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Ni-Cu alloy nanoparticles loaded on various metal oxides acting as efficient catalysts for photocatalytic H₂ evolution

Yusuke Yamada,*^{ab} Shinya Shikano^a and Shunichi Fukuzumi*^{acd}

Catalysis of Al₂O₃-SiO₂, TiO₂, SiO₂ and CeO₂ (MOx) impregnated with pre-formed Ni-Cu alloy nanoparticles (Ni-CuNPs/MOx) for photocatalytic hydrogen (H₂) evolution was compared with that of MOx impregnated with Ni²⁺ and Cu²⁺ ions followed by reduction (Ni-Cu/MOx). The photocatalytic H₂ evolution was conducted by photoirradiation ($\lambda > 340$ nm) of a deaerated mixed solution of ⁻ phthalate buffer (pH 4.5) and acetonitrile [1:1 (v/v)] containing β -dihydronicotinamide adenine dinucleotide (NADH), 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh⁺–NA), and Ni-CuNPs/MOx or L... Cu/MOx as an electron donor, a photosensitiser and an H₂-evolution catalyst, respectively. Ni-CuNPs/Al₂O₃-SiO₂ exhibited activity for the photocatalytic H₂ evolution, whereas Ni-Cu/Al₂O₃-SiO₂ showed no activity. Such precursor dependent catalysis can be elucidated by the ion-exchangeable nature and high surface area of Al₂O₃-SiO₂ on which Ni-Cu alloy particles hardly form from metal salt. On the other hand, Ni-Cu/TiO₂ and Ni-Cu/SiO₂ exhibited higher activity than Ni-CuNPs/TiO₂ and Ni-CuNPs/SiO₂, respectively, resulting from formation of smaller Ni-Cu alloy nanoparticles on TiO₂ and SiO₂ by reducing Ni²⁺ and Cu²⁺ on the surfaces. When CeO₂ was used as the support, no catalytic activity was observed for either Ni-CuNPs/CeO₂ or Ni-Cu/CeO₂. Kinetic study for thermal H₂ evolution suggested that Ni-CuNPs were severely deactivated for H₂ evolution by being loaded on CeO₂.

1. Introduction

Hydrogen (H₂) has been regarded as the most promising energy carrier of the next generation,¹⁻³ however, most part of H₂ supplied to chemical industry is currently produced by the steam forming of fossil fuels such as natural gas, which is a large energy consuming process and emitting carbon dioxide as a main by-product.⁴ It is highly desired that H₂ is produced from renewable chemicals by utilizing natural energy.⁵ In this context, H₂ production utilizing solar energy has attracted much attention in this research field.⁶⁻¹³ Visible light-driven photocatalytic H₂-evolution systems composed of a photosensitiser, an electron relay and an H₂-evolution catalyst have so far been extensively studied.¹⁴⁻²⁵ Recently, efficient photocatalytic H₂-evolution systems were developed by employing electron donor-acceptor linked dyads,²⁶⁻³² which electron long-lived form transfer states under photoirradiation.33-35 The long lifetime of the electron-transfer states allows to eliminate electron relays in the H₂-evolution systems.27-32

Pt nanoparticles has been widely used as a high performance H_2 -evolution catalyst,^{36,37} however, Pt is a most expensive metal because of its limited reserve.³⁸ Thus,

reduction of usage of precious metals and development of alternative catalysts composed of cheaper metals are high demanded. For reduction of using amount of precious metals, Ru nanoparticles supported on a silica support have been developed.³⁹ As a catalyst using a base metal, Ni nanoparticles has been reported although catalytic activity was half that of Pt nanoparticles.⁴⁰ Recently, Ni and Cu loaded on silica or titania prepared by a conventional impregnation method using Ni(NO₃)₂ and Cu(NO₃)₂ as precursors followed by reduction have been reported to exhibit high catalytic activity with *a* synergistic effect.⁴¹ Although the catalytic activity highly depends on the preparation procedures and supports of the catalysts,⁴¹ requisites to obtain the synergistic effect between Ni and Cu and the origin of the support effect have yet to be clarified.

