Photocatalytic production of hydrogen on Ni/NiO/KNbO₃/CdS nanocomposites using visible light†

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The photocatalytic production of H₂ from water splitting was demonstrated on Ni/NiO/KNbO₃/CdS nanocomposites using visible light irradiation at wavelengths >400 nm in the presence of isopropanol. The inherent photocatalytic activity of bulk-phase CdS was enhanced by combining Q-sized CdS with KNbO₃ and Ni deposited on KNbO₃. Enhanced activity is most likely due to effective charge separation of photogenerated electrons and holes in CdS that is achieved by electron injection into the conduction band of KNbO₃ and the reduced states of niobium (*e.g.*, Nb(IV) and Nb(III)) are shown to contribute to enhanced reactivity in the KNbO₃ composites by mediating effective electron transfer to bound protons. We also observed that the efficient attachment of Q-size CdS and the deposition of nickel on the KNbO₃ surface increases H₂ production rates. Other factors that influence the rate of H₂ production including the nature of the electron donors and the solution pH were also determined. The Ni/NiO/KNbO₃/CdS nanocomposite system appears to be a promising candidate for possible practical applications including the production of H₂ under visible light.

Introduction

Hydrogen (H₂) production from water splitting using semiconductor photocatalysts has attracted considerable interest since the pioneering work of Fujishima and Honda,¹ who discovered that water can be photo-electrochemically decomposed into hydrogen and oxygen using a semiconductor (TiO₂) electrode under UV irradiation. A large number of metal oxides and sulfides (*e.g.* TiO₂,^{1–3} WO₃,^{4–6} SrTiO₃,^{7,8} ZnO,^{9–11} CdS,^{12–17} ZnS,^{13,16,18,19} niobates,^{20–24} and tantalates^{25–28}) have been examined as photocatalysts for hydrogen production from splitting water. However, the majority of the simple and mixed-metal oxides photocatalysts are primarily active for H₂ production under UV irradiation ($\lambda < 385$ nm or $E_g \geq 3.0$ eV) present in only a small portion of solar light. More recently, there is a focused effort on the development of photocatalysts that are capable of using visible light ($\lambda = 400$ –700 nm) for the photocatalytic production of H₂ including transition metal doping (*e.g.*, platinum,²⁹ chromium,³⁰ and vanadium³¹) and nonmetallic element doping (*e.g.*, nitrogen,^{32–35} sulfur,^{36,37} and carbon^{35,38}).

CdS, n-type semiconductor with $E_g = 2.4$ eV, has been shown to have photocatalytic activity for H₂ production under visible light irradiation, although, sacrificial electron donors such as C₂H₅OH,³⁹ HS[–],^{40,41} or SO₃^{2–}¹⁹ are used to obtain measurable rates of H₂ production and to avoid the photocorrosion of CdS in the presence of O₂. On the other hand, the electronic levels and photoactivity of CdS can be tuned by changing or controlling

particle size without changing the chemical composition. For example in the case of nanoparticulate ZnO, Hoffmann and co-workers^{9,42} reported a ten-fold increase in photoefficiency for the photocatalytic production of hydrogen peroxide with a decrease in particle size from 40 to 23 nm. In another example, Hoffman *et al.*⁴³ found an increase in quantum efficiency for photo-polymerization of methyl methacrylate with a corresponding decrease in particle size using Q-size CdS.

