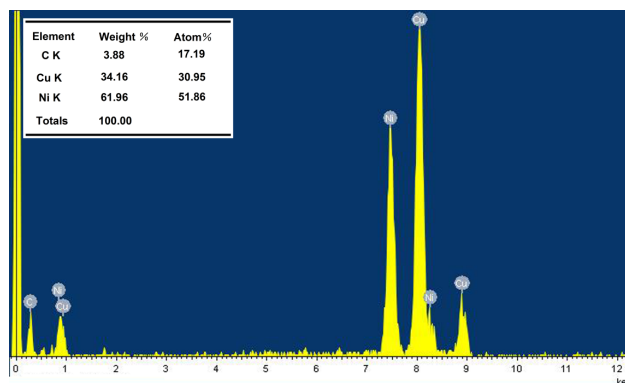


Fig. S8 HRTEM-EDX image of *in situ* generated Ni(0) nanoparticles.

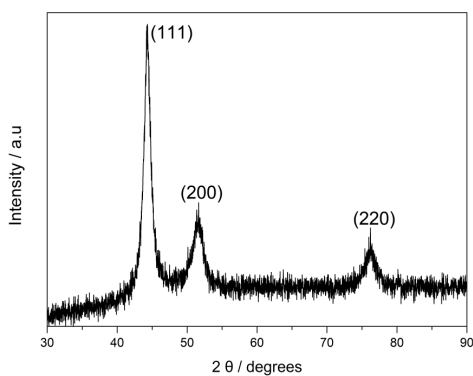


Fig. S9 XRD of *in situ* generated Ni(0) nanoparticles.

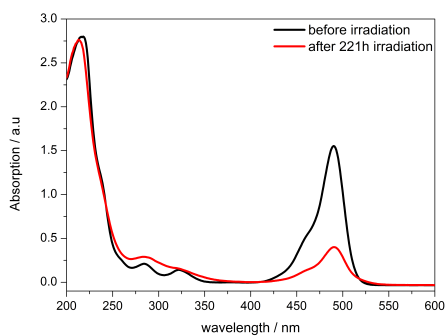


Fig. S10 UV-vis absorption changes before and after 221 h irradiation of a system containing 2.0

mM FI (5%, v/v) TEOA and 5 mg *in situ* generated Ni(0) nanoparticles in 28.5 mL H₂O.

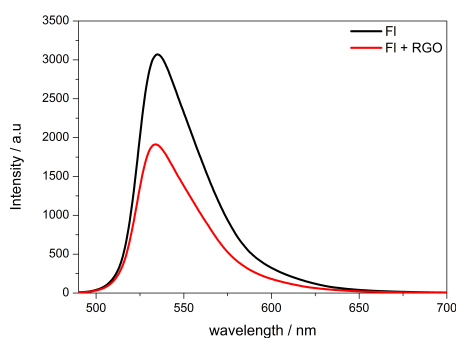


Fig. S11 Fluorescence quenching of FI (3 mL, 1.0 mM) by RGO (0.15 mL, 1 mg/mL).

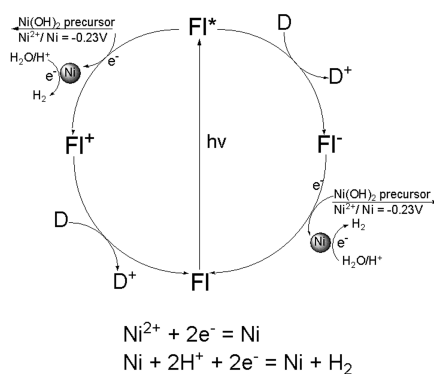


Fig. S12. Schematic representation of the photoinduced electron transfer processes from excited state FI* (-1.7V vs SCE) or FI⁻ (-1.3V vs SCE) to Ni(OH)₂ precatalyst for reduction of Ni²⁺ to Ni nanoparticles, and simultaneous electron transfer to the generated Ni nanoparticles for photocatalytic hydrogen production reactions.

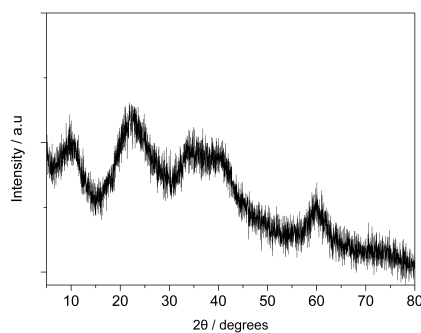


Fig. S13 XRD of green precipitate formed by NiCl₂ and TEA in water, showing the pattern of α-Ni(OH)₂.

