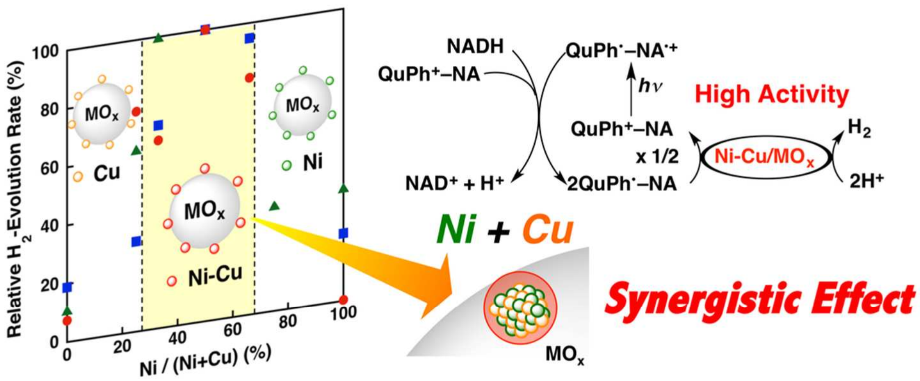

Ni and Cu supported on TiO2 or SiO2 synergistically acted as H2-evolution catalysts in a photocatalytic system.
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Synergistic effects of Ni and Cu supported on TiO_2 and SiO_2 on photocatalytic H_2 evolution with an electron donor-acceptor linked molecule

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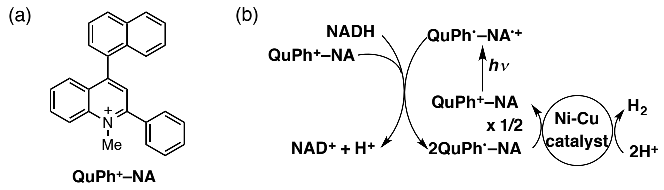
Synergistic effects of Ni and Cu supported on metal oxides on their catalytic activity for hydrogen evolution were observed in photocatalytic hydrogen evolution with 2-phenyl-4-(1-naphthyl)quinolinium ion ($QuPh^+$–NA) and β-dihydronicotinamide adenine dinucleotide (NADH) as a photocatalyst and an electron donor, respectively. Among the catalysts of Ni and Cu supported on TiO_2, SiO_2, SiO_2-Al_2O_3 and CeO_2, Ni and Cu supported on TiO_2 and SiO_2 exhibited high catalytic activity at the wide range of Ni contents [Ni/(Ni+Cu)] from 30 to 70%, while TiO_2 and SiO_2 solely supporting Ni or Cu showed insignificant catalytic activity. The catalytic activity of Ni and Cu supported on TiO_2 and SiO_2 depends on preparation methods of the catalysts. The catalysts prepared by a co-impregnation method, in which a precursor solution containing both $Ni(NO_3)_2$ and $Cu(NO_3)_2$ was used for the impregnation, showed high catalytic activity, whilst catalysts prepared by a sequential impregnation method, in which $Ni(NO_3)_2$ and $Cu(NO_3)_2$ were impregnated and calcined successively, exhibited low catalytic activity. TEM observations with the energy dispersive X-ray spectroscopy (EDS) elemental mapping of these catalysts revealed that Ni and Cu were closely located on support surfaces in a catalyst prepared by the co-impregnation method, whereas Ni and Cu were separated in the catalyst prepared by the sequential impregnation method. These results suggest that the close location of Ni and Cu is necessary to exhibit the high catalytic activity. Such synergistic effect among base metals and metal oxide supports would be a key to develop active catalysts for the hydrogen evolution without using platinum group metals.

Introduction

Hydrogen (H_2) production utilising solar energy attracts much attention from the viewpoint of storage of natural energy as chemical energy.[1-11] A photocatalytic H_2-evolution system, which mimics the natural photosynthesis, can be constructed by using an electron donor, a photosensitiser, an electron mediator and an H_2-evolution catalyst.[12-20] For example, H_2 evolution can be observed by the photoirradiation of a solution containing ethylenediamine tetraacetic acid disodium salt, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), methyl viologen and Pt particles as an electron donor, a photosensitiser, an electron mediator and a hydrogen evolution catalyst, respectively.[21] This type of H_2-evolution systems requires a sacrificial electron donor, however, a high quantum efficiency and rational improvement in catalysis are achievable by replacing each component after modifications.[8,22,23] As a component of H_2-evolution catalyst, Pt particles have been most widely used because of its very low overpotential for proton reduction.[24-26] However, avoiding or reducing the use of Pt metal is strongly demanded because of its high cost and limited supply.[22,27]

Alternative to Pt nanoparticles (PtNPs), Ru nanoparticles (RuNPs) and Ni nanoparticles (NiNPs) have been demonstrated to act as H_2-evolution catalysts in reaction systems using organic electron donor-acceptor linked dyads as photocatalysts.[28,29] RuNPs exhibit virtually the same activity of PtNPs, however, the catalytic activity of NiNPs was lower than those of PtNPs and RuNPs.[28-30] For the improvement of Ni catalysis, concomitant use of other metals such as Cu, Pd and Co is promising as reported for various catalytic reactions.[31-33] For example, Ni-Cu alloy nanoparticles have been reported to exhibit catalytic activity for thermal H_2 evolution by hydrolysis of sodium borohydride higher than nanoparticles solely composed of Ni or Cu.[34] Such synergistic effect between Ni and Cu has been also reported for supporting catalysts using SiO_2,[35] Al_2O_3,[36-38] CeO_2[39], ZrO_2[40] and TiO_2[41] for high temperature reactions such as ethanol steam reforming. In general, supporting catalytically active metals on a metal oxide is beneficial for improvements not only in catalytic activity by metal-support interaction but also in durability of the metal nanoparticles. However, there have been no systematic studies on the synergistic and support effects of Ni and Cu catalysts in photocatalytic H_2 evolution.