We report herein catalytic activity of Ni-Cu alloy nanoparticles, which were prepared *ex situ* by thermal decomposition of Ni(acac)₂ and Cu(acac)₂ (acac acetylacetonato), loaded on a metal oxide support chosen from SiO₂, TiO₂, Al₂O₃-SiO₂ and CeO₂ (MOx) for photocatalytic H₂ evolution. The photocatalytic H₂ evolution was conducted 1_y photoirradiation ($\lambda > 340$ nm) of a mixed solution of phthalate buffer (pH 4.5) and MeCN containing β dihydronicotinamide adenine dinucleotide (NADH), 2-phenyl-4-(1-naphthyl)quinolinium ion (QuPh⁺–NA) and Ni-CuNPs/MOx as an electron donor, a photosensitiser and an H₂evolution catalyst, respectively. The chemical structure of QuPh⁺–NA and the overall photocatalytic cycle of H₂ evolution are depicted in Scheme 1. The catalytic activity of Ni-CuNPs/MOx was compared with that of Ni-Cu/MOx, which are prepared by the impregnation method using Ni(NO₃)₂ and Cu(NO₃)₂ as precursors to clarify the requisites for high catalytic activity with each support.



Scheme 1 (a) Molecular structure of $\mathsf{QuPh}^{\!\!+}\text{-}\mathsf{NA}$ and (b) the overall photocatalytic cycle of H_2 evolution

2. Results and discussion

2.1 Effect of Ni-Cu alloy formation on catalysis

Ni and Ni-Cu alloy nanoparticles (NiNPs and Ni-CuNPs) were prepared by thermal decomposition of Ni(acac)₂ and/or Cu(acac)₂ in deaerated oleylamine and 1-ocatadecene at 230 °C by changing the ratio of Ni/Cu between 1/0 and 5/5.42 Cu nanoparticles (CuNPs) were obtained by Cu(OAc)₂ reduction by NaBH₄ in the presence of polyvinylpyrrolidone (PVP).⁴³ The molar ratio of Ni/Cu in the Ni-CuNPs determined by the X-ray fluorescence measurements was 55/45. The particles sizes of the as-prepared nanoparticles determined by dynamic laser scattering (DLS) were 25, 15 and 50 nm for NiNPs, Ni-CuNPs and CuNPs, respectively (Fig. S1). The sizes of NiNPs and Ni-CuNPs agreed with those determined by the TEM observation (Figs. 1b and 1c), however, the sizes of CuNPs determined by TEM were larger than 100 nm (Fig. 1a), which is double of those determined by DLS measurements. Growing of CuNPs resulted from the exposure to the electron beam for TEM observation, or intrinsic instability of CuNPs after removal of excess stabiliser during washing process.

Alloy formation in Ni-CuNPs was clearly confirmed by powder X-ray diffraction measurements. In general, both Cu and Ni metals take the face–centred–cubic structure.⁴⁴ The reflection peaks from (111) surfaces of CuNPs and NiNPs appeared at $2\theta = 43.4^{\circ}$ and 44.7° , respectively (Figs. 1d and 1f), which are agreed with the values reported for Cu metal and Ni metal, 43.38° and 44.53° , respectively,⁴⁴ although the peak position of CuNPs is inaccurate owing to concomitant formation of Cu₂O species as evidenced by the peak appeared at 36.58° .⁴⁴ The (111) diffraction peak of Ni-CuNPs appeared at 43.5° , which is in between those from NiNPs and CuNPs, without an accompanied peak. Thus, Ni-CuNPs used as a precursor for preparation of Ni-CuNPs/MOX (*vide infra*) are



Fig. 1 TEM images and powder X-ray diffraction peaks of (a,d) Cu nanoparticles, (b,e) Ni-Cu alloy nanoparticles and (c,f) Ni nanoparticles from (111) plane.

regarded as Ni-Cu alloy with the size of 15 nm.

