On the Synergism between Cu and Ni for Photocatalytic Hydrogen Production and their Potential as Substitutes of Noble Metals

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A series of Cu(OH)₂-Ni(OH)₂/P25 photocatalysts was prepared by co-deposition-precipitation (total metal loading $\approx 1 \text{ wt \%}$) and their performance was evaluated for H₂ production. Among this series, the 0.8Cu(OH)₂-0.2Ni(OH)₂/P25 photocatalyst demonstrated very high H₂ production rates in 20 vol% ethanol/water and 5 vol% glycerol/water mixtures (10 and 22 mmol h⁻¹g⁻¹, respectively). Detailed analyses based on reaction kinetics, photoluminescence, X-ray photoelectron spectroscopy (XPS), and charge carrier scavenging suggest that both working catalysts are composed of Cu and Ni metals in their active phases. Cu⁰ is produced directly by the transfer of electrons from the conduction band of TiO₂ to surface Cu(OH)₂ nanoclusters, whereas Ni⁰ is formed indirectly through a process of gradual dissolution of Ni(OH)₂ to yield aqueous Ni²⁺ owing to the acidic environment of the medium, followed by Ni²⁺ reduction by electrons from the TiO₂ conduction band. The high rates of H₂ production that match those obtained with noble metals can be explained owing to a considerably less negative ΔG° of Cu oxide formation when compared with that of Ni oxide formation^[1] and higher work function of Ni than that of Cu.^[2]

Introduction

Hydrogen is widely regarded as the logical energy carrier to replace fossil fuels for electricity generation and transportation. The development of the so-called "hydrogen economy" requires new technologies for H₂ generation, of which photocatalytic water splitting or alcohol photoreforming by using direct sunlight are viewed as two of the most promising pathways. Many photocatalysts have been reported that are capable of producing hydrogen from water in the presence of sacrificial agents, with M/TiO₂ systems (M=Pd, Au, or Pt) generally showing the best and most stable performances.^[3] Photocatalysis relies on capturing the energy of incident photons with $E > E_{gr}$ through excitation of electrons from the valence band of a semiconductor into its conduction band. Electrons and

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holes thus produced then drive oxidation and reduction reactions on the semiconductor surface. TiO_2 is an ideal support for photocatalytic hydrogen production from water and alcohols because of its high chemical stability and resistance to photocorrosion in aqueous media, as well as its low cost and wellmatched energy bands with water redox levels.^[4] The addition of noble metals such as platinum, gold, and palladium to TiO_2 is needed for photocatalytic H₂ production.^[3,5] However, noble metals are expensive, with low natural abundance, hence they are not especially practical for the design and development of industrial photocatalysts for hydrogen production. The identification of alternative low-cost co-catalysts that enhance the photocatalytic activity of TiO_2 for hydrogen production is a priority.

Cu/TiO₂ and Ni/TiO₂ systems are particularly promising in this regard and represent cost-effective and efficient photocatalyst systems for solar hydrogen production.^[6] Yu and coworkers deposited Ni(OH)₂ nanoclusters on TiO₂ by a simple precipitation method and observed a hydrogen production rate of 3.0 mmolg⁻¹h⁻¹ in 25 vol% aqueous methanol under UV excitation.^[7] Hydrogen evolution was attributed to the more positive redox potential of the Ni²⁺/Ni couple compared with the conduction band of TiO_2 , which serves as the active sites for the reduction of H^+ to H_2 . The same group also fabricated Cu(OH)₂/TiO₂ photocatalysts by using the same method, and reported a hydrogen production rate of 3.4 mmolg⁻¹h⁻¹ in a 0.09 M ethylene glycol solution in water under UV irradiation. The enhanced activity was attributed to the transfer of electrons from the TiO₂ conduction band to Cu(OH)₂, which then reduced H^+ to H_2 . However, it is not clear if Cu(OH)₂

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acted as the cathodic site or Cu(OH)₂ was reduced to Cu₂O or Cu^o under reaction conditions, which then acted as the site for H₂ evolution. In previous work, some of us have evaluated the hydrogen production activities of a series of Ni/TiO₂ photocatalysts in ethanol/water mixtures.^[2a] The photocatalytic activity of Ni/TiO₂ photocatalysts was found to be highly dependent on the Ni loading, with a loading of 0.38 wt% being optimal, affording a rate of 24.3 mmol $g^{-1}h^{-1}$ in 95 vol % aqueous ethanol under UV irradiation. The high activity of the Ni/TiO₂ photocatalyst was rationalized in terms of the high work function of metallic Ni and the excellent Schottky junction formed at the TiO₂ surface. In the same work, 0.63 wt % NiO/TiO₂ was tested. A long induction period was observed before a constant hydrogen production rate was obtained, reaching about one fourth of that of Ni/TiO₂. This later was simply prepared by in situ hydrogen production. We have explained this induction period as being due to in situ reduction of a fraction of NiO by hydrogen, produced in the initial stage of the reaction, to Ni⁰. The Fermi level of Ni⁰ is below that of the conduction band of TiO₂ anatase. In another work, we have previously studied the CuO/TiO₂ system and found that activity was dependent on the nominal CuO loading, with 1.25 wt% CuO being optimal $(H_2 \text{ production rate} = 20.3 \text{ mmol g}^{-1} \text{ h}^{-1} \text{ in } 80:20 \text{ EtOH}/H_2\text{O}).^{[8]}$ Highly dispersed sub-monolayer Cu^{II} species on TiO₂ surfaces, rather than supported CuO nanoparticles, were proposed as the active site for hydrogen production. In another recent work, some of us have investigated Au/Cu₂O-TiO₂ and found that Cu⁺ reduction to Cu⁰ is behind the main catalytic activity. The redox potentials of Cu⁺ and Cu²⁺ are within the band gap of TiO₂. These latter results further confirm the results seen for the CuO/TiO₂ system.^[9]