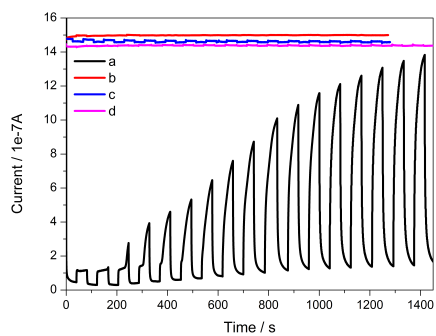
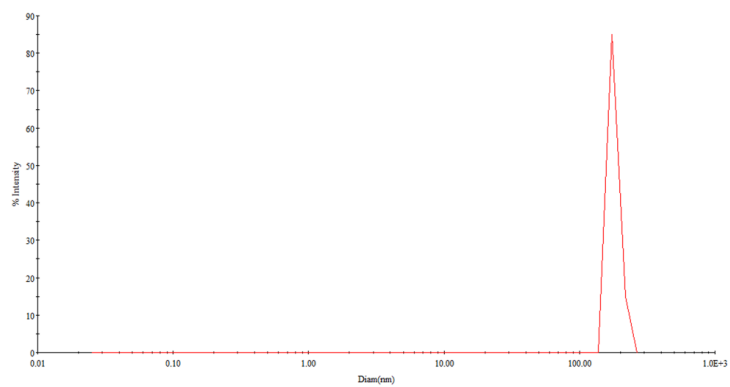
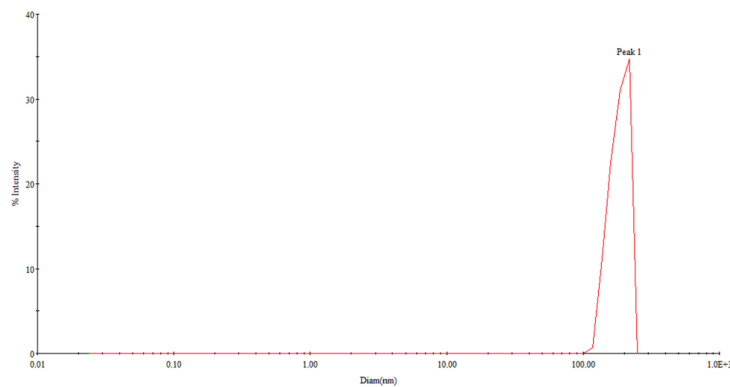


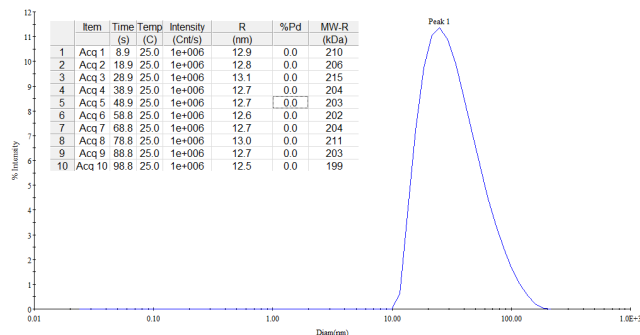
Fig. S14 Photocurrent responses of systems composed of aqueous solutions (30 mL) at pH 10.40 of a. KCl (0.1 M), NiCl₂ (1.0 mM), TEA (5%, v/v) and Fl (1.0 mM); b. KCl (0.1 M); c. KCl (0.1 M), NiCl₂ (1.0 mM) and Fl (1.0 mM); d. KCl (0.1 M), NiCl₂ (1.0 mM) and 5% TEA.



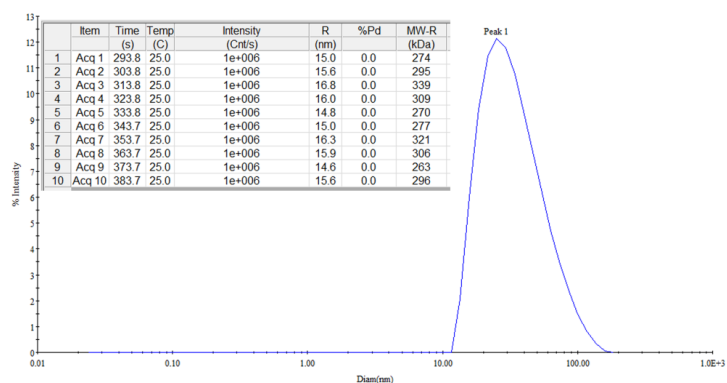
(a)



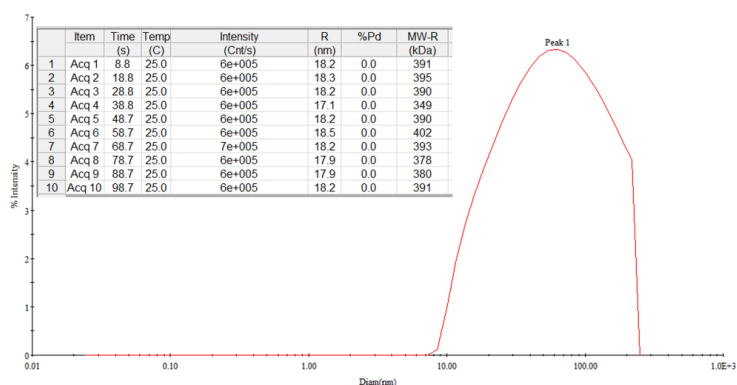
(b)



(c)



(d)



(e)

Fig. S15 (a) Particle size distribution determined by DLS measurements with NiCl₂ (1.0 mM), TEA (5%, v/v) and FI (1.0 mM) at irradiation time of 0 min. **(b)** Particle size distribution determined by DLS measurements with NiCl₂ (1.0 mM), TEOA (5%, v/v) and FI (1.0 mM) at

irradiation time of 0 min, (c) 10 min and (d) 30 min, (e) 60 min.