We report herein H_2-evolution catalysis of Ni-Cu/TiO_2 and Ni-Cu/SiO_2 in an efficient photocatalytic H_2-evolution system composed of a donor-acceptor linked dyad, 2-phenyl-4-(1-naphthyl)quinolinium ion ($QuPh^+$–NA), as a photocatalyst and β-dihydronicotinamide adenine dinucleotide (NADH) as a sacrificial electron donor. The chemical structure of the organic photocatalyst used in this study and the overall reaction scheme are depicted in Scheme 1. Upon photoexcitation of $QuPh^+$–NA,



Scheme 1 (a) Structure of $QuPh^+$–NA and (b) the overall photocatalytic cycle for H_2 evolution using $QuPh^+$–NA and an Ni-Cu catalyst.

electron transfer from the NA moiety to the singlet excited state of the $QuPh^+$ moiety occurs to produce the electron-transfer state ($QuPh^•$–$NA^{•+}$).[42,43] Then, electron transfer from NADH to $QuPh^•$–$NA^{•+}$ occurs to produce $NADH^{•+}$ and $QuPh^•$–NA.[28] $NADH^{•+}$ undergoes deprotonation releasing one proton to afford $NAD^•$ that can transfer an electron to $QuPh^+$–NA to produce NAD^+ and $QuPh^•$–NA.[28] Two equivalents of $QuPh^•$–NA thus produced can inject two electrons to Ni-Cu catalysts to evolve H_2 from two protons.[28] It should be noted that no electron mediator, which is frequently used in homogeneous photocatalytic H_2 production, is required in the present photocatalytic system, because the electron-transfer state of $QuPh^+$–NA has a sufficient lifetime for the oxidation of NADH and also for electron injection to Ni-Cu catalysts.[25,28-30] In this reaction system, effects of Ni/Cu ratio, preparation methods, surface area and morphology of SiO_2, and surface area and crystal structure of TiO_2 on the catalysis of Ni-Cu/TiO_2 and Ni-Cu/SiO_2 for H_2 evolution were examined to clarify the conditions to achieve the synergistic and support effect, which would be a key to develop active catalysts alternative to platinum group metals.

2. Result and discussion

2.1 Photocatalytic H_2 evolution with Ni and a transition metal supported on metal oxides

Effect of concomitant use of Ni with another metal, Cu, Co or Fe, supported on TiO_2 or SiO_2 was examined on the H_2-evolution catalysis of Ni. These catalysts were prepared by a co-impregnation method. Photocatalytic H_2 evolution was performed by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of MeCN and a phthalate buffer (pH 4.5) [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and TiO_2 or SiO_2 supporting Ni and another metal (M) (100 mg L^{-1}, M = Cu, Co or Fe), in which the loading amount was 1.5 wt% for each of Ni and M, as shown in Fig. 1.

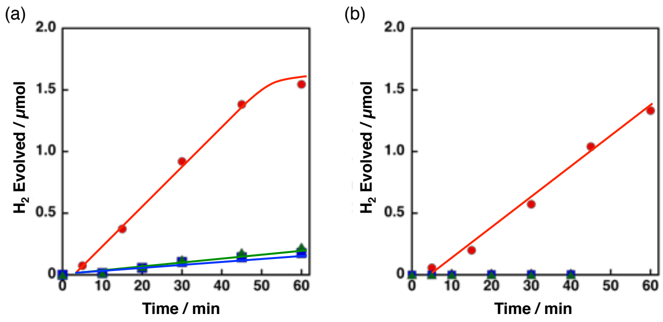


Fig. 1 Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and (a) 3 wt% Ni-M/TiO_2 or (b) 3 wt% Ni-M/SiO_2 (100 mg L^{-1}, M = Cu (red circle), Co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

Significant amount of H_2 evolution was observed only for Ni-Cu/TiO_2. TiO_2 is a well-known photocatalyst, however, no H_2 evolution was confirmed for a reaction suspension without $QuPh^+$–NA under the present reaction conditions (Fig. S1a†). From the reaction suspension using Ni-Cu/TiO_2 as an H_2-evolution catalyst in the presence of $QuPh^+$–NA, continuous H_2 evolution was observed after a short induction period for ca. 5 min. This induction period is for the reduction of NiO, $NiCuO_2$ and/or Cu_2O species to be catalytically active metallic species, because the presence of NiO (JCPDS card No. 78-0643) species in as-prepared Ni-Cu/TiO_2 was confirmed by the diffraction peak around 2θ = 43.4° in the powder X-ray diffraction (Fig. 2). This peak may overlap with the diffraction peaks from $NiCuO_2$ (JCPDS card No. 6-720) and Cu_2O (JCPDS card No. 05-0667), which have been reported to provide the diffraction peaks at 2θ = 43.8° and 42.5°, respectively, because no diffraction peak was observed at 2θ = 35.6°, which indicates formation of CuO (JCPDS card No. 05-0661). Powder XRD measurements were also performed for the Ni-Cu/TiO_2 after the photocatalytic

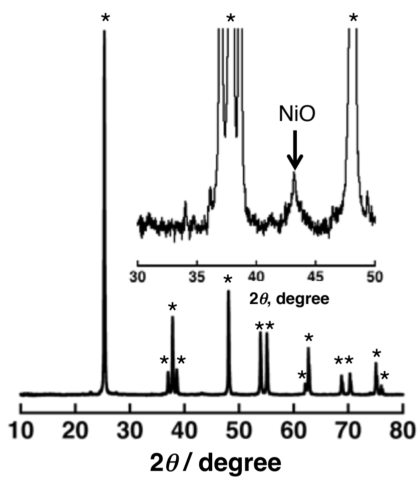


Fig. 2 Powder X-ray diffraction patterns of 3 wt% Ni-Cu/TiO_2 [Ni/Cu = 1:1 (w/w)]. The peaks with * originate from TiO_2 (anatase).

reaction. No diffraction peak indicating formation of Ni^0 or Cu^0 species was clearly observed in the peak appeared around 43° (Fig. S2).