The enhancement in photocatalytic activity regarding Nicontaining TiO₂ photocatalyst systems is, however, more complex. It is postulated that Ni(OH)₂ is converted into NiO after prolonged exposure to irradiation in the oxidizing environment provided by the reaction mixture.^[10] NiO cannot trap photogenerated electrons because the conduction band of NiO is more negative than that of TiO₂. There is some controversy in the literature about the valence and conduction band energies of NiO.^[11] Values in the ranges of -0.3 to -1.0 eV are reported for the conduction band, and 2.4 to 4.3 eV for the valence band (with respect to the standard hydrogen electrode (SHE)).^[12] Theoretical calculations indicate that H-H recombination on NiO (100) is exothermic, with an activation barrier of only 40 kJ mol⁻¹.^[13] High hydrogen production rates observed on Ni(OH)₂-containing catalysts can be rationalized in terms of the ability of NiO to act as an adsorbed atomic hydrogen recombination site after H⁺ has accepted an electron directly from the conduction band of TiO2.^[10] Bimetallic heterogeneous catalysts demonstrate excellent performance in many reactions, offering increased activity and selectivity to the desired products. Bimetallic nanoparticles deposited on TiO₂ can create surface electronic states and active sites different to those realized in monometallic systems owing to synergistic physical and chemical interactions amongst the different atoms and phases.^[14] For example, Pt–Cu/TiO₂ photocatalysts can selectively reduce nitrate to N₂ under UV irradiation. In contrast, nitrate is converted to ammonia or nitrite over Pt/TiO₂ or Cu/TiO₂, respectively.^[15] Similarly, highly selective ammonia synthesis from nitrate can be observed over Pd–Cu/TiO₂ photocatalysts compared with their monometallic counterparts.^[16]

Herein, we report the successful synthesis of a series of Cu(OH)₂-Ni(OH)₂/TiO₂ photocatalysts by a simple precipitation method, and the subsequent application of these photocatalysts for hydrogen production in different alcohol/water systems under UV excitation. An oxidized Ni atom in contact with a Cu atom may become reduced owing to a considerably less negative ΔG° of Cu oxide formation (-129 kJ mol⁻¹) compared with that of Ni oxide formation $(-430 \text{ kJmol}^{-1})$.^[1] This would then increase hydrogen production because the work function of Ni is higher than that of Cu.^[2] Of particular interest were the chemical and morphological evolution of the co-catalysts under the reaction conditions, the synergistic effects of Cu and Ni co-deposition for H₂ evolution, and the effect of the Cu/Ni ratio on H₂ production rates. Results are expected to guide the future development of efficient, low-cost semiconductor photocatalysts for solar H₂ production.

Results and Discussion

Materials characterization

Powder XRD patterns for all $Cu(OH)_2-Ni(OH)_2/P25$ photocatalysts are shown in Figure S1 in the Supporting Information, and are dominated by peaks resulting from anatase and rutile. No clear change in the anatase and rutile diffraction peak positions is seen, suggesting that the metal hydroxide species are finely dispersed over the support. The low loadings would also make identification of Ni(OH)₂ and Cu(OH)₂ difficult. The anatase and rutile crystallite sizes determined from the powder XRD data by using the Scherrer equation were 28 nm and 36 nm, respectively.

Figure 1 (a) shows the UV/Vis diffuse reflectance spectra (DRS) for the different mono- and bimetallic photocatalysts, whilst Figure 1 (b) compares fresh and used 0.8 Cu(OH)₂-0.2 Ni(OH)₂/TiO₂. All catalysts showed intense absorption below 400 nm, owing to the P25 support ($E_g = 3.15 \text{ eV}$). All metal-containing photocatalysts showed absorption in the visible region owing to overlap between the TiO₂ and metal hydroxide complexes. The Ni3d and Cu3d states can mix with the TiO_2 conduction band at the interface region and thus decrease the band gap energy between the Ti3d and O2p states of TiO₂.^[17] The absorption spectra of fresh bimetallic photocatalysts show a broad band centered above 600 nm and a small absorption shoulder at 450 nm. The absorption shoulder at 450 nm is partly due to the interfacial charge transfer (IFCT) from TiO₂ conduction band to M^{2+} cations (where M = Cu and Ni).^[15, 18] The enhanced absorption above 600 nm can be assigned to Ni^{2+} d–d (600–800 nm) and Cu^{2+} d–d (700-800 nm) transitions. The increased absorption around 450-600 nm for the used photocatalyst in Figure 1 (b) is likely due to the formation of Cu⁺ oxide species during photoreactions.^[29]

Figure S2 in the Supporting Information shows digital photographs of the as-prepared photocatalysts under UV irradia-



Figure 1. (a) UV/Vis spectra of P25, "as prepared" mono- and bimetallic photocatalysts as indicated; (b) UV/Vis of as prepared and used 0.8Cu(OH)2-0.2 Ni(OH)₂/TiO₂.

tion (20 mg of each of photocatalyst suspended in 20 vol% ethanol/water mixtures with total volumes of 25 mL). For the as-prepared photocatalysts, the light blue-green color increased with an increase in Cu(OH)₂ loading owing to the presence of octahedrally coordinated Cu^{2+} ions. $^{[20]}$ The grey color of calcined 0.8Cu(OH)2-0.2Ni(OH)2/P25 catalyst indicates the formation of metal oxides.^[8] Under photoreaction conditions, the color change increases gradually with the increase of the amount of Cu(OH)₂ whereas no change is observed for the Ni(OH)2-containing catalysts. The latter observation might be due to the fact that Ni²⁺ in Ni(OH)₂ cannot be reduced under the given conditions. Upon exposure to air, the change in Cu(OH)₂/P25 color reverts back to the original color, which is most likely due to re-oxidation of Cu⁰.