In order to enhance the photocatalytic activity of CdS, efforts have been made to combine CdS with other semiconductors having different band energies (*e.g.*, TiO₂,^{44–47} ZnS,^{13,48,49} K₄Nb₆O₁₇,⁵⁰ or K₂Ti₄O₉^{51,52}) since the coupling of two semiconductor particles with different energy levels is useful to achieve effective charge separation. For example in a colloidal TiO₂/CdS composite system, the electrons photogenerated from CdS band gap excitation can be transferred to the conduction band (CB) of TiO₂ particles, while the holes remain in the CdS particle. It is also observed that this charge separation in a colloidal composite system can accelerate the degradation of azo dyes⁴⁴ and increase H₂ production in aqueous H₂S solution.⁴⁶

In this study, we synthesized nanocomposites of potassium niobate (KNbO₃) and CdS by solid-state reactions and investigated their properties and photoactivity for H₂ production under visible light irradiation ($\lambda > 400$ nm) in the presence of isopropanol as an electron donor. KNbO₃ is used in optical waveguides, in nonlinear optical devices (*e.g.*, frequency doubling and wavelength mixing), in piezoelectric devices (*e.g.*, tunable frequency ultrasound transducers), in holographic image storage, and as a wide-band gap photocatalyst ($\Delta E_g = 3.4$ eV) because of its unusual chemical and physical properties. KNbO₃/CdS nanocomposites are characterized by XRD, SEM, TEM, UV-vis reflectance spectra and show better visible-light photoactivity for H₂ production than other composites (*e.g.*, TiO₂ or K₄Nb₆O₁₇). Moreover, the efficiency of H₂ production is significantly enhanced by loading Ni on KNbO₃.

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Experimental

Sample preparation

Stoichiometric KNbO_3 was synthesized from Nb_2O_5 (Aldrich) and K_2CO_3 (Aldrich) in a standard solid-state reaction. K_2CO_3 and Nb_2O_5 were mixed together in a mortar at 1 : 1 mole ratio and the powdered mixture was pressed into a pellet at 27.6 MPa and then heated at 650–925 °C for 10 h with a heating and cooling temperature ramp of $\pm 200\text{ }^\circ\text{C h}^{-1}$. With slight variations of the K : Nb mole ratio of 1 : 1.1 and a heating temperature at 1025 °C, a mixture of KNbO_3 and $\text{K}_4\text{Nb}_6\text{O}_{17}$ is obtained. Synthesis of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was carried out for comparison using K_2CO_3 and Nb_2O_5 in the K : Nb mole ratio of 1 : 1.5 and calcination at 1150 °C for 10 h. The crystal structures were confirmed by X-ray diffraction (XRD) at room temperature.

KNbO_3/CdS composite samples were prepared by stirring KNbO_3 powders in a 20 mL of ethanol of $2 \times 10^{-2}\text{ M}$ $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ for 1 day, followed by sulfurization with 20 mL of ethanol of $2 \times 10^{-2}\text{ M}$ Na_2S for 1 day. Composite samples were collected by filtration, which was followed by washing and subsequent drying.

Elemental nickel (Ni) and NiO (0.1–3.6 wt%) were loaded on the surface of KNbO_3 by a method that Domen and co-workers^{23,53,54} reported. KNbO_3 samples were suspended in a $\text{Ni}(\text{NO}_3)_2$ aqueous solution for 1 day, followed by it being filtered, washed and dried. The solid was reduced in H_2 atmosphere at 500 °C for 2 h, and subsequently oxidized in an O_2 atmosphere at 200 °C for 1 h. In the case of elemental Ni-loaded KNbO_3 samples (Ni/KNbO_3), the O_2 oxidation step was eliminated. The NiO-loaded KNbO_3 samples (NiO/KNbO_3) were obtained by complete O_2 oxidation at 500 °C for 1 h. A schematic flow chart is shown in Fig. 1.

Fig. 1 Schematic flow chart outlining the synthetic procedures for the composite $\text{Ni}/\text{NiO}/\text{KNbO}_3/\text{CdS}$ catalyst preparation.