The initial H_2-evolution rate for the reaction system using Ni-Cu/TiO_2 was determined to be 1.7 μmol h^{-1} from the initial (45 min) slope the reaction system. The apparent quantum yield obtained under photoirradiation (λ = 350±10 nm) for 1 h was 1.1%, where photon flux determined by using actinometer was 2.89×10^{-9} einstein s^{-1}. The rate was 10 times slower compared with the H_2-evolution rate determined for the reaction system using Pt nanoparticles instead of Ni-Cu/TiO_2, in which the weight of used Pt was the same as that of Ni-Cu in the Ni-Cu/TiO_2, however, the maximum H_2 yield based on the amount of NADH reached as high as 87% (1.7 μmol) without using precious metals. The H_2 evolution ceasing by cutting off the light in the course of the reaction assures that the H_2 evolution proceeds photocatalytically (Fig. S1b†). Also a photocatalytic system using a reduced amount of $QuPh^+$–NA (0.11 mM) evolved H_2 repeatedly for five times by the addition of NADH to the reaction solution after ceasing H_2 evolution (Fig. S3†) and the turnover number based on $QuPh^+$–NA reached 21. On the other hand, the amount of H_2 evolution was less than 0.1 μmol from the suspensions containing TiO_2 supporting Ni-Fe and Ni-Co as H_2-evolution catalysts by photoirradiation for 60 min (Fig. 1a, green triangle and blue square, respectively). Similarly, a negligible amount of H_2 evolution was observed from the reaction suspensions containing Ni/TiO_2 and Cu/TiO_2 as the H_2-evolution catalysts (Fig. S4a†). Thus, Cu acts as the only suitable counterpart of Ni to achieve synergistic effects on the H_2-evolution catalysis.

Similar synergistic effects of Ni and Cu in the photocatalytic H_2 evolution were observed for Ni-Cu/SiO_2 as shown in Fig. 1b, in which the maximum H_2 yield reached to 77% (1.5 μmol) with the H_2-evolution rate of 1.3 μmol h^{-1} determined from the initial (60 min) slope. No H_2 evolution was confirmed for Ni-Fe/SiO_2 and Ni-Co/SiO_2 by photoirradiation for 60 min. Insignificant amount of H_2 evolution was observed from the reaction suspensions employing Ni/SiO_2 and Cu/SiO_2 as the H_2-evolution catalysts (Fig. S4b†). These results obviously indicate that addition of Cu is effective to improve the catalysis of both Ni supported on TiO_2 and SiO_2 although the addition of Fe or Co was unprofitable.

Support effects on the catalytic activity of Ni-Cu catalysts were also examined by employing TiO_2, SiO_2, SiO_2-Al_2O_3 and CeO_2 as supports. Ni and Cu were loaded on the supports by a co-impregnation method where the loading amount was 1.5 wt% for each of Cu and Ni. The Brunauer-Emmett-Teller (BET) surface areas of TiO_2, SiO_2, SiO_2-Al_2O_3, CeO_2 were determined to be 6.8, 52, 118 and 162 m^2 g^{-1}, respectively. The surface area of the TiO_2 is significantly low compared with others, however, the effect of surface areas on the catalytic activity of Ni-Cu/TiO_2 is limited (vide infra, Fig. 12). Powder X-ray diffraction patterns of these metal oxides suggested that SiO_2 and SiO_2-Al_2O_3 are amorphous nature, whilst TiO_2 and CeO_2 are crystalline in the anatase and fluorite structures, respectively (Fig. S5†). These metal oxide supports were chosen from those often used for supporting Ni for various reactions.[39-41] As mentioned above, both TiO_2 and SiO_2 supporting Ni-Cu showed high catalytic activity in terms of both H_2 yields and H_2-evolution rates (dashed lines in Fig. 3) in the photocatalytic H_2 evolution. On the other hand, Ni-Cu supported on SiO_2-Al_2O_3 (red triangle) and CeO_2 (blue inverse triangle) showed no significant activity for the photocatalytic H_2 evolution as shown in Fig. 3. Although the origin of the support effect is still unclear, the readily reducible nature may be beneficial to produce active sites at perimeter between Ni-Cu species and the supports. The small negative standard enthalpies of formation for TiO_2 and SiO_2 (-940 and -910 kJ mol^{-1}, respectively) compared to those for CeO_2 and Al_2O_3 (-1089 and -1676 kJ mol^{-1}, respectively) suggest that TiO_2 and SiO_2 are more readily reducible than CeO_2 and SiO_2-Al_2O_3.[44] Thus, SiO_2 and TiO_2 could be suitable supports to achieve Ni-Cu species active for photocatalytic H_2 evolution.

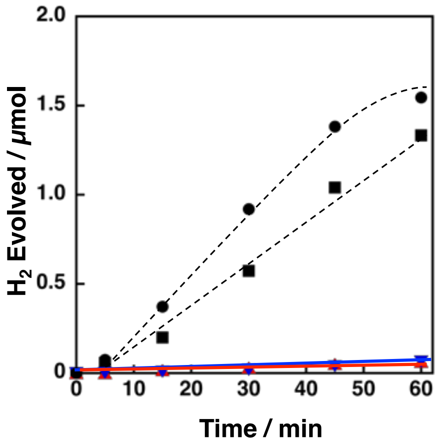


Fig. 3 Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and 3 wt% Ni-Cu/MO_x (100 mg L^{-1}, MO_x = TiO_2, circle; SiO_2, square; SiO_2-Al_2O_3, red triangle; CeO_2, blue inverse triangle).

2.2 Effect of preparation methods on H_2-evolution catalysis of Ni-Cu supported on TiO_2 and SiO_2

The catalytic activity of Ni-Cu/TiO_2 and Ni-Cu/SiO_2 was highly influenced by preparation methods. When Ni-Cu/TiO_2 prepared by a co-impregnation method using the solution containing both $Cu(NO_3)_2$ and $Ni(NO_3)_2$ was examined for the photocatalytic H_2 evolution, a fast H_2-evolution rate was observed (Fig. 1a, 1.7 μmol h^{-1}). On the other hand, the H_2-evolution rates were as low as 0.5 and 0.3 μmol h^{-1} with catalysts prepared by a sequential impregnation method, in which a $Cu(NO_3)_2$ solution was impregnated to Ni/TiO_2 or an $Ni(NO_3)_2$ solution to Cu/TiO_2 (red circle and blue square in Fig. 4a, respectively). Similar influence of preparation methods was also observed for Ni-Cu/SiO_2 as shown in Fig. 4b. The H_2-evolution rate obtained for Ni-Cu/SiO_2 prepared by co-impregnation was significantly larger (Fig. 1b, 1.3 μmol h^{-1}) than those obtained for Ni-Cu/SiO_2 catalysts prepared by the sequential impregnation method, 0.1 and 0.2 μmol h^{-1}.