TEM images for 1.0Cu(OH)₂/P25 photocatalyst are shown in Figure 2 at different magnifications. P25 is known to be composed of small nearly spherical anatase crystallites of average size 20-30 nm, and larger rutile crystallites with average size 40-60 nm, both of which are evident in the TEM images. It is

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Figure 2. TEM images of fresh 1.0 Cu(OH)₂/P25 photocatalyst.

difficult to discern metal hydroxide nanoparticles on the surface of the TiO₂ by using TEM owing to the similarity in the atomic number of Ni, Cu, and Ti, among other factors (Figure 2a and b). It has been reported that hydroxide nanoparticles on TiO₂ support could only be identified with any certainty at a metal loadings of greater than $5 \text{ wt} \% \text{ M(OH)}_2$ (M = Ni, Cu).^[7,21] It is likely that the hydroxide nanoparticles are present in a very small size (1-3 nm) as seen in the magnified TEM image only (Figure 2b).^[22] The presence of small metal hydroxide particles suggest a strong interaction with the P25 support. Energy-dispersive X-ray (EDX) analysis of the same photocatalyst indicates the presence of both Cu and Ni species (Figure S3 in the Supporting Information).

Figure 3 presents the Cu2p, Ni2p, Ti2p, C1s, and O1s XPS spectra of fresh 0.8 Cu(OH)₂-0.2 Ni(OH)₂/P25 photocatalyst whereas the Cu2p and Ni2p spectra of all fresh photocatalysts are given in Figure S4 in the Supporting Information. Nitrogen was the only other element detected with an overall atomic percentage of less than 0.5%. The X-ray photoelectron spectroscopy (XPS) of the Cu2p region for different Cu oxidation



Figure 3. XPS results of fresh bimetallic 0.8 Cu(OH)2-0.2 Ni(OH)2/P25 photocatalvst.



states has been studied thoroughly.^[23] Typical XPS Cu 2p_{3/2} values for Cu⁰ and Cu⁺ are observed between 932.3–932.5 eV. making Cu⁰ and Cu⁺ difficult to distinguish, whereas that of Cu²⁺ is 1 eV higher at about 933.6 eV. The XPS of Cu 2p of Cu²⁺ has characteristic satellites at about 6 eV above the Cu 2p peaks. It can be noted that copper is detected in its reduced state (Cu⁰/Cu⁺) whereas nickel is detected as Ni(OH)₂ in 0.98 and 0.19 at%, respectively (Table 1). Ni 2p_{3/2} and Ni 2p_{1/2} peaks are observed at 855.6 eV and 873.2 eV, respectively. The binding energy position, absence of multiple splittings, and additional "shake-up" satellite features at approximately 6 eV above the Ni 2p peaks indicate that Ni is present as Ni(OH)₂.

Table 1. XPS analysis of fresh bimetallic 0.8 Cu(OH) ₂ -0.2 Ni(OH) ₂ /P25 photocatalyst.								
Chemical composition	Core level	Peak position [eV]	FWHM [eV]	at%				
TiO ₂	Ti 2p _{3/2}	458.7	1.0	33.8				
TiO ₂	Ti 2p _{1/2}	464.4	1.9					
Metal oxide	O1s	530	1.1	46.4				
Metal hydroxide		532.1	2.1					
Carbon (adv.)	C1s	284.8	1.4	19.6				
C–O–C (adv.)		286.4	1.3					
C–O=C (adv.)		288.6	1.3					
Cu/Cu ₂ O	Cu 2p _{3/2}	932.4	1.7	0.39				
	Cu 2p _{1/2}	952.2	2.1					
Ni(OH) ₂	Ni 2p _{3/2}	855.6	2.1	0.10				
	Ni 2p _{1/2}	873.2	2.5					
	Ni 2p _{1/2}	873.2	2.5					

To gain insight regarding the electron transfer dynamics, steady-state and time-resolved photoluminescence (PL) of the P25, $1.0 \text{Cu}(\text{OH})_2/\text{P25}$ and $1.0 \text{Ni}(\text{OH})_2/\text{P25}$ samples were conducted and the results are presented in Figure 4a and b. Fig-



Figure 4. (a) Steady-state PL and (b) time-resolved PL spectra following excitation at 305 nm.

ure 4a demonstrates that 1.0Cu(OH)₂/P25 exhibits PL approximately 2 times lower in intensity compared with P25. This is a clear indication of photo-excited electron transfer from the conduction band of the P25 to the Cu(OH)₂. Conversely, P25 and 1.0NiOH)₂/P25 exhibit similar intensities. The presence of Ni may also passivate some surface defects, thus resulting in a slight increase in the PL intensity. To confirm this, PL measurements as a function of Ni(OH)₂ loading were performed. PL intensity was observed to increase with an increase in loading. To understand the electron transfer rate, time-resolved PL was conducted. We were anticipating a decrease in the PL lifetimes of 1.0 Cu(OH)₂/P25 compared with P25 as a result of electron transfer from the photo-excited P25 to Cu(OH)₂. However, instead we observed the same PL kinetics behavior for all three samples. This strongly suggests that the electron transfer occurs much faster than the instrument response function \approx 500 ps of our time-correlated single photon set-up. The measured PL kinetics was best fitted by the built-in single exponential model ($\tau = Ae^{-kt}$, where τ , A, k, and t are the time constant, amplitude in counts, first-order rate constant, and time, respectively) suggesting a time constant of \approx 1.24 \pm 0.006 ns.

Photoreactions

H₂ production

Photocatalytic H_2 production was evaluated by using either ethanol or glycerol as sacrificial agents. Degussa P25 showed negligible activity because of the rapid recombination of conduction band electrons and valence band holes and as a result of the absence of H⁻ recombination centers for hydrogen evolution.^[10,24] Figure 5 a shows the effect of the precipitation



Figure 5. (a) Effect of NaOH concentration on H₂ production with $0.5 \text{ Cu}(\text{OH})_2$ -0.5 Ni(OH)₂/P25 photocatalysts. (b) Effect of metal loading amount on H₂ production in 20 vol% ethanol/water mixtures by using $x \text{Cu}(\text{OH})_2$ -yNi(OH)₂/P25 photocatalysts where x = y.

agent (NaOH) concentration, during catalyst preparation, on the hydrogen production rate when using $0.5 \text{Cu}(\text{OH})_2$ - $0.5 \text{Ni}(\text{OH})_2/\text{P25}$ catalysts. The small observed dependence of the hydrogen production rate on NaOH concentration might be due to the better dispersion or agglomeration of metal hydroxides particles on the P25 surface. The effect of metal loading concentration was studied by increasing the overall loading amount from 0.5 to 3 wt% (Figure 5 b).