The instability of CuNPs prevents their direct use for photocatalytic H₂ evolution. Thus, NiNPs, CuNPs and Ni-CuNPs were loaded on TiO₂ by the impregnation method to compare catalysis of Ni-CuNPs/TiO₂ for photocatalytic I⁺ evolution with those of NiNPs/TiO₂ and CuNPs/TiO₂. The photocatalytic H₂ evolution was conducted by photoirradiation $(\lambda > 340 \text{ nm})$ of a deaerated mixed solution (2.0 mL) of a phthalate buffer (50 mM, pH 4.5) and acetonitrile (MeCN) [1:1 (v/v)] containing NADH (1.0×10^{-3} M), QuPh⁺–NA (8.8 × 10⁻⁴ M) and Ni-CuNPs/TiO₂, NiNPs/TiO₂ or CuNPs/TiO₂ (100 mg L⁻¹). Continuous H₂ evolution was observed for the reactior system employing Ni-CuNPs/TiO₂ with an H₂-evolution rate of 0.9 µmol h⁻¹, whereas no or insignificant amount of *I* evolution was observed for the reaction systems employing CuNPs/TiO₂ and NiNPs/TiO₂ (Fig. 2). Thus, alloy formation of



Fig. 2 Time courses of H₂ evolution under photoirradiation (λ > 340 nm) of an N₂-saturated mixed solution (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh⁺–NA (8.8 x 10⁻⁴ M), NADH (1.0 x 10⁻³ M) and 3.5 wt% CuNPs/TiO₂ (red circle), 1.3 wt% NiNPs/TiO₂ (green square) or (c) 3.2 w % CuNPs/TiO₂ (blue triangle) (100 mg L⁻¹).

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Ni and Cu is necessary for high catalytic activity. The high catalytic activity could result from the optimisation of metalhydrogen bond strength, because the nickel-hydrogen bond seems too strong, on the contrary, the copper-hydrogen bond seems too weak for H₂ evolution as predicted by the density functional theory (DFT) calculations.⁴⁵ The induction period (5 min) before H₂ evolution may result from the reduction of native oxide formed on the surface of Ni-CuNPs.

2.2 Precursors effect of Ni–Cu alloy nanoparticles loaded on TiO_2 and SiO_2 on photocatalytic H_2 evolution

The surface structures of Ni-CuNPs/TiO₂ and Ni-Cu/TiO₂ were observed by a transmission electron microscope (TEM). Ni-CuNPs/TiO₂ were prepared by the impregnation method using pre-formed Ni-CuNPs as a precursor, on the other hand, Ni-Cu/TiO₂ samples were prepared by the impregnation method using Ni(NO₃)₂ and Cu(NO₃)₂ as precursors with the reductive treatment. Particles with the size of 10-20 nm were observed on TiO₂ surfaces of Ni-CuNPs/TiO₂ (Fig. 3a), whilst smaller particles with the size of ~5 nm were observed on TiO₂ surfaces of Ni-Cu/TiO₂ (Fig. 3c). Formation of Ni-Cu alloy for both samples was evidenced by identical peak positions of the diffraction peaks around 43.5° in powder XRD patterns (Figs. 3b and 3d). The loading amounts of Ni-Cu alloy were determined by X-ray fluorescence measurements as 3.5 and 3.0 wt% for Ni-CuNPs/TiO₂ and Ni-Cu/TiO₂, respectively.



Fig. 3 (a,c) TEM images and (b,d) powder X-ray diffraction peaks of Ni-Cu/TiO₂ prepared by the impregnation method using (a, b) Ni-Cu nanoparticles or (c,d) Ni(NO₃)₂ and Cu(NO₃)₂. The diffraction peaks with the "*" mark originate from the TiO₂ support.