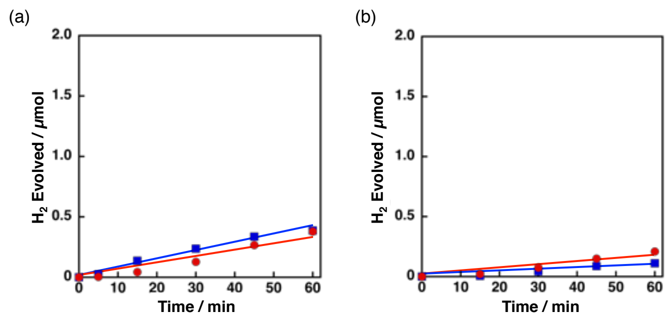


Fig. 4 Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8×10^{-4} M), NADH (1.0×10^{-3} M) and (a) 3 wt% Ni-Cu/TiO_2 (100 mg L^{-1}) prepared by a sequential impregnation method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

2.3 Characterisation of Ni-Cu supported on TiO_2 and SiO_2 by UV-vis and TEM with EDS elemental mapping

The Ni-Cu/TiO_2 and Ni-Cu/SiO_2 catalysts prepared by co-impregnation and sequential impregnation methods were characterised by diffuse reflectance UV-vis spectroscopy (DRS). The DRS of Ni-Cu/TiO_2 catalysts prepared by different procedures are shown in Fig. 5a. Ni-Cu/TiO_2 prepared by the co-impregnation method (red) showed strong absorption in the visible region (400-800 nm) compared with Ni-Cu/TiO_2 catalysts prepared by the sequential impregnation method, Cu impregnated to Ni/TiO_2 (blue) or Ni impregnated to Cu/TiO_2 (green). The peaks appeared around 600-800 nm in DRS of Ni-Cu/TiO_2 catalysts differ from superposition of DRS of Ni/TiO_2 and Cu/TiO_2 depicted in Fig. S6a†, suggesting that a part of Ni and Cu species have electronic interaction on the TiO_2 surfaces.

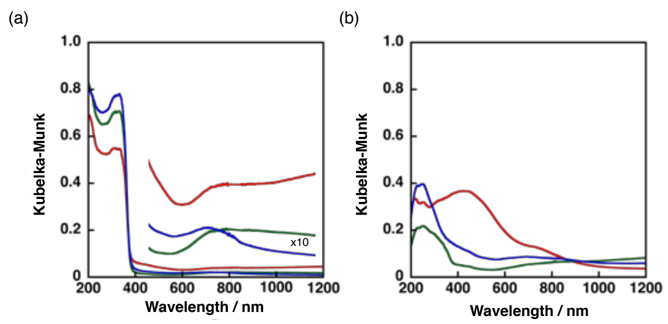


Fig. 5 Diffuse reflectance UV-vis spectra of (a) Ni-Cu/TiO_2 and (b) Ni-Cu/SiO_2 catalysts prepared by co-impregnation (red) and sequential impregnation method (Cu impregnated to Ni/MO_2, blue and Ni impregnated to Cu/MO_2, green. M = Ti or Si).

More obvious difference in DRS was observed among Ni-Cu/SiO_2 catalysts prepared by different methods as shown in Fig. 5b. The DRS of Ni/SiO_2 and Cu/SiO_2 are depicted in Fig. S6b†. The DRS of the Ni-Cu/SiO_2 catalyst prepared by the co-impregnation method (red) showed absorption maxima around 480 nm, whereas small shoulder around 400 nm was observed for the Ni-Cu/SiO_2 catalysts prepared by the sequential impregnation method. The difference in the absorption at the visible region provides the difference in colour. The origin of brownish colour of the Ni-Cu/SiO_2 catalyst prepared by the co-impregnation method can be ascribed to the formation of $NiCuO_2$ on SiO_2 surfaces, which has been proposed for Ni-Cu supported on cordierite in the literature.[45]

The difference in the structures of the Ni-Cu/SiO_2 catalysts prepared by the co-impregnation and the sequential impregnation methods was confirmed by TEM measurements in the atomic level with the energy dispersive X-ray spectroscopy (EDS) elemental mapping for Si, Cu and Ni. Fig. 6 shows a high-angle annular dark field scanning TEM (HAADF-STEM) image of a particles in size of 20 nm formed on Ni-Cu/SiO_2 prepared by the co-impregnation method. The

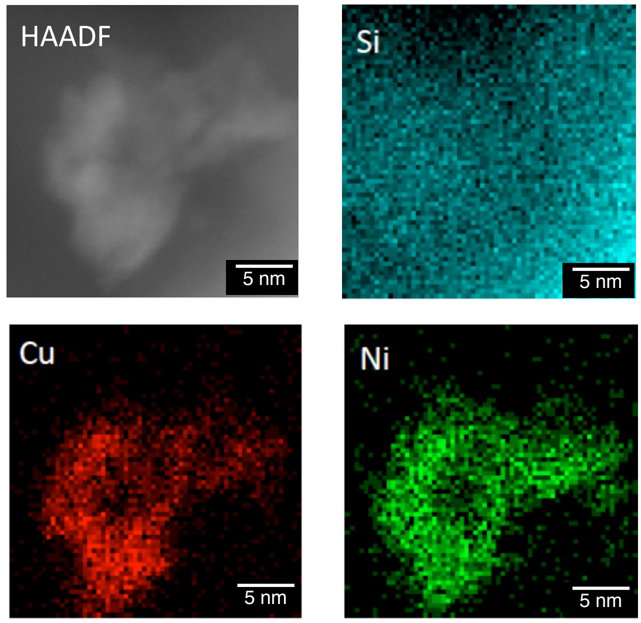


Fig. 6 HAADF-STEM and energy dispersive X-ray spectroscopy (EDS) elemental mapping of Ni-Cu/SiO_2 prepared by the co-impregnation method for Si, Cu and Ni.