The optimum hydrogen production rate was obtained for a nominal loading amount of 1 wt%. A slight decrease in activity at 1.5 wt% metal loading was observed and after that a sharp decrease in activity was observed from 2 to 3% loadings. The decrease in photocatalytic activity with increasing metal loading has been observed by many other groups, how-



ever, no clear explanation is yet known.^[8,25] Upon increasing of metal particle coverage, a larger fraction of the semiconductor surface may become unavailable for light adsorption. It can also result in increased surface defects at the metal–semicon-ductor interface, leading to an increase in electron–hole recombination centers. For further study, the overall nominal metal loading was kept at 1 wt% and 0.5 M NaOH solution was used as the precipitating agent.

Comparison of hydrogen production in 20 vol% ethanol/ water mixture with various samples is shown in Figure 6. Hydrogen production experiments in different ethanol to water volume ratios with the $0.8 \text{Cu}(\text{OH})_2$ - $0.2 \text{Ni}(\text{OH})_2$ /P25 catalyst



Figure 6. Comparison of the photocatalytic activities of $0.8 \text{Cu}(OH)_2 0.2 \text{Ni}(OH)_2/\text{P25}$, $1.0 \text{Cu}(OH)_2/\text{P25}$, $0.5 \text{Cu}(OH)_2 0.8 \text{Ni}(OH)_2/\text{P25}$, $1.0 \text{Ni}(OH)_2/\text{P25}$, and $0.8 \text{Cu}(OH)_2 0.2 \text{Ni}(OH)_2/\text{P25}$, $1.0 \text{Ni}(OH)_2/\text{P25}$, and $0.8 \text{Cu}(OH)_2 0.2 \text{Ni}(OH)_2/\text{P25}$ (calcined) samples for the photocatalytic H₂ production in 20 vol% ethanol/water mixture.

were also performed. An increase in rates with increasing ethanol proportion, was noticed (Figure S5 in the Supporting Information). Further investigations were performed in 20 vol% ethanol/water mixtures while keeping the ethanol concentration to a minimum to afford reliable measurements owing to the amount of hydrogen produced with our experimental set up. Catalyst $1.0 \text{Ni}(\text{OH})_2/\text{TiO}_2$ was the least active with a hydrogen production rate two times lower than 1.0 Cu(OH)₂/TiO₂. Hydrogen production rates increase with increasing Cu wt% ratio in bimetallic catalysts and 0.8Cu(OH)2-0.2Ni(OH)2/TiO2 was found to be the most active. However, the 0.8Cu(OH)₂-0.2Ni(OH)₂/ TiO₂ catalyst losses its activity considerably if calcined at 300 °C. As the Brunauer-Emmett-Teller (BET) surface area of TiO₂ P25 did not change upon calcination at 300 °C, the deactivation could be linked to the formation of larger particles of oxides of Cu and Ni, which are more difficult to reduce and therefore do not provide the needed Schottky barrier for electron transfer to occur.

In comparison with ethanol/water mixtures, glycerol/water mixtures showed higher rates of hydrogen production (Figure 7). In general, alcohols with lower oxidation potential,

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Figure 7. Comparison of the photocatalytic activities of $0.8 \text{ Cu}(\text{OH})_2$ - $0.2 \text{ Ni}(\text{OH})_2/\text{P25}$, $0.2 \text{ Cu}(\text{OH})_2$ - $0.8 \text{ Ni}(\text{OH})_2/\text{P25}$, $0.5 \text{ Cu}(\text{OH})_2$ - $0.5 \text{ Ni}(\text{OH})_2/\text{P25}$, $1.0 \text{ Cu}(\text{OH})_2/\text{P25}$, and $1.0 \text{ Ni}(\text{OH})_2/\text{P25}$ samples for the photocatalytic H₂ production in 5 vol% glycerol/water mixtures.

larger numbers of α -H atoms, and hydroxyl groups deliver higher hydrogen production rates.^[26] The oxidation potential, number of α -H atoms, and hydroxyl groups are 0.004 V, 5, and 3 for glycerol whereas they are 0.084 V, 2, and 1 for ethanol, respectively.^[26] In alcohol/water mixtures, the photoreaction is initiated by the reaction of an alcohol with a hole in the TiO₂ valence band to form α -hydroxyl radicals. The formation of α hydroxyl radicals have been identified previously on TiO₂ by using EPR and has been proposed by many others.^[27] Lower hydrogen production rates were observed for glycerol concentrations greater than 30 vol% (data not shown) owing to an increase in reaction mixture viscosity. Inspection of the hydrogen production with time indicates an induction period in both cases. Two particular points are, however, worth mentioning. First, Ni(OH)₂ catalysts had the longer induction period in both cases, also Ni-containing catalysts showed longer induction periods, which increased with concentration. Second, glycerol and water mixtures showed much shorter induction periods compared with that of ethanol and water mixtures. In previous work,^[26] we have shown a relationship between hydrogen production rates and the exponential of redox potential, by following Marcus theory.^[28] The rates for glycerol were about twice as fast compared with those for ethanol reactions. The results reported in this study on Cu and Ni are thus not too different, indicating that the main drive for the reaction (at least on TiO₂) is the difference in the oxidation potential of the donor molecules and the valence band of the semiconductor.

Table 2 presents a compilation of results from other work to compare with the ones presented here. It can be noted that better hydrogen production rates are obtained with the bimetallic composition used in this study compared with monometallic catalysts reported in literature.