Characterization

The crystal structures of synthesized KNbO_3 samples were confirmed by powder X-ray diffraction (XRD) using a Philips diffractometer (X'pert Pro) with $\text{Cu-K}\alpha$ radiation. Diffuse reflectance spectra were obtained with a UV-vis spectrometer (Shimadzu UV-2101 PC) and were converted from reflection to absorption spectra by the Kubelka–Munk method. Brunauer–Emmett–Teller (BET) surface area analyses were also performed to compare the surface areas of KNbO_3 samples that were prepared under different conditions. Microstructures and composition were also analyzed with a LEO 1550 VP Field Emission Scanning Electron Microscope (SEM) and a Philips EM201 Transmission Electron Microscope (TEM). Inductively Coupled Plasma-Mass Spectrometry (HP 4500 ICP-MS) was used to determine the amounts of Ni^{2+} and Cd^{2+} adsorbed on the surface of KNbO_3 . Potassium ions released from KNbO_3 during ion exchange with Ni^{2+} were determined by a Dionex DX-500 Ion Chromatography system. X-Ray Photoelectron Spectroscopy (XPS) was used to observe the changes in the oxidation state of Nb species and Ni species adsorbed on the surface of KNbO_3 with $\text{Al-K}\alpha$ radiation.

Photocatalytic reaction

Photocatalytic reactions for hydrogen production were carried out in an air-tight reactor vessel under visible light irradiation ($\lambda > 400\text{ nm}$). Catalyst samples (0.2 g) were suspended in 50 mL of a water–isopropanol mixture (30 v/v%) in a Pyrex glass reactor. Samples were purged with Ar or N_2 gas for 30 min before reaction in order to eliminate dissolved O_2 . A high-pressure 500 W Hg–Xe arc lamp in combination with a 400 nm cut-off filter was used as the primary light source. The intensity of incident light was determined by ferrioxalate actinometry to obtain quantum yields for H_2 production. The amount of H_2 evolved during photolysis was analyzed by GC/TCD (HP 5890, N_2 carrier) with a molecular sieve column (30 m $\times$ 0.32 mm $\times$ 12.00 μm).

Results and discussion

Ni/NiO/ KNbO_3 /CdS nanocomposite characterization

Fig. 2 shows XRD patterns of synthesized KNbO_3 under different calcination temperatures and mole ratios. XRD pattern for KNbO_3 calcined at 925 °C with 1 : 1 mole ratio of K : Nb (Fig. 2(a)) shows exactly the same 2θ peaks that correspond to standard KNbO_3 . Samples calcined over the range of temperatures from 650 to 925 °C also show the same peak patterns. However, the sample produced at 1025 °C with 1 : 1.1 mole ratio of K : Nb (Fig. 2(b)) has extra 2θ peaks that are attributed to potassium hexaniobate ($\text{K}_4\text{Nb}_6\text{O}_{17}$). $\text{K}_4\text{Nb}_6\text{O}_{17}$ has a perovskite structure similar to KNbO_3 , but it consists of a layered structure composed of two different types of niobate sheets. The material structures were also confirmed by SEM images. A layered structure is only observed for the sample calcined at 1025 °C by SEM as shown in Fig. 3. The diffraction peaks of KNbO_3 samples are more intense and sharper with an increase in calcination temperature. The broadening of XRD peaks at low calcination temperatures may be due to smaller crystallite sizes.

Fig. 2 X-Ray diffraction patterns for (a) KNbO_3 powder sample synthesized from 1 : 1 mole ratio of K_2CO_3 and Nb_2O_5 at 925°C and (b) KNbO_3 powder sample synthesized from 1 : 1.1 mole ratio of K_2CO_3 and Nb_2O_5 at 1025°C . (●) KNbO_3 , (○) $\text{K}_4\text{Nb}_6\text{O}_{17}$.

The particle sizes of KNbO_3 at different calcination temperatures can be estimated with the Scherrer equation; the estimated particle sizes were 28, 32 and 39 nm for KNbO_3 samples prepared at 650°C , 775°C and 925°C , respectively. BET surface areas were found to be 4.35, 3.08 and $2.14\text{ m}^2\text{ g}^{-1}$ for 650°C , 775°C and 925°C samples, respectively, and it is apparent that the specific surface area decreases with an increase in calcination temperature. Furthermore, there appears to be no observable structural difference between KNbO_3 samples before and after Ni deposition or with the addition of nanoparticulate CdS. Fig. 4 is the TEM picture of a nanocomposite sample of Ni/NiO/ KNbO_3 /CdS which shows that Ni or CdS nanoparticles were loaded on the surface of KNbO_3 .