Photocatalytic H_2 evolution was performed by employing Ni-Cu/TiO₂ as an H₂-evolution catalyst (Fig. 4a, square). The average H₂-evolution rate for the reaction time between 5 to 30 min was 1.5 µmol h⁻¹ with an H₂ yield higher than 80%. The

photocatalytic H₂ evolution was also examined by employing Ni-CuNPs/TiO₂ instead of Ni-Cu/TiO₂ under otherwise the same conditions (Fig. 4a, circle). The H₂ evolution rate and H₂ and 50%, respectively, suggesting that Ni-Cu/TiO₂ is superior to Ni-CuNPs/TiO₂ in terms of the H₂-evolution rate and H₂ yield. The lower catalytic activity of Ni-CuNPs/TiO₂ resulted from larger particles size as implied previously where the optimum loading amount of Ni and Cu is between 3-4 wt% and further increase in the loading amount resulted in lower catalytic activity.⁴¹

More obvious precursor effect was observed when SiO₂ was employed as the support. Ni-Cu/SiO₂ prepared by using Ni(NO₃)₂ and Cu(NO₃)₂ exhibited high catalytic activity in terms of an H₂ yield higher than 70% and an H₂-evolution rate of 1.3 µmol h⁻¹ (Fig. 4b, square). On the other hand, Ni-CuNPs/SiO₂ exhibited a lower H₂ yield of 20% and an H₂evolution rate of 0.2 µmol h⁻¹ (Fig. 4b, circle). TEM observations suggest that the sizes of Ni-CuNPs supported (SiO₂ were ~2 nm and 10-15 nm for Ni-Cu/SiO₂ and Ni-CuNPs/SiO₂, respectively (Fig. S2). Thus, decreasing the size of Ni-CuNPs would be important for catalysis improvement. Additionally, the higher catalytic activity of Ni-CuNPs/TiO₂ than that of Ni-CuNPs/SiO₂ may result from the higher reducibility of TiO₂.⁴¹



Fig. 4 Time courses of H₂ evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh^{*}–NA (8.8 x 10⁻⁴ M), NADH (1.0 x 10⁻³ M) and (a) 3 wt% Ni-Cu/TiO₂ (100 mg L⁻¹, black square) and 3.5 wt% Ni-CuNPs/TiO₂ (100 mg L⁻¹, red circle) and (b) 3 wt% Ni-Cu/SiO₂ (100 mg L⁻¹, black square) and 3.5 wt% Ni-CuNPs/SiO₂ (100 mg L⁻¹, red circle).

2.3 Photocatalytic H₂ evolution with Ni-CuNPs supported on Al₂O₃-SiO₂

On the contrary to Ni-CuNPs/TiO₂ and Ni-CuNPs/SiO₂, Ni-CuNPs/Al₂O₃-SiO₂ exhibited higher catalytic activity for the photocatalytic H₂ evolution than Ni-Cu/Al₂O₃-SiO₂. H₂evolution rate was 0.6 µmol h⁻¹ for the photocatalytic H₂evolution system employing Ni-CuNPs/Al₂O₃-SiO₂, which was prepared by using pre-formed Ni-Cu nanoparticles, as an H₂ evolution catalyst under otherwise the same reaction conditio for Ni-CuNPs/TiO₂. The H₂-evolution rate was slightly slower but comparable to that of Ni-CuNPs/TiO₂ (0.9 µmol h⁻¹). On the contrary, Ni-Cu/Al₂O₃-SiO₂, which was prepared by t e impregnation method using Ni(NO₃)₂ and Cu(NO₃)₂ a.

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activity for the photocatalytic H_2 evolution (Fig. 5). Thus, the structure of Ni and Cu species on the surface of Al_2O_3 -SiO₂ should be different for these catalysts.



Fig. 5 Time courses of H₂ evolution under photoirradiation (λ > 340 nm) of a deaerated mixed solution of a phthalate buffer and MeCN [1:1 (v/v)] containing QuPh⁺–NA (8.8 x 10⁻⁴ M), NADH (1.0 x 10⁻³ M) and 3 wt% Ni-Cu/Al₂O₃-SiO₂ (100 mg L⁻¹, black square) or 6.5 wt% Ni-Cu/Al₂O₃-SiO₂ (100 mg L⁻¹, red circle).