The activity and stability of $0.8 \text{Cu}(\text{OH})_2$ - $0.2 \text{Ni}(\text{OH})_2$ /P25 catalysts was investigated in 20 vol% ethanol/water mixtures. As can be seen from Figure 8, stable photocatalytic hydrogen production was observed over the duration of the experiments (16 h). The slight decrease in rate with time (up to 15% for the



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Table 2. Comparison of hydrogen production rates over Cu- and Ni-containing catalysts reported in the literature with those of the present study.							
Photocatalyst (metal loading method)	Sacrificial reagents [vol%]	Irradiation source	H_2 production [mmol g ⁻¹ h ⁻¹]	Ref.			
1 wt % Cu–Ni/P25	5% glycerol/water	100 W lamp (UV)	22.32	Present study			
1 wt % Cu–Ni/P25 (solvothermal)	37% methanol/water	300 W lamp (UV)	13.5	[29]			
1.25 wt% CuO/TiO ₂ (complex precipitation)	80% ethanol/water	100 W lamp (UV)	20.3	[8]			
29 mol % Cu(OH) ₂ /P25 (precipitation)	0.09 м ethylene glycol/water	3 W LEDs (UV)	3.42	[21]			
0.5 mol % Ni(OH) ₂ /P25 (precipitation-deposition)	25% methanol/water	3 W LEDs (UV)	3.056	[7]			
1.3 wt % CuO/P25 (impregnation)	0.1 м glycerol/water	3 W LEDs (UV)	2.06	[30]			
8 at %Cu/P25 (chemical reduction)	10% methanol/water	400 W lamp (UV)	20	[31]			
1 wt % Cu ₂ O/P25 (impregnation)	20% ethanol/water	200 W lamp (UV)	3.48	[32]			
1.2 wt % Cu/TiO ₂ anatase (incipient wetness)	30% methanol/water	208 W (UV) lights	3.2	[6c]			
1.25 wt % Ni/P25 (complex precipitation)	95% ethanol/water	100 W lamp (UV)	20.7	[2a]			
0.5 mol % Ni(OH) ₂ /P25 (precipitation deposition)	25% of methanol/water	3 W UV-LEDs (UV)	3.056	[7]			
1.5 wt % NiO/TiO ₂ -anatase (sol–gel)	10% methanol/water	300 W lamp (UV)	0.162	[6e]			
0.8 wt % Au/TiO ₂ -anatase (photodeposition)	25% methanol/water	400 W lamp (UV)	1.54	[33]			
4 wt % Au/P25 (photodeposition)	5% ethanol/water	450 W (UV/Vis)	6.12	[34]			
1 wt % Au/TiO ₂₋ anatase (photodeposition)	50% methanol/water	2.4 W lamp (UV)	8.4	[35]			
1 wt % Au/TiO ₂ -anatase (flame spray pyrolysis)	6% methanol/water	250 W (UV/Vis)	8	[36]			
1 wt % Pd/TiO ₂ -anatase + rutile nanofibers (impregnation)	50% ethanol/water	8 W (UV-B)	16.2	[37]			
0.5 wt % Au–0.5 wt % Pt/TiO ₂ -anatase (impregnation)	50% ethanol/water	125 W (UV lamp)	8	[38]			
0.25 wt % Au-0.75 wt % Pd/P25 (sol-immobilization)	25% glycerol/water	LED (365 nm)	19.6	[39]			
1.5 wt % Au/P25 (deposition precipitation with urea)	80% ethanol/water	100 W (365 nm)	32.2	[40]			
2 wt % NiO/TiO ₂ -anatase + rutile (impregnation)	16% glycerol/water	500 W (UV)	1.23	[41]			
1 wt % Pt/P25 (deposition precipitation with urea)	10% glycerol/water	200 W (UV)	27.1	[42]			
1.5 wt% Au/P25 (deposition precipitation with urea)	10% glycerol/water	100 W (365 nm)	27.9	[27]			



Figure 8. Different successive runs for the hydrogen production experiments with $0.8 Cu(OH)_2$ - $0.2 Ni(OH)_2$ /P25 catalysts by using 20 vol% ethanol/water mixtures.

fourth run) was due to the deposition of catalyst particles (clearly seen with the naked eye) on the reactor walls with time, thus scattering away the incoming radiation. We performed recyclability tests with similar bimetallic loadings on TiO₂ nanofibers, and no decrease in hydrogen production rates was observed over the same length of time. The effect of pH on H₂ generation with $0.8 \text{Cu}(OH)_2$ – $0.2 \text{Ni}(OH)_2$ /P25 catalysts was investigated in a 5 vol% glycerol/water mixture (Figure S6 in the Supporting Information). In general, a decrease in rate with an increase in pH was observed. We did observe negligible H₂ production in water alone. H₂ production in the case of pure water on metal supported TiO₂ is about two orders of magnitudes smaller compared with that in the presence of the sacrificial agents.⁽⁴³⁾

Electron/hole transfer

Table 3 presents Rhodamine B dye degradation over P25, $1.0 \operatorname{Ni}(OH)_2/P25$, $1.0 \operatorname{Cu}(OH)_2/P25$, and $0.8 \operatorname{Cu}(OH)_2-0.2 \operatorname{Ni}(OH)_2/P25$ catalysts in the absence or presence of either a hole (Na₂EDTA) or an electron scavenger (benzoquinone).^[45] The objective here is to further probe the electron/hole transfer process in the presence of Cu and Ni hydroxides. The absorption spectra were collected in 400–600 nm range during the monitoring process. To test the activity, we have measured the time needed for dye degradation, specifically, the time needed to decompose 80% of the dye. It was noted that the time required to degrade the dye is longer in the case of metal-

Table 3. Results of Rhodamine B dye degradation over different photocatalysts. Degradation time is taken as that needed to decompose 80% of the dye.