EDS elemental mapping for Si (blue), Cu (red) and Ni (green) indicates that the particle observed in the HAADF-STEM image is composed of both Cu and Ni. On the other hand, the particles on Ni-Cu/SiO_2 prepared by the sequential method, in which Cu was impregnated to Ni/SiO_2, showed separated deposition of Cu and Ni. As shown in Fig. 7, comparison of EDS elemental mapping for Cu (red) and Ni (green) with the HAADF-STEM image indicates that the brightest part of the HAADF-STEM image is a Cu-rich region and small particles appeared in the upper middle are Ni-rich or only Ni. These observations suggest that suitable selection of preparation methods is necessary to achieve close location of Ni and Cu on the surfaces of Ni-Cu/SiO_2.

2.4 Optimisation of Ni/Cu ratio, loading amount of Ni-Cu and structure of TiO_2 and SiO_2 supports

The catalytic activity of Ni-Cu/SiO_2 with different loading amounts of Ni-Cu [1:1 (w/w)] ranging from 2 to 5 wt% was examined for the photocatalytic H_2 evolution. The H_2-evolution

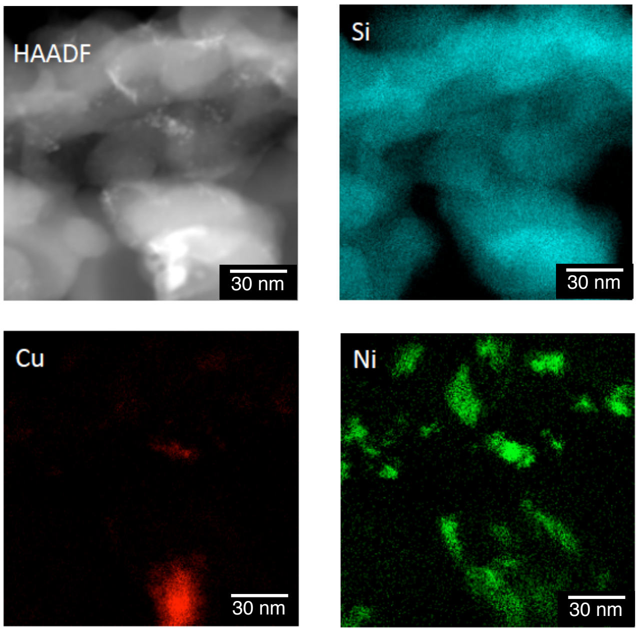


Fig. 7 HAADF-STEM and EDS elemental mapping of Ni-Cu/SiO_2 prepared by the sequential impregnation method (Ni impregnated to Cu/SiO_2) for Si, Cu and Ni.

rates determined from the slopes of time courses of H_2 evolution (Fig. 8a) at the reaction time from 5 to 30 min were 0.8, 1.2, 1.3 and 1.0 μmol h^{-1} for Ni-Cu/SiO_2 with the loading amount of Ni-Cu of 2, 3, 4 and 5 wt%, respectively. The total H_2 yield obtained for 3 wt% Ni-Cu/SiO_2 was 77%, which is higher than those of 2, 4 and 5 wt% Ni-Cu/SiO_2 (28, 54 and 45%, respectively). Thus, loading amount of Ni-Cu around 3-4 wt% is optimum to achieve high catalytic activity for Ni-Cu/SiO_2.

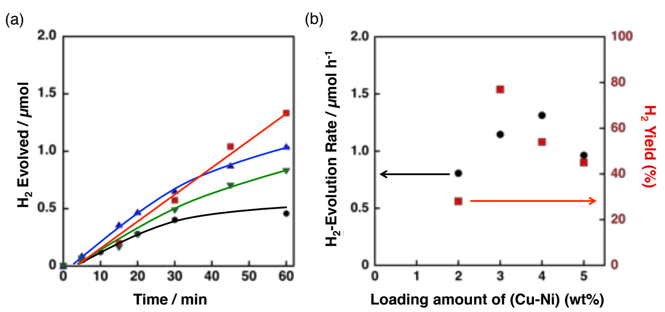


Fig. 8 (a) Time course of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8 × 10^{-4} M), NADH (1.0 × 10^{-3} M) and Ni-Cu/SiO_2 [Ni/Cu = 1/1 (w/w)] (100 mg L^{-1}; 2 wt%, black circle; 3 wt%, red square; 4 wt%, blue triangle; 5 wt%, inverse triangle) prepared by a co-impregnation. (b) Effect of loading amount of Cu and Ni on initial (30 min) H_2-evolution rate and H_2 yield.

The effect of the ratio between Ni and Cu on the catalytic activity of 3 wt% Ni-Cu/SiO_2 was also examined. Fig. 9a shows the time courses of H_2 evolution in the photocatalytic H_2 evolution using Ni-Cu/SiO_2 catalysts with Ni contents, Ni/(Ni+Cu) ratio, from 0 to 100%. H_2-evolution rates higher than 0.8 μmol h^{-1} was observed for the catalysts with Ni contents from 25 to 67% as shown in Fig. 9b. The effect of Cu

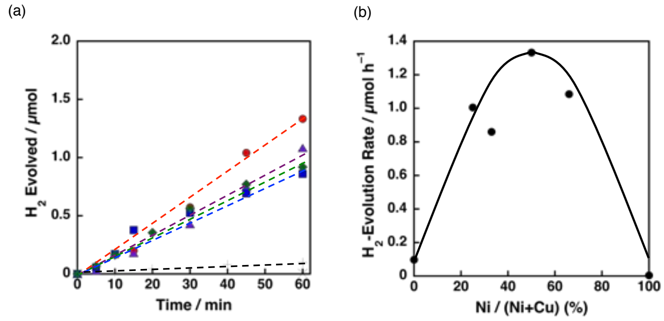


Fig. 9 (a) Time courses of H_2 evolution by photoirradiation (λ > 340 nm) of an mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8 × 10^{-4} M), NADH (1.0 × 10^{-3} M) and 3 wt% Ni-Cu/SiO_2 (100 mg L^{-1}) with various Ni contents prepared by the co-impregnation method. [Ni/(Ni+Cu) = 0% (plus), 25% (green diamond), 33% (blue square), 50% (red circle), 67% (purple triangle) and 100% (inverse triangle)] (b) Plot of initial H_2-evolution rate *vs.* Ni contents.