The structure of Ni-CuNPs loaded on Al_2O_3 -SiO₂ was confirmed by TEM observations. As shown in Fig. 6a, deposition of Ni-CuNPs with the size of 10-20 nm on Al_2O_3 -SiO₂ surfaces was observed as the cases of Ni-CuNPs/TiO₂ and Ni-CuNPs/SiO₂. Fewer and much smaller Ni and/or Cu metal



Fig. 6 (a,c) TEM images and (b,d) powder X-ray diffraction peaks of Ni-Cu/Al₂O₃-SiO₂ prepared by the impregnation method using (a, b) Ni-Cu nanoparticles or (c,d) Cu(NO₃)₂ and Ni(NO₃)₂. The diffraction peaks with the "*" mark originate from the Al₂O₃-SiO₂ support.

nanoparticles on Al₂O₃-SiO₂ were observed for Ni-Cu/Al₂O₃-SiO₂ as the cases of Ni-Cu/TiO₂ and Ni-Cu/SiO₂. The XRD peak around $2\theta = 43^{\circ}$ assignable to metal particles was observed for Ni-Cu/Ps/Al₂O₃-SiO₂, however, a weak shoulder peak was observed for Ni-Cu/Al₂O₃-SiO₂, suggesting that little

formation of metal particles including Ni, Cu and Ni-Cu alloy on Ni-Cu/Al₂O₃-SiO₂. Thus, the low catalytic activity of Ni-Cu/Al₂O₃-SiO₂ may be ascribed to little formation of Active alloy particles on Al₂O₃-SiO₂.

Little formation of Ni-CuNPs on Ni-Cu/Al₂O₃-SiO₂ can be explained by the presence of cation exchange sites of Al₂O₃-SiO₂ with a high surface area. In an aqueous solution, Ni²⁺ and Cu²⁺ ions can be adsorbed on cation exchange sites by electrostatic interaction. The strongly adsorbed metal ions are hardly reduced to form metal nanoparticles on the surfaces of Al₂O₃-SiO₂ with a high surface area (Scheme 2). When a support has no cation exchange sites, physisorbed Ni²⁺ and Cu²⁺, which weakly bound to the surfaces, can move around to form Ni-Cu alloy particles during the heat and reduction treatment.



Scheme 2 Formation of Ni-CuNPs on electroneutral surfaces and non-formation of Ni-CuNPs on cation exchangeable surfaces

2.4 Photocatalytic H_2 evolution with Ni-CuNPs supported on CeO₂

Both Ni-Cu/CeO₂ and Ni-CuNPs/CeO₂ exhibited very low catalytic activity for the photocatalytic H_2 evolution (Fig. 7),



Fig. 7 Time courses of H₂ evolution under photoirradiation ($\lambda > 340$ nm) of a deaerated mixed solution of a phthalate buffer and MeCN [1:1 (v/v)] containing QuPh^{*}–NA (8.8 x 10⁻⁴ M), NADH (1.0 x 10⁻³ M) and Ni-Cu/CeO₂ (100 mg⁻¹) prepared by impregnation method using Ni and Cu salts (black square, 3wt%, and Ni-Cu nanoparticles (red circle, 2.4wt%).

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although TEM measurements for Ni-CuNPs/CeO₂ indicated that Ni-CuNPs were successfully loaded on CeO₂ surfaces as same as Ni-CuNPs/Al₂O₃-SiO₂ (Fig. S3). However, the H₂ yields calculated from the amount of NADH in the reaction solutions were less than 5% and the H₂-evolution rates were lower than 0.1 µmol h⁻¹ for both Ni-Cu/CeO₂ and Ni-CuNPs/CeO₂. There are two possible reasons for such low catalytic activity of Ni-Cu/CeO₂. One is the overlapping of absorption of CeO₂ and QuPh⁺–NA (Fig. 8). Stronger light absorption (< 460 nm) by CeO₂ disturbs the light absorption by QuPh⁺–NA to form QuPh⁻–NA. The other possible reason is electronic interaction between CeO₂ and Ni-CuNPs. High mobility of lattice oxygen of CeO₂ may result in oxidation of Ni-CuNPs, which is unsuitable for proton reduction.



Fig. 8 (a) Diffuse reflectance UV-vis spectra of CeO₂ (black) and QuPh^{*}–NA (red) and (b) photographs of CeO₂ and QuPh^{*}–NA.