Photocatalyst	Hole	Superoxide	Degradation
	scavenger	scavenger	time [min]
P25	-	-	32
1.0 Ni(OH) ₂ /P25 1.0 Ni(OH) ₂ /P25 1.0 Ni(OH) ₂ /P25	– Na₂EDTA	- benzoquinone	38 38 70
1.0 Cu(OH)₂/P25	–	–	110
1.0 Cu(OH)₂/P25	Na₂EDTA	–	105
1.0 Cu(OH)₂/P25	–	benzoquinone	170
$\begin{array}{l} 0.8Cu(OH)_2-0.2Ni(OH)_2/P25\\ 0.8Cu(OH)_2-0.2Ni(OH)_2/P25\\ 0.8Cu(OH)_2-0.2Ni(OH)_2/P25 \end{array}$	–	–	90
	Na₂EDTA	–	90
	–	benzoquinone	135



loaded catalysts compared with P25 alone in all cases. This indicates that doping TiO₂ with these elements decreases its activity, in sharp contrast with hydrogen production. More specifically, the dye degradation time is longer over all Cu supported catalysts compared with 1.0 Ni(OH)₂/P25 (with almost the same activity as TiO₂ alone). It is to be noted that this last observation is also opposite to the hydrogen production results. The reason is most likely competition of conduction band (CB) electrons. In other words, Cu in Cu(OH)₂/P25 has a suitable reduction potential, as a result of which there is competition between $(Cu^{2+} + 2e^{-}(CB) \rightarrow Cu^{0})$ -not needed for the dye degradation—and $(O_2 + e^{-}(CB) \rightarrow O_2^{-}$ —needed for the dye degradation reaction. However, in the case of Ni(OH)₂/P25, the conduction band electrons are unable to reduce the Ni in Ni(OH)₂, and thus are therefore exclusively used to form superoxide radicals that in turn oxidize the dye. To probe further into this, we have investigated the effect of hole and electron scavengers on the dye degradation time. In the presence of Na₂EDTA, a hole scavenger, the rate of dye degradation all catalysts was close to that obtained without any scavenger. However, the degradation was much slower in the presence of benzoquinone, a superoxide radical scavenger (Table 3). These results also suggest that the role of OH radicals or h⁺ is negligible in this degradation process whereas electrons/superoxide radicals are the main active species.

The reduction potential of Cu(OH)₂/Cu is slightly lower than the conduction band potential of anatase and rutile TiO₂ (Cu(OH)₂+2e⁻=Cu+2OH⁻, E° =-0.224 V; Figure 9). Under photoreaction conditions, electrons can directly transfer from the CB of TiO₂ to Cu(OH)₂ nanoclusters to reduce Cu²⁺ to Cu⁰ as shown in Figure 10. This direct conversion can be supported by four observations in this study. 1) Instant color change on exposing the catalysts slurry to UV radiation in the presence of a sacrificial regent. This change in color gradually decreases



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*Ni(OH)₂ + 2H⁺ \rightarrow Ni²⁺ + 2H₂O **Ni²⁺ + 2e \rightarrow Ni ***Cu(OH)₂ + 2e \rightarrow Cu + 2OH⁺

Figure 10. Schematic illustration of the hydrogen production, charge transfer, separation, and chemical conversions with Ni(OH)₂ and Cu(OH)₂ nanoclusters on TiO₂ under photoreaction conditions.

with the decrease in Cu content (Figure S2). 2) The presence of Cu in its reduced state in all XPS results owing to the excitation of TiO₂ electrons by X-rays and their subsequent transfer to Cu(OH)₂ nanoclusters. 3) Two times lower PL intensity in the case of $1.0 \text{ Cu}(OH)_2/P25$ compared with P25, indicating photoexcited electron transfer from the CB of the P25 to the Cu(OH)₂. 4) The approximately three-fold decrease in dye degradation rate on Cu(OH)₂ loaded P25 compared with P25 alone owing to the competition between electron transfer from the conduction band of TiO₂ to Cu(OH)₂ and dye molecule, probably via superoxide radical (O₂⁻⁺) formation. This is further supported by an increase in dye degradation time in the presence of superoxide scavenger benzoquinone whereas no change in



Figure 9. Schematic illustration of the hydrogen production, charge transfer, separation, and chemical conversions with Ni(OH)₂ and Cu(OH)₂ nanoclusters on TiO₂,^[2a,7,9,21,47]

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dye degradation time was observed in the presence of a hole scavenger, Na_2EDTA (Table 3).^[44] In the metallic state, Cu acts as a co-catalyst for electron transfer to proton for hydrogen production.^[45]

The rate of hydrogen production observed with a similar loading of Ni was far less than that with Cu (Figures 6 and 7). The reduction potential of $Ni(OH)_2/Ni$ $[Ni(OH)_2 + 2e^- = Ni + Ni(OH)_2 + Ni(OH)_2 + 2e^- = Ni + Ni(OH)_2 + Ni(O$ $2 \text{OH}^- E^\circ = -0.76 \text{ V}$] is more negative than the conduction band potential of TiO₂. Thus, the electron transfer from the CB band of TiO₂ to Ni(OH)₂ is thermodynamically unfavorable. Although there is evidence from photoluminescence and dye degradation experiments that the Ni(OH)₂ level lies above the TiO₂ CB for the photocatalysts used in this study, stable H₂ production on monometallic Ni(OH)₂ loaded catalysts is observed during the hydrogen production experiments. Furthermore, 0.8Cu(OH)₂-0.2Ni(OH)₂/P25 exhibits higher activity to that of the sum of both 0.2 Ni(OH)₂/P25 and 1.0 Cu(OH)₂/P25. These observations reject the possibility of Ni(OH)₂ remaining inactive under photoreaction conditions. Typically, in a photoreaction experiment involving ethanol or glycerol as sacrificial agent, the pH of the reaction mixture drops to approximately 4 within the first hour as a result of their oxidation. There is a possibility of Ni(OH)₂ dissolution in the reaction mixture as a Ni^{2+} concentration of 0.1 mol L⁻¹ at pH 6 is predicted in equilibrium with Ni(OH)₂^[46]