Fig. 5 shows the light absorption properties of nanocomposite samples. The KNbO_3 /CdS nanocomposite absorbs visible light at $\lambda > 400\text{ nm}$. This is primarily due to the band gap excitation of Q-size CdS, since KNbO_3 does not absorb visible light. The respective band gaps are estimated to be 3.4 eV and 2.6 eV for KNbO_3 and Q-CdS, from the plots of Kubelka–Munk functions *vs.* photon energy. It should be noted that absorption edge of Q-size CdS synthesized for the CdS/ KNbO_3 nanocomposite is blue-shifted from absorption edge of bulk CdS particles.⁴³

The synthesized KNbO_3 samples were suspended in an aqueous $\text{Ni}(\text{NO}_3)_2$ solution for 1 day to load Ni^{2+} as a co-catalyst. ICP-MS and IC results show that most of the Ni^{2+} ions are adsorbed on the surface of KNbO_3 particles and some of them

Fig. 3 SEM images of (a), (b) KNbO_3 synthesized at 925°C (K : Nb = 1 : 1) and (c) KNbO_3 synthesized at 1025°C (K : Nb = 1 : 1.1).

Fig. 4 TEM image of Ni/NiO/ KNbO_3 /CdS nanocomposite.

are ion-exchanged with K^+ ions located in the KNbO_3 framework. However, in the synthesis of CdS nanoparticles on the KNbO_3 surface, only 20–30% of Cd^{2+} ions are adsorbed on the surface and ion exchange with K^+ is not observed. Then Ni^{2+} -adsorbed (or ion-exchanged) KNbO_3 samples were treated under proper conditions, *i.e.* H_2 reduction at 500°C followed by O_2 oxidation at 200°C . After thermal reduction by H_2 , the doped samples turned gray from the initial white undoped KNbO_3 .

Fig. 5 UV-vis diffuse reflectance spectra for (a) KNbO₃, (b) KNbO₃/CdS, (c) Ni/NiO/KNbO₃/CdS.

However, oxidation at 500 °C converts elemental nickel to NiO with a corresponding change in color from gray to light yellow. XPS analysis of the various samples was used to identify the oxidation states of Ni in each sample.

Photocatalytic H₂ production

The measured H₂ production rates in illuminated aqueous isopropanol solutions under visible light with CdS, KNbO₃, Ni/NiO/KNbO₃, and Ni/NiO/KNbO₃/CdS composites are compiled in Table 1. The naked KNbO₃, nickel-doped KNbO₃, and Ni/NiO/KNbO₃ samples showed no activity for H₂ production under visible light since its band gap energy (3.4 eV) was larger than the excitation energies ($\lambda > 400$ nm). Simple Q-CdS nanoparticle suspensions produce H₂, but at very low rates. However, H₂ production rates increase significantly in the KNbO₃/CdS nanocomposites. This may be because effective charge separation of electrons and holes in illuminated CdS with electron injection into the conduction band of KNbO₃ may be

Table 1 Photocatalytic activities of potassium niobate nanocomposites for H₂ production from water–isopropanol mixed solution

Sample	Weight% of Ni _T	Calcination temp./°C	H ₂ production ^a /μmol h ⁻¹ g ⁻¹
KNbO ₃	0	925	0
Ni/NiO/KNbO ₃	0.1	925	0
CdS	0	—	3
TiO ₂ /CdS	0	—	12
Ni/NiO/K ₄ Nb ₆ O ₁₇ /CdS	0.1	1150	37
Ni/NiO/KNbO ₃ /CdS	0	925	50
	0.1	925	150
	0.3	925	125
	0.5	925	75
	1.0	925	80
	3.6	925	65
	0.5	650	110
	0.5	775	80
	1.0	650	120
	1.0	775	80