The rate-determining step of the photocatalytic H₂ evolution is the proton reduction on a catalyst surface or H₂ evolution. To evaluate the proton reduction and H2-evolution catalysis of Ni-CuNPs/CeO₂ under thermal reaction conditions, the proton reduction by QuPh'-NA was executed as follows: QuPh'-NA was generated by photoirradiation of a mixed solution containing QuPh⁺-NA in the presence of NADH. After QuPh⁻-NA formed, an aliquot of dispersion containing an H₂-evolution catalyst such as Ni-CuNPs/CeO2 was injected to the solution in the dark. When Ni-Cu/TiO₂ was employed as the H₂-evolution catalyst, a considerable amount of H₂ evolution was observed within 15 min (Fig. 9, circle). On the other hand, much slower H₂ evolution was observed when Ni-Cu/CeO₂ or Ni-CuNPs/CeO₂ was employed as the catalyst (Fig. 9, square and triangle). The slower H₂ evolution suggests that Ni-CuNPs are deactivated on the surfaces of CeO2. Thus, electronic interaction between CeO2 and Ni-CuNPs is the predominant reason for the low catalytic activity of Ni-CuNPs/CeO2.

3. Conclusions

Various metal oxide catalysts supporting Ni and Cu alloy nanoparticles (Ni-CuNPs) were prepared and employed for the photocatalytic H₂ evolution. Catalytically active smaller Ni-CuNPs were formed on TiO₂ and SiO₂ by impregnation of Ni(NO₃)₂ and Cu(NO₃)₂ followed by the reduction. On the contrary, Ni-CuNPs formation was not observed when Al₂O₃-SiO₂ was employed as a support instead of TiO₂ or SiO₂. To



Fig. 9 Time courses of H₂ evolution by the thermal reduction of protons by QuPh–NA (0.44 mM) in the presence of 3 wt% Ni-Cu/TiO₂ (red circle) and Ni-Cu/CeO₂ prepared by the impregnation method using Ni-Cu nanoparticles (green triangle, 2.4 wt%) or Ni(NO₃)₂ and Cu(NO₃)₂ as precursors (blue square, 3 wt%).

achieve high catalytic activity, pre-formed Ni-CuNPs (Ni-Cu/Al₂O₃-SiO₂) should be used as a precursor of Ni-CuNPs/Al₂O₃-SiO₂. These results clearly indicate t importance of Ni-Cu alloy formation, in which metal-hydrogen bond strength may be optimized. When CeO₂ was used as t... support, no active catalyst for H₂ evolution was obtained irrespective of precursors, suggesting that CeO₂ is unsuitable support for Ni-CuNPs acting as H₂ evolution catalysts. By employing pre-formed Ni-CuNPs as a precursor of a. impregnation method, the synergistic effect between Ni and Cu and the support effect can be considered separately.

4. Experimental section

4.1 Materials

All chemicals were obtained from chemical companies and used without further purification. SiO₂ (10-20 nm), TiO₂ (anatase), nickel acetylacetonate [Ni(acac)₂] and oleylaming (70%) were purchased from Sigma-Aldrich. Copper nitrate, nickel nitrate, copper acetate [Cu(OAc)₂], sodium hydroxide and sodium aluminate were obtained from Wako Pure Chemical Industries. Copper acetylacetonate [Cu(acac)₂], 1 octadecene, polyvinylpyrrolidone (PVP) and ß dihydronicotinamide adenine dinucleotide disodium salt (reduced form) (NADH) were obtained from Tokyo Chemical Industry. Acetonitrile was obtained from Nacalai Tesque. CeO2 was provided by Daiichi Kigenso Kagaku Kogyo Co., Ltd. 2-Phenyl-4-(1-naphthyl)quinolinium perchlorate (QuPh⁺-NA),³⁴ Ni-Cu alloy nanoparticles,⁴² Ni nanoparticles,⁴² Cu nanoparticles,⁴³ and Al₂O₃-SiO₂^{46,47} were prepared by literature methods. Purified water was provided by using a Millipore DIRECT-Q UV3 water purification system (18.2 MΩ cm).