To confirm this, we performed photoreactions with the high concentration of 1% Ni(OH)₂/P25 catalyst (100 mg) to allow Ni²⁺ detection in the reaction mixture, by using dimethylglyoxime (DMG) as a complexing agent. The appearance of a red color after 3 h clearly indicated the dissolution of Ni²⁺ in the alcohol/water mixture. Based on these observations, the stable hydrogen production, and the appropriate redox potential of Ni²⁺/Ni couple (-0.23 V), we propose that Ni(OH)₂ is first dissolved into the reaction mixture and Ni²⁺(aq) thus formed is then photodeposited on P25 as shown in Figures 9 and 10. This is also supported by the observation that relatively longer induction time is needed to observe hydrogen production in the case of Ni-containing catalysts (Figures 6 and 7).

The considerable hydrogen production rate in the case of 1.0 Cu(OH)₂/TiO₂ was due to its appropriate work function (5.1 eV). The very high rate of hydrogen production, 10 mmol h⁻¹g⁻¹, in the ethanol/water mixture observed for 0.8 Cu(OH)₂–0.2 Ni(OH)₂/P25 and that of 22 mmol h⁻¹g⁻¹ in the glycerol/water mixture observed for 0.5 Cu(OH)₂-0.5 Ni(OH)₂/ P25 is a result of the synergistic effect of Cu deposited directly from Cu(OH)₂ precipitates and re-adsorption of Ni²⁺ cations in the solution. These Ni²⁺ ions may selectively be photodeposited over electron-rich sites on the P25 surface, which are away from the Cu nanoclusters or on the Cu nanoclusters themselves, forming a Cu/Ni alloy (Figure 10). It has been reported that for an ideal composition of Cu/Ni alloy, a more suitable Schottky barrier height can be made.^[29] The reducibility of Ni is enhanced in the Cu/Ni alloy owing to the considerably less negative ΔG° of Cu oxide formation (-129 kJ mol⁻¹) compared with that of Ni oxide formation $(-430 \text{ kJmol}^{-1})$,^[1] which is favorable for water reduction.^[29] The decrease in the hydrogen production rate on going from 0.5 Cu(OH)₂-0.5 Ni(OH)₂/P25 to $0.2 \text{ Cu}(\text{OH})_2$ – $0.8 \text{ Ni}(\text{OH})_2$ /TiO₂ is due to the gradual decrease of the Cu amount. The very small hydrogen production rate observed with $0.8 \text{ Cu}(\text{OH})_2$ – $0.2 \text{ Ni}(\text{OH})_2$ /TiO₂ calcined at 300 °C in air might be due to conversion of Cu(OH)₂ and Ni(OH)₂ to their oxides (CuO and NiO, respectively) and their subsequent growth into larger particles by sintering. This explanation is also in line with what has been reported previously where a decrease in H₂ production rate with an increase of CuO particle size was observed.^[8]

Conclusions

A series of Cu(OH)₂-Ni(OH)₂/P25 photocatalysts were prepared by co-deposition-precipitation (total metal loading $\approx 1 \text{ wt \%}$), characterized, and their performance evaluated for H₂ production in different alcohol/water mixtures under UV excitation. Among this series, the 0.8Cu(OH)₂-0.2Ni(OH)₂/P25 photocatalyst demonstrated very high hydrogen production rates in 20 vol% ethanol/water and 5 vol% glycerol/water mixtures $(10 \text{ mmol } h^{-1}g^{-1} \text{ and } 22 \text{ mmol } h^{-1}g^{-1}, \text{ respectively}).$ Detailed analyses based on reaction kinetics, photoluminescence, XPS, and charge carrier scavenging suggest that both working catalysts are composed of Cu and Ni metals in their active phase. Cu^o is produced directly by the transfer of electrons from the conduction band of TiO₂ to surface Cu(OH)₂ nanoclusters, whilst Ni⁰ is formed indirectly through a process of gradual dissolution of Ni(OH)₂ to yield aqueous Ni²⁺ as a result of the acidic environment of the medium, followed by Ni²⁺ reduction by electrons from the conduction band of the semiconductor. The high rates of H₂ production, which match those obtained with noble metals, can be explained by the following rationale. An oxidized Ni atom in contact with a Cu atom may become reduced owing to the considerably less negative ΔG° of Cu oxide formation (-129 kJ mol⁻¹) compared with that of Ni oxide formation (-430 kJ mol⁻¹).^[1] This would then increase hydrogen production because the work function of Ni is higher than that of Cu.^[2] The present work suggests that bimetallic Cu-Ni catalysts formed on TiO₂ are promising alternatives to noble metals for hydrogen production.[25a, 26]

Experimental Section

Catalyst preparation

All the reagents used were of analytical grade and used without further purification. Distilled water was used in all experiments. Commercially available Degussa P25 was obtained from Evonik Industries, Germany. In a typical synthesis, P25 (500 mg) was added to 0.5 μ NaOH (50 mL) and sonicated well to give a homogeneous slurry. Specific volumes of aqueous solutions of Cu(NO₃)₂·3 H₂O and Ni(NO₃)₂·6 H₂O were then added dropwise to the P25 dispersion with continuous stirring. The resulting dispersions were sonicated for 10 min and then stirred for a further 2 h. Finally, the Cu(OH)₂ and Ni(OH)₂ impregnated P25 photocatalysts were collected by vacuum filtration, washed several times with water, and then dried in air at 80 °C for 24 h. The nominal weight percentages of Ni and Cu in the photocatalysts were 1.0 Cu(OH)₂, 1.0 Ni(OH)₂, 0.5 Cu(OH)₂– 0.5 Ni(OH)₂, 0.8 Cu(OH)₂–0.2 Ni(OH)₂, and 0.2 Cu(OH)₂–0.8 Ni(OH)₂, where the prefixes represent the weight percentage of each metal.