on the reducibility of NiO on SiO_2 has been discussed by temperature-programmed reaction with flowing H_2/Ar in the literature.[35c-e] The reduction temperature of NiO on SiO_2 around 580 °C decreased to below 300 °C for Ni-Cu/SiO_2 under 10%H_2/Ar flowing.[35c] The enhanced reducibility of NiO on Ni-Cu/SiO_2 catalysts resulted in high catalytic activity for ethanol steam reforming.[35c] The promotional effect of Cu(O) on the reduction of NiO can be also expected for the present photocatalytic H_2-evolution system although the reaction temperature was as low as room temperature.

Effects of the morphologies and the surface areas of SiO_2 supports on the catalysis of Ni-Cu/SiO_2 for H_2 evolution were also examined by employing additional two SiO_2 supports, which have a spherical morphology with the BET surface area similar to that of an SiO_2 support [unshaped, low surface area (unshaped LS)] used in above experiments and an unshaped morphology with higher BET surface area. The morphologies of SiO_2 supports were confirmed by TEM observations as shown in Fig. S7[†] and the BET surface areas were determined to be 59 m^2 g^{-1} and 420 m^2 g^{-1} for the SiO_2 (spherical) and the SiO_2 [unshaped, high surface area (unshaped HS)], respectively. With these SiO_2 supports, 3 wt% Ni-Cu/SiO_2 [Ni/Cu = 1:1 (w/w)] were prepared by the co-impregnation method and used as the H_2-evolution catalysts in the photocatalytic H_2-evolution system. The time courses of the H_2 evolution are shown in Fig. 10a. The H_2-evolution rates were 0.4 and 0.8 μmol h^{-1} for Ni-Cu/SiO_2 catalysts with spherical and unshaped (high surface area) morphologies, respectively. The H_2-evolution rate for Ni-Cu/SiO_2 (spherical) significantly lower than that for Ni-Cu/SiO_2 [unshaped LS (52 m^2 g^{-1})] (1.3 μmol h^{-1}) indicates that the morphology of SiO_2 affects the catalysis of Ni-Cu/SiO_2. The lower catalytic activity by employing SiO_2 (spherical) as a support has been reported for Ru/SiO_2 in the photocatalytic H_2 evolution.[30] The smooth surfaces of the SiO_2 (spherical) more readily promote the adhesive interaction among the SiO_2 particles through supporting metals than the rough surfaces of the SiO_2 (unshaped).[30] Thus, a part of supporting metals acting as the adhesive among SiO_2 particles hardly work as the H_2-

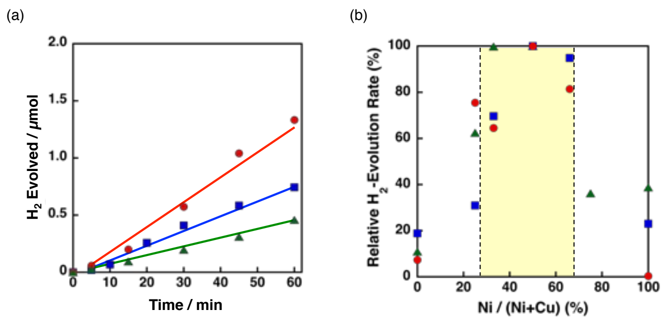


Fig. 10 (a) Time course of H_2 evolution by photoirradiation (λ > 340 nm) of an mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8 × 10^{-4} M), NADH (1.0 × 10^{-3} M) and 3 wt% Ni-Cu/SiO_2 (100 mg L^{-1}). (a) SiO_2 with spherical morphology (green triangle) and unshaped LS (red circle) and unshaped HS (blue square). (b) Plot of initial H_2-evolution rate *vs.* Ni contents.

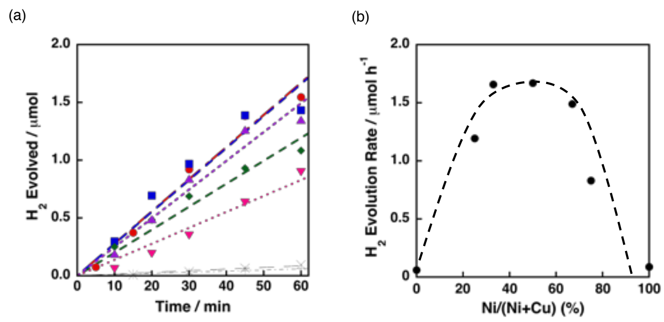


Fig. 11 (a) Time course of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8 × 10^{-4} M), NADH (1.0 × 10^{-3} M) and 3 wt% Ni-Cu/TiO_2 (100 mg L^{-1}) with various Ni contents prepared by a co-impregnation. [Ni/(Ni+Cu) = 0% (plus), 25% (green diamond), 33% (blue square), 50% (red circle), 67% (purple triangle), 75% (pink inverse triangle) and 100% (cross)] (b) Plot of initial H_2-evolution rate *vs.* Ni contents.

evolution catalyst. A similar mechanism is applicable to the present Ni-Cu/SiO_2 (spherical) catalysts. For the effects of surface areas, the catalytic activity of Ni-Cu/SiO_2 (unshaped LS) was higher than that of Ni-Cu/SiO_2 (unshaped HS). This result may suggest that lower surface area of the SiO_2 is favourable to closely locate Ni and Cu to each other. Thus, both morphologies and surface areas of SiO_2 supports affect the catalysis of Ni-Cu/SiO_2.