4.2 Preparation of Ni-Cu alloy nanoparticles⁴²

Ni-Cu alloy nanoparticles were prepared by a literature method.⁴² Ni(acac)₂ (26 mg, 0.10 mmol) and Cu(acac)₂ (26 mg, 0.10 mmol) were dissolved in dry oleylamine (1.0 mL) at 85 °C under an Ar atmosphere. A mixed solution of oleylamine (1^o mL) and 1-octadecene (10 mL) in a 50 mL three-neck roun ¹-bottom flask was degassed under reduced pressure for 30 min at

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140 °C to remove water and oxygen, then heated to 230 °C (ramp rate: 10 °C min⁻¹) under an Ar atmosphere. The solution containing metal precursors was injected into the mixed solvents in 20 s, and was allowed to further react for 10 min at the temperature under an Ar atmosphere. After cooled to room temperature, the obtained suspension was centrifuged (9000 rpm, 10 min) to separate black precipitates. The black precipitates were washed three times by dispersion/precipitation (*n*-hexane/ethanol) cycles. The final product was dispersed in *n*-hexane (5 mL).

4.3 Preparation of Ni nanoparticles⁴²

Ni(acac)₂ (51 mg, 0.20 mmol) was dissolved in dry oleylamine (1.0 mL) at 85 °C under an Ar atmosphere. A mixed solution of oleylamine (15 mL) and 1-octadecene (5 mL) in a 50 mL threeneck round-bottom flask was degassed under reduced pressure for 30 min at 140 °C to remove water and oxygen, then heated to 230 °C (ramp rate: 5 °C min⁻¹) under an Ar atmosphere. The solution of the nickel precursor was injected into the mixed solvents in 20 s, and allowed to react for 5 min at this temperature under an Ar atmosphere. After cooled to room temperature, the obtained suspension was centrifuged (9000 rpm, 10 min) to separate black precipitates. The black precipitates were washed three times by dispersion/precipitation (*n*-hexane/ethanol) cycles. The final product was dispersed in *n*-hexane (5 mL).

4.4 Preparation of Cu nanoparticles⁴³

 $Cu(OAc)_2$ (60 mg, 0.30 mmol) and PVP (0.40 g) were dissolved in water (20 mL) in a 50 mL three-neck round-bottom flask at room temperature. Then, an aqueous solution of NaBH₄ (11 mg, 0.30 mmol) and NaOH (12 mg, 0.30 mmol) was injected into the Cu(OAc)₂/PVP aqueous solution and stirred for 15 min under an Ar atmosphere at room temperature. After the reaction, acetone was added to cause flocculation and then the suspension was centrifuged (9000 rpm, 10 min) to separate black precipitates. The black precipitates were washed three times by dispersion/precipitation (acetone/ethanol) cycles. The final product was dispersed in ethanol (5 mL).

4.5 Preparation of Al₂O₃-SiO₂^{46,47}

 SiO_2 was suspended in an aqueous solution (50 mL) containing sodium aluminate (1.3 g, 16 mmol) and stirred for 20 h at room temperature. The precipitate was collected by filtration and dried at 120 °C. The dried sample was calcined at 550 °C (ramp rate: 5 °C min⁻¹) for 6 h in air.

4.6 Preparation of Ni-Cu loaded on metal oxides by using Ni(NO₃)₂ and Cu(NO₃)₂ as precursors

A typical procedure for the preparation of metal oxides loading Ni and Cu by an impregnation method is as follows: A metal oxide support (350 mg) was immersed in an aqueous solution containing Ni(NO₃)₂· θ_2O (27 mg, 92 mmol) and Cu(NO₃)₂· θ_2O (21 mg, 85 mmol) and sonicated for 30 min. The obtained catalyst precursor was dried at 60 °C in an oven and calcined at 350 °C (ramp rate: 5 °C min⁻¹) for 4 h under air. The obtained powder was immersed in an aqueous solution containing NaBH₄ to reduce oxides of Cu and Ni before catalysis evaluation.