^a Catalyst, 0.2 g; volume, 50 ml; light source, Hg–Xe lamp (500 W) with $\lambda > 400$ nm, 30 v/v% isopropanol.

possible in the KNbO₃/CdS nanocomposites. H₂ production with TiO₂ (Degussa P-25)/CdS nanocomposites was also performed for comparison. TiO₂/CdS had lower H₂ production activity than KNbO₃/CdS. H₂ production rates for the KNbO₃/CdS nanocomposites were enhanced significantly in the presence of the deposited Ni/NiO co-catalysts. Ni most likely serves to collect conduction band electrons. However, a significant enhancement of H₂ production rate was not observed in a Pt deposited KNbO₃ sample (Pt/KNbO₃/CdS) as compared to Ni/KNbO₃/CdS nanocomposites. We also synthesized potassium hexaniobate (K₄Nb₆O₁₇) for comparison because K₄Nb₆O₁₇ is known as a good photocatalyst for H₂ production under UV light irradiation.^{20,22,23} However, the result shows that KNbO₃/CdS nanocomposite produces more H₂ than K₄Nb₆O₁₇/CdS under visible light irradiation.

The enhanced reactivity of the KNbO₃ nanocomposites may be due to involvement of the reduced states of niobium and/or oxygen vacancies that allow for the photoexcitation of mobile electrons with visible light. For example, Ewart *et al.*⁵⁵ reported that mobile electrons are generated in electrochemically reduced and Fe-doped KNbO₃ upon excitation at 532 nm. The electrons photoexcited at 532 nm had lifetimes of 4 ns and electron mobilities of 0.5 cm² V⁻¹ s⁻¹. They concluded that the photoexcited electrons are trapped within 4 ns (*i.e.*, loss of detectable mobility), however, the trapped-state electrons are thermally activated on a millisecond timeframe and eventually recombine with the internal donor states. Kesselman *et al.*⁵⁶ observed a similar reduction in Nb₂O₅/TiO₂ composites that were reduced over hydrogen at high temperatures. Reduction of Nb₂O₅ is known to form a variety of phases such as Nb₁₂O₂₉, Nb₂₂O₅₄, Nb₂₅O₆₂, and Nb₄₇O₁₁₆ that involve partial oxygen loss coupled with the formation of Nb(IV). Therefore, the longer lifetimes ($\tau_{tr} > \text{ms}$) of the trapped electrons may contribute to the higher reduction rates for bound protons or hydroxides. Similar mixed valence state phase should coexist within the framework of reduced KNbO₃ and contribute to the photo-excitation of electrons and to the overall photoactivity with visible light. The Ni/NiO/KNbO₃ samples were thermally treated at 500 °C under H₂ atmosphere to reduce Ni²⁺ to elemental nickel. This treatment step may lead to creation of oxygen vacancies or formation of the reduced states (*e.g.*, Nb(IV) and Nb(III) states) of niobium. The thermal treatment of pure, white KNbO₃ at 500 °C under H₂ produced a light gray product that is consistent with Nb(V) reduction. We performed XPS analysis to compare the oxidation states of Nb between KNbO₃ samples before and after H₂ reduction, however, the reduced states were not readily observed. However, it was measured that reduced states of Nb are formed during the photolytic reaction. Another relevant feature of the metal niobates (*e.g.*, LiNbO₃⁵⁷ and KNbO₃⁵⁸), which is critical for electro-optic and photorefractive applications, is the activation of surface protons (*i.e.*, protons bound in hydroxyl ions, ⁻OH). The hydroxyl bound protons have activation energies in the range of 1 eV for mobility in KNbO₃ crystals.