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A 0.8Cu(OH)₂-0.2Ni(OH)₂/P25 sample was also calcined at 300 °C for 2 h to examine the effect of metal oxide formation on photocatalytic activity. The Brunauer–Emmett–Teller (BET) surface area of TiO₂ is approximately 50 m²g⁻¹ in all the catalysts.

Photocatalysts characterization

Powder XRD patterns were collected with a Siemens D5000 Diffractometer equipped with a curved graphite filter monochromator. XRD data was collected over the 2θ range $20-70^{\circ}$ (step size 0.05° , scan rate 2° min⁻¹) by using CuK_{α} X-rays ($\lambda = 1.5418$ Å, 40 mA, 40 kV). Anatase and rutile crystallite sizes (L) were determined by using the Scherrer equation ($L = 0.9\lambda/\beta \cos\theta$) and line-widths of the anatase (101) reflection at $2\theta = 25.3^{\circ}$ and the rutile (110) reflection at $2\theta = 27.4^{\circ}$. UV/Vis absorbance spectra of the photocatalysts were collected over the wavelength range 200-900 nm with a Thermo Fisher Scientific UV/Vis spectrophotometer equipped with a praying mantis diffuse reflectance accessory. TEM analyses were performed by using a Philips CM12/STEM Electron Microscope, PW 6030 (120 kV). XPS data was collected by using a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyzer and an analysis chamber at base pressure $\approx 1 \times 10^{-9}$ Torr. Samples were excited by using monochromatic AlK_{α} X-rays (1486.69 eV) with the X-ray source operating at 150 W. Samples were gently pressed into thin pellets of \approx 0.1 mm thickness for the analyses. A charge neutralization system was used to alleviate sample charge build up during analysis. Survey scans were collected at a pass energy of 80 eV over the binding energy range 1200-0 eV, whereas core level scans were collected with a pass energy of 20 eV. The spectra were calibrated against the C1s signal at 284.80 eV from adventitious hydrocarbons. Steady-state and timeresolved photoluminescence (PL) measurements were carried out by using a Flau Time 300 (FT-300) steady-state and lifetime spectrometer, PicoQuant GmbH, Germany. The PL was measured by using a pulsed LED laser excitation source, PLS-300, centered at 305 nm with full-width half-maximum (FWHM) of \approx 416 ps and pulse energy 0.077 pJ. The PL curves were fitted by using Easy Tau and FluoFit software.

Hydrogen production experiments

Photocatalytic hydrogen production tests were conducted in a Pyrex reactor (140 mL). Photocatalyst (2.5 mg) was loaded in the reactor containing 25 mL of an aqueous alcohol/water mixture (20 vol% ethanol or 5 vol% glycerol). Prior to the start of each photocatalytic experiment, the reactor was continuously bubbled with nitrogen at a flow rate of 10 mLmin⁻¹ for 30 min to remove dissolved and headspace oxygen. A Spectroline model SB-100P/F lamp (100 W, 365 nm) at a distance of 10 cm from the reactor was used for UV light excitation of the photocatalysts. The photon flux measured at the sample was \approx 6.5 mW cm⁻² (comparable to UV flux in sunlight). Hydrogen generation was monitored by taking gas head space samples (0.5 mL) at regular time intervals and injecting them into the gas chromatograph (Shimadzu GC 2014) equipped with a TCD detector and molecular sieve capillary column (length = 25 mm; ID = 0.32 mm; average thickness 0.50 μ m). H₂ produced through the photoreaction was quantified against an internal calibration curve. The photocatalytic tests for each sample were repeated at least three times for accuracy. Catalyst stability tests were performed by using 0.8 Cu(OH)₂-0.2 Ni(OH)₂/P25 and 20 vol% ethanol/water mixture. The test was started by using the same experimental set up as explained above then continued for the duration of the experiments (16 h). The

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only difference was that the reactor was purged with nitrogen at a flow rate of 10 mLmin⁻¹ for 30 min at 4 h increments to remove dissolved and headspace gases.

 $0.05\,\,\text{m}$ HCl or $0.05\,\,\text{m}$ NH4OH solutions were used to adjust the pH for experiments performed to see the effect of pH on H2 generation rate.

Dye degradation experiments

Rhodamine B photodegradation experiments were conducted in a 140 mL Pyrex reactor containing aqueous Rhodamine B (40 mL, 12 mg L^{-1}) and photocatalyst (10 mg). Prior to starting an experiment, the reaction mixture was stirred in the dark for one hour to establish the adsorption–desorption equilibrium of the dye on the catalyst surface. The same irradiation set up was used as that described in the hydrogen production experiment section. At regular intervals, a small portion of the reaction mixture was collected by pipette, centrifuged to remove suspended photocatalyst particles, and its absorbance (400–600 nm) was measured by using a UV spectrophotometer (lambda 25 PerkinElmer). For radical trap experiments, 5 mL of 50 mmol solutions of Na₂EDTA or benzoquinone were added directly into the initial reaction mixture. Negligible Rhodamine B degradation was observed under UV irradiation in the absence of a photocatalyst.

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Noble metal substitutes: A series of $Cu(OH)_2$ -Ni $(OH)_2$ /P25 photocatalysts was prepared by co-deposition-precipitation (total metal loading ≈ 1 wt%) and their performance was evaluated for H₂ production. Among this series, the 0.8 Cu(OH)₂-0.2 Ni(OH)₂/P25 photocatalyst demonstrated very high H₂ production rates in 20 vol% ethanol/water and 5 vol% glycerol/water mixtures (10 and 22 mmolh⁻¹g⁻¹, respectively).



*Ni(OH)₂ + 2H⁺ → Ni²⁺ + 2H₂O **Ni²⁺ + 2e → Ni ***Cu(OH)₂ + 2e → Cu + 2OH

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On the Synergism between Cu and Ni for Photocatalytic Hydrogen Production and their Potential as Substitutes of Noble Metals