The effect of the ratio between Ni and Cu was also investigated for 3 wt% Ni-Cu/SiO_2 (spherical) and 3 wt% Ni-Cu/SiO_2 (unshaped HS) in the photocatalytic H_2 evolution. The time courses of the H_2-evolution rates in the photocatalytic H_2 evolution are shown in Fig. S8[††]. Fig. 10b shows the relative H_2-evolution rates depending on the Ni/(Ni+Cu). High catalytic activity was achieved at the content of Ni between 30 and 67% as observed for Ni-Cu/SiO_2 (unshaped LS) shown in Fig. 9b.

Catalytic activity of Ni-Cu/TiO_2 for the H_2 evolution dependent on the Ni content was also investigated in the photocatalytic H_2 evolution. Fig. 11a demonstrates the time courses of H_2 evolution in the photocatalytic reaction systems using Ni-Cu/TiO_2 with different Ni contents. H_2-evolution rates higher than 1.5 μmol h^{-1} were obtained for the Ni-Cu/TiO_2 catalysts with 33-67% of Ni contents. The origin of synergistic effect of Ni and Cu on TiO_2 has been discussed by H_2-TPR measurements in the literature.[41a] The reduction temperature of NiO on TiO_2 was lowered in the presence of CuO from ca. 500 °C to 300 °C by increasing the content of CuO.[41a] Although the photocatalytic H_2 evolution was performed at room temperature, readily reducible nature of NiO influenced by the addition of Cu would be beneficial to form metallic Ni species on the TiO_2 support.

Effects of crystal structures and the BET surface areas of TiO_2 supports were examined by using a series of 3 wt% Ni-Cu/TiO_2 catalysts in the photocatalytic H_2 evolution. The crystal structures confirmed by XRD (Fig. S9[†]) and BET surface areas of the TiO_2 supports were rutile with high surface area (rutile HS, 250 m^2 g^{-1}), rutile with low surface area (rutile LS, 0.3 m^2 g^{-1}) and anatase with high surface area (anatase HS, 46 m^2 g^{-1}). The TiO_2 support used in the above mentioned experiments has anatase structure with low surface area (anatase LS, 6.8 m^2 g^{-1}) (vide supra). With these TiO_2 supports, 3 wt% Ni-Cu/TiO_2 [Ni/Cu = 1:1 (w/w)] catalysts were prepared by the co-impregnation method. Fig. 12 shows the time courses of H_2 evolution in the photocatalytic H_2 evolution performed with these Ni-Cu/TiO_2 (rutile HS, rutile LS, anatase HS) catalysts as the H_2-evolution catalysts. The H_2-evolution rates determined from the initial (60 min) slopes were 1.5, 1.3 and 1.3 μmol h^{-1} for Ni-Cu/TiO_2 (rutile HS, rutile LS and anatase HS), respectively, which are comparable to that for Ni-Cu/TiO_2 (anatase LS) (1.7 μmol h^{-1}). Although the surface area of TiO_2 (rutile LS) is only ca. 1/1000 that of TiO_2 (rutile HS), the catalytic activity of Ni-Cu on these TiO_2 supports is comparable. These results suggest that neither crystal structures nor the BET surface areas of the TiO_2 supports are insignificant factor to determine the catalytic activity of Ni-Cu/TiO_2.

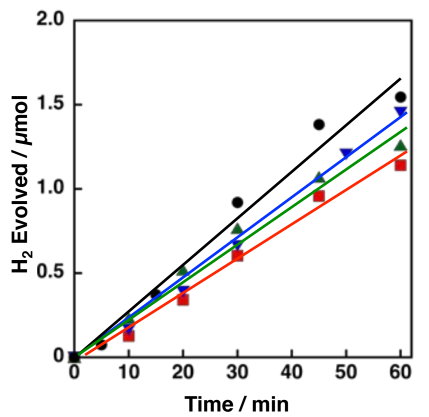


Fig. 12 Time course of H_2 evolution by photoirradiation (λ > 340 nm) of a mixed suspension (2.0 mL) of a phthalate buffer (pH 4.5) and MeCN [1:1 (v/v)] containing $QuPh^+$–NA (8.8 × 10^{-4} M), NADH (1.0 × 10^{-3} M) and 3 wt% Ni-Cu supported on TiO_2 (100 mg L^{-1}) with different crystal structures. (anatase LS, black circle; rutile HS, blue inverse triangle; anatase HS, red square; rutile LS, green triangle)

3. Conclusions

The catalytic activity of Ni-Cu/TiO_2 and Ni-Cu/SiO_2 for H_2 evolution was greatly enhanced by synergistic effects of Ni and Cu in the photocatalytic H_2-evolution system using 2-phenyl-4-(1-naphthyl)quinolinium ion and NADH as a photocatalyst and an electron donor, respectively. Such a synergistic effect between Ni and Cu was not observed for Ni-Fe and Ni-Co catalysts and for Ni-Cu/SiO_2-Al_2O_3 and Ni-Cu/CeO_2. TEM observation and EDS elemental mapping of Ni-Cu/SiO_2 prepared by the co-impregnation method and Ni-Cu/SiO_2 prepared by the co-impregnation and the sequential impregnation methods suggest that the close location of Ni and Cu is important to achieve the high catalytic activity. The synergistic effect between Ni and Cu was observed in the wide range of Ni contents, Ni/(Ni+Cu), from 30 to 70%. This study has demonstrated that suitable choices of an additives, a support, a catalyst preparation method are all important to achieve highly active H_2-evolution catalysts composed of base metals with synergistic effect.