In light of the above photophysical properties related to surface hydroxyl groups, an alternative pathway may involve excitation of reduced KNbO₃ with visible light followed by conduction band reduction of surface bound protons on KNbO₃. The pH of zero point of charge, pH_{zpc}, of KNbO₃ was measured as pH $\sim$ 3.2, thus the KNbO₃ surface may be dominated by

$>\text{NbOH}$ and $>\text{NbO}^-$ under our optimal experimental conditions ($\text{pH} \sim 8$). Given this situation, we can write the following set of reactions that may result in H_2 production on KNbO_3 surface sites or Ni/NiO/KNbO_3 composite sites:

In addition, we compared three different procedures for attachment of CdS particles on the KNbO_3 surface as shown in Fig. 6. To form KNbO_3/CdS nanocomposites, we first added Cd^{2+} ions in KNbO_3 suspension, and then we added sulfide ($\text{HS}^-/\text{S}^{2-}$) ions after stirring for 1 day (Fig. 6(a)). ICP-MS results show that only 20–30% of the Cd in CdS particles are directly synthesized on KNbO_3 surface and the remainder of the CdS particles are suspended freely in the solution. One sample was prepared by mechanical mixing of CdS and KNbO_3 by addition of KNbO_3 after Q-CdS synthesis in ethanol (Fig. 6(b)) and another sample has only CdS adsorbed on the KNbO_3 surface by removing free Cd^{2+} ions in suspension before adding S^{2-} ions (Fig. 6(c)). The CdS surface adsorption sample (Fig. 6(c)) shows reasonable photoactivity even though the amounts of CdS are quite small (20–30%) compared to samples having CdS synthesized both on KNbO_3 surface and in solution (Fig. 6(a)). As a consequence, we conclude that direct CdS contact with the KNbO_3 surface plays an important role for effective charge separation with increased H_2 production rates. Although, the

Fig. 6 Effect of CdS loading on KNbO_3 surface on photocatalytic activities for H_2 production: (a) CdS synthesized both on KNbO_3 surface and in solution, (b) CdS synthesized by external mixing with KNbO_3 , (c) CdS adsorbed on KNbO_3 , (d) Q-size CdS only.

externally mixed sample (Fig. 6(b)) also has measurable H_2 production rates. From these results, we can infer that Q-CdS particles are attached to the surface of KNbO_3 under our experimental conditions ($\text{pH} \sim 8$) even though CdS was synthesized initially in solution phase.

The KNbO_3 surface is negatively charged under the pH conditions of our experiments since the pH_{zpc} of KNbO_3 is measured as $\text{pH} \sim 3.2$. The actual determination of pH_{zpc} of the nanoparticulate CdS colloids is more difficult. Park and Huang⁵⁹ reported a $\text{pH}_{\text{zpc}} = 7.5$ for colloidal CdS based on electrophoretic mobility measurements and acid–base titrations. At an ionic strength of $\mu = 0.05$ M, they determined that $\text{p}K_{\text{a}1} = 6.1$ and $\text{p}K_{\text{a}2} = 9.0$ for $[\text{Cd}^{2+}] = 2.5$ μM and $\sigma_0 = 20$ mC cm^{-2} . Liu and Huang⁶⁰ subsequently reported a pH_{zpc} for cubic CdS of 7.0 and $\text{pH}_{\text{zpc}} = 7.5$ for hexagonal CdS. In contrast, other researchers^{61–63} have reported substantially lower values for the pH_{zpc} for CdS in aqueous suspensions. Under experimental conditions that were quite different from those employed by Park and Huang,⁵⁹ Nicolau and Menard⁶³ determined a $\text{pH}_{\text{zpc}} = 1.8$ for 0.01 M Na_2SO_4 and KCl as background electrolytes based on electrophoretic mobility measurements. Guindo *et al.*⁶² found even lower values of pH_{zpc} between 1 and 1.5 for differently prepared spherical CdS particles. However, they pointed out that the IEP (isoelectric point) was sensitive to the specific surface characteristics of CdS which depend on the degree of oxidation or aging as noted by the shift in IEP to higher values for samples that were synthesized over longer periods of time. According to our observations, it may be true that pH_{zpc} of CdS is relatively high under our experimental conditions, so that CdS colloid in solution are positively charged and then electrostatically attracted to the negatively charged KNbO_3 particles under our experimental pH conditions.