4.7 Preparation of Ni-Cu alloy nanoparticles loaded on metal oxides

A metal oxide support (50 mg) was $\operatorname{immersed}_{341^{\circ} \oplus 445^{\circ} \oplus 455^{\circ} \oplus 455^{\circ}$

4.8 Transmission electron microscopy (TEM)

The sizes and shapes of nanoparticles were determined from bright field images using a JEOL JEM-2100 that has a thermal field emission gun with an accelerating voltage of 200 kV. The observed samples were prepared by dropping a dispersion of catalysts and allowing the solvent to evaporate and then scooped up with an amorphous carbon supporting film on a (grid.

4.9 Catalysts characterisation by powder X-ray diffraction, diffused reflectance UV-vis spectroscopy and dynamic laser scattering

X-ray diffraction patterns were recorded by a Rigaku MiniFlex 600. Incident X-ray radiation was produced by a Cu X-ray tube operating at 40 kV and 15 mA with Cu $K\alpha$ radiation of 1.54 Å. The scanning rate was 2° min⁻¹ from 10° to 80° in 2 θ . The diffuse reflectance UV-vis spectra were recorded with a Jasco V-670 spectrophotometer equipped with an integrating sphere module (SIN-768). Reflectance obtained for each sample was converted to $f(R_{\infty})$ values according to the Kubelka-Munk theory, $f(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty}$, where R_{∞} is the reflectance of the sample layer. BaSO₄ was used for back ground spectra measurements. Dynamic light scattering (DLS) measurements were performed with a Zetasizer Nano ZS instrument (Malvern Instruments Ltd., U.S.A.).

4.10 N₂ adsorption for BET surface area determination

Nitrogen adsorption-desorption at 77 K was performed with a Belsorp-mini (BEL Japan, Inc.) within a relative pressure range from 0.01 to 101.3 kPa. A sample mass of ~100 mg was used for adsorption analysis after pretreatment at 120 °C for 1 h under vacuum conditions and kept in N₂ atmosphere until N₂, adsorption measurements. The samples were exposed to a mixed gas of He and N₂ with a programmed ratio and adsorbed amount of N₂ was calculated from the change of pressure in a cell after reaching the equilibrium (at least 5 min). The surface area of each catalyst was determined by the Brunauer-Emmett-Teller (BET) method for multiple N₂ adsorption amounts under the conditions of partial pressure less than 0.3. The Brunaue Emmett-Teller (BET) surface areas of TiO₂, SiO₂, SiO₂-Al₂O₃, CeO₂ were determined to be 6.8, 52, 118 and 162 m² g⁻¹, respectively.

4.11 Photocatalytic H₂ evolution

A mixed solution (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh⁺–NA (0.88 mM), NAE \pm (1.0 mM) and an H₂-evolution catalyst was flushed with N₂ gas. The solution was then irradiated for a certain time with a xen⁻¹

lamp (Ushio Optical, Model X SX-UID 500X AMQ) through a colour filter glass (Asahi Techno Glass L39) transmitting $\lambda >$ 340 nm at room temperature. After 1 min stirring in the dark, gas in a headspace was analysed by Shimadzu GC-14B gas chromatography (detector: TCD, column temperature: 50 °C, column: active carbon with the particle size 60-80 mesh, carrier gas: N₂ gas) to determine the amount of evolved H₂.

4.12 H₂ evolution with QuPh'-NA in the dark^{39,41}

Typically, a mixed solution (2.0 mL) of a deaerated phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing QuPh⁺–NA (0.44 mM) and NADH (1.0 mM) was photoirradiated for 5 min with a Xe lamp through a colour filter glass transmitting $\lambda >$ 340 nm. Formation of QuPh–NA was confirmed by the change of UV-vis absorption spectra. Next, a deaerated aqueous solution containing Ni-Cu/MOx (0.1 mg) was added to the photoirradiated solution in the dark with stirring. The absorbance change at 420 nm due to QuPh–NA was continuously monitored by UV-vis spectrometer.²⁹ Evolved H₂ in the headspace of a reaction vial was intermittently quantified by a gas chromatograph.

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Notes and references

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Which is the better precursor to be an H₂ evolution catalyst?



Catalysis of Ni-Cu alloy nanoparticles loaded on various metal oxides for photocatalytic H₂ evolution depends on preparation methods and supports.