4. Experimental Section

4.1 Materials

All chemicals were obtained from chemical companies and used without further purification. SiO_2 (unshaped, low surface area), TiO_2 (anatase, low surface area) and TiO_2 (anatase, high surface area) were purchased from Sigma–Aldrich. SiO_2 (unshaped, high surface area) was obtained by Merck. Iron nitrate, copper nitrate, nickel nitrate, 2-propanol, hydrochloric acid (37%), sodium aluminate and titanium(IV) chloride were obtained from Wako Pure Chemical Industries. An aqueous ammonia (28%) and *β*-dihydronicotinamide adenine dinucleotide disodium salt (reduced form) (NADH) was obtained from Tokyo Chemical Industry. Tetraethyl orthosilicate (TEOS) was delivered by Shin-Etsu Chemical. Acetonitrile was obtained from Nacalai Tesque. CeO_2 was provided by Daiichi Kigenso Kagaku Kogyo Co., Ltd. 2-Phenyl-4-(1-naphthyl)quinolinium perchlorate ($QuPh^+$–NA),[42] SiO_2-Al_2O_3,[46] spherical SiO_2,[47] and TiO_2 (rutile, high surface area)[48] were prepared by literature methods. Purified water was provided by a Millipore DIRECT-Q UV3 water purification system (18.2 MΩ cm).

4.2 Preparation of Ni-Cu supported on metal oxides by a co-impregnation method

A typical procedure for the preparation of metal oxides supporting Ni and Cu by a one-step impregnation method is as follows: Metal oxides (350 mg) was soaked in an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (26.8 mg, 92.2 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (20.6 mg, 85.3 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 ºC min^{-1}) for 4 h under air. The obtained powder was soaked in an aqueous solution containing $NaBH_4$ to reduce oxides of Cu and Ni before catalysis evaluation.

4.3 Preparation of Ni-Cu supported on TiO_2 and SiO_2 by a sequential impregnation method

A typical procedure for the preparation of TiO_2 and SiO_2 catalysts supporting Cu and Ni by a sequential impregnation method is as follows: TiO_2 or SiO_2 (350 mg) was immersed in an aqueous solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (20.6 mg, 85.3 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 ºC min^{-1}) for 4 h under air. Then, the calcined sample was immersed in an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (26.8 mg, 92.2 mmol). The obtained slurry was dried and calcined. The obtained powder was soaked in an aqueous solution containing $NaBH_4$ to reduce oxides of Cu and Ni before catalysis evaluation.

4.4 Preparation of Ni-Co and Ni-Fe supported on TiO_2 and SiO_2 by a co-impregnation method

These catalysts were prepared by a one-step impregnation method is as follows: TiO_2 or SiO_2 (350 mg) was soaked in an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (26.8 mg, 92.2 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (26.8 mg, 92.1 mmol) or $Fe(NO_3)_3 \cdot 9H_2O$ (37.2 mg, 92.1 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 ºC min^{-1}) for 4 h under air. The obtained powder was soaked in an aqueous solution containing $NaBH_4$ to reduce oxides of Cu and Ni before catalysis evaluation.

4.5 Preparation of SiO_2-Al_2O_3

SiO_2 was suspended to 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 ºC min^{-1}) for 6 h under air.

4.6 Preparation of spherical silica

TEOS (18 mL, 80 mmol) was dissolved in a mixture solution of water (31 mL), ethanol (300 mL) and 28% ammonia solution (5.4 mL) and stirred for 4 h at room temperature. After the reaction, obtained white precipitate was collected by centrifugation (9000 rpm, 10 min) and washed three times by water. The obtained powder was dried at 70 °C in an oven and calcined at 350 °C (ramp rate: 5 ºC min^{-1}) for 4 h under air to remove residual ammonia.

4.7 Preparation of TiO_2 (rutile, high surface area)[48]

Titanium(IV) chloride (5.7 g, 30 mmol) was dissolved in a mixture solution of water (100 mL), 2-propanol (200 mL) and hydrochloric acid (10 mL) and refluxed for 20 h at 90 °C. After the solution was cooled to room temperature, the suspension was neutralised by 28% ammonia solution to pH 9. The white precipitate was collected by centrifugation (9000 rpm, 10 min) and washed three times by water.

4.8 Preparation of TiO_2 (rutile, low surface area)

TiO_2 (rutile, high surface area) was calcined at 1000 °C (ramp rate: 10 ºC min^{-1}) for 3 h under air.

4.9 Transmission electron microscopy (TEM)

The sizes and shapes of SiO_2 supports 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 Cu grid. High-angle annular dark field scanning TEM (HAADF-STEM) images and the energy dispersive X-ray spectroscopy (EDS) elemental mapping of Ni-Cu/SiO_2 were obtained by a FEI Titan G2 60-300 with an accelerating voltage of 300 kV. The observed samples were directly put on Mo meshes.

4.10 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 5° to 80° in 2θ. 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. $BaSO_4$ 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.).

4.11 N_2 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 N_2 atmosphere until N_2-adsorption measurements. The samples were exposed to a mixed gas of He and N_2 with a programmed ratio and adsorbed amount of N_2 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 N_2 adsorption amounts under the conditions of partial pressure less than 0.3.

4.12 Photocatalytic H_2 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), NADH (1.0 mM) and an H_2-evolution catalyst was flushed with N_2 gas. The solution was then irradiated for a certain time with a xenon 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 ºC, column: active carbon with the particle size 60-80 mesh, carrier gas: N_2 gas) to determine the amount of evolved H_2.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Time courses of H_2 evolution (Figs. S1, S4 and S8), powder X-ray diffraction (Figs. S2, S5 and S9), the amount of H_2 evolved in the repetitive experiments (Fig. S3), diffused reflectance spectra (Fig. S6), TEM images (Fig. S7). See DOI: 10.1039/b000000x/

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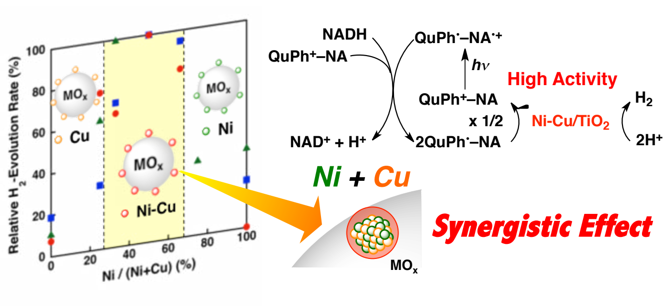

Ni and Cu supported on TiO_2 or SiO_2 synergistically acted as H_2-evolution catalysts in a photocatalytic system.