The rates of H_2 production on the four-component composite, $\text{Ni/NiO/KNbO}_3/\text{CdS}$, are compared to the three-component composite containing only Ni or NiO. The data presented in Fig. 7 show that elemental Ni on KNbO_3 is a more active species than NiO on KNbO_3 to improve H_2 production although its external surface is partially oxidized to NiO. However, the H_2 production rates are not greatly enhanced in the three-component composite containing only NiO. This tendency is consistent

Fig. 7 Effect of oxidation states of Ni deposited KNbO_3 (0.1 wt% loading as Ni^+) on photocatalytic H_2 production from water–isopropanol mixed solution.

with previous results obtained for Ni/NiO loaded onto SrTiO₃ as reported by Domen *et al.*⁵³ They reported that Ni/NiO/SrTiO₃ produced substantially more H₂ from aqueous methanol than the simpler NiO/SrTiO₃ system under UV irradiation. They concluded that the presence of Ni metal in contact with the SrTiO₃ surface plays an important role in the H₂ production activity. Domen *et al.*⁶⁴ also found small amounts of H₂ evolved under the band gap irradiation of Ni/SrTiO₃. They attributed their low activity to loss of Ni by release of Ni²⁺ due to oxidation of Ni metal by direct hole transfer from SrTiO₃ during band gap irradiation. In contrast, our results show that the three-component, Ni/KNbO₃/CdS, composite can produce a comparable amount of H₂ compared to the four-component, Ni/NiO/KNbO₃/CdS, composite. In both the 3- and 4-component catalysts, the primary absorption occurs at $\lambda > 400$ nm (compared to SrTiO₃ with $\lambda < 400$ nm) with CdS as a chromophore. Thus, elemental nickel deposited on KNbO₃ is unlikely to be directly oxidized by holes in our composite material.

As shown in Table 1, the highest H₂ production rates were obtained with a Ni-deposition level of 0.1 wt% as Ni_T (= Ni + NiO), and above this level enhancement due to nickel deposition was marginal. However, we observed the enhanced H₂ production with higher wt% of Ni deposition on KNbO₃ samples prepared at low calcination temperatures. The increase of photoactivities with 0.5–1.0 wt% Ni-loaded on KNbO₃ prepared at low calcination temperatures may be only due to simply an increase in the total reactive surface area. It is noted that a KNbO₃ sample mixed with the K₄Nb₆O₁₇ structure which was calcined at 1025 °C produces comparable amounts of H₂ to KNbO₃ samples calcined at 925 °C.

We observed fairly dramatic color changes taking place during irradiation of the Q-size CdS and the CdS nanocomposite materials. In all cases, the catalysts suspensions are yellow before illumination because of the CdS chromophore. However, after exposure to a focused beam of light at $\lambda > 400$ nm, the color changes very quickly to a silver gray. As the color changes from yellow to gray, H₂ production is observed as a steady stream of gas bubbles rising up in the photolysis cell. The observed color change may be due to the rapid photoreduction of Cd(II) to Cd(I) and then to Cd(0) on the surface of CdS in the absence of oxygen. There is also some probability that S²⁻ in the CdS matrix is also oxidized partially by trapped valence band holes to form S(0) and eventually polysulfide ion (S₂²⁻). Upon exposure to oxygen, the yellow color is regenerated over several hours with the return of yellow CdS on the nanocomposite structures.

Apparent quantum yields, ϕ , for H₂ production, were determined as follows:

$$\phi = \frac{dm_{H_2}/dt}{I_{abs}^0} \times 2 \quad (7)$$

where dm_{H_2}/dt is the initial production rate of H₂ (mol s⁻¹) and I_{abs}^0 is the photon absorption rate in units of Einstein s⁻¹ (mol(e⁻) s⁻¹). We also considered the fact that two electrons are consumed to produce one hydrogen molecule from two protons for quantum yield calculation. The photon flux through the cell was 2.3×10^{17} photons s⁻¹ as determined by ferrioxalate actinometry with an apparent quantum yield for H₂ production of 4.4% for $\lambda > 400$ nm. It should be noted that the amount of light scattered

Fig. 8 H₂ production rate from water–isopropanol mixed solution with Ni/NiO/KNbO₃/CdS under natural sunlight (August 13, 2006; Pasadena, California).

from the nanocomposite suspension was not considered here and therefore the actual quantum yield may be higher.

Photocatalytic H₂ production under natural sunlight

Substantial amounts of hydrogen gas are also produced readily using natural sunlight as the irradiation source. For example, the 4-component composite was exposed to solar light between 11:30 am and 3:30 pm on the roof of W. M. Keck Laboratories at Caltech on August 13, 2006. Experimental procedures were identical to those employed in the controlled laboratory experiments except the use of different types of pyrex reactors. As shown in Fig. 8, H₂ is readily produced from aqueous isopropanol solutions under natural sunlight; however, the amount of H₂ produced is actually larger than that produced over the same period of time under UV light irradiation in the laboratory. This simple demonstration illustrates the potential of practical application of Ni/NiO/KNbO₃/CdS nanocomposite for H₂ production with sunlight.

Influence of solvent composition on photocatalytic H₂ production

The relative effects of a variation of solvent–water mixtures on H₂ production for KNbO₃/CdS at $\lambda > 400$ nm are illustrated as shown in Fig. 9. 30 v/v% of isopropanol (IPA), ethanol (EtOH), and methanol (MeOH) solution were used in the photoreaction. The order of photoreactivity is IPA > EtOH > MeOH, which is in inverse order of their dielectric constants (*i.e.*, $\epsilon_{IPA} = 19 < \epsilon_{EtOH} = 24.3 < \epsilon_{MeOH} = 33$).

Alcohols function primarily as hole traps that prevent rapid electron–hole recombination. The presence of an electron donor other than water is crucial for photocatalytic H₂ production, since little H₂ is produced without added electron donors even under UV light irradiation. However, the interaction of the various electron donors with the charged CdS surface will also depend on their chemical and physical properties. Alcohols have a substantially lower dielectric constants than H₂O ($\epsilon = 80.4$). As a consequence, we predict that the relative thickness of the electrical double layer (EDL) should decrease when alcohols are

Fig. 9 Solvent effects on photocatalytic H₂ production with Ni/NiO/KNbO₃/CdS under visible light ($\lambda > 400$ nm).

added. The EDL thickness should decrease in the order of dielectric constants, as given by the Debye equation:

$$\kappa \equiv \left(\frac{2F^2\mu}{\varepsilon\varepsilon_0 RT} \right)^{0.5} \quad (8)$$

where ε is the dielectric constant of the solvent or mixed solvent system, ε_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$), μ is the ionic strength of the background electrolyte (mol m^{-3}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is temperature in units of K, and F is the Faraday constant (96485 C mol^{-1}). Electrical double layer compression will enhance the physico-chemical interaction of the electron donors with the charged CdS surface. Thus, more efficient hole trapping by the electron donors should increase H₂ production rates.

We note that SO_3^{2-} and S^{2-} are also frequently used as sacrificial donors to prevent the photocorrosion of metal sulfide semiconductors;^{19,46,47,65} however, the H₂ production rate of KNbO₃/CdS nanocomposites with the addition of 0.01 M SO_3^{2-} and 0.1 M S^{2-} was very low relative to those with the addition of alcohols as electron donors.

Influence of pH on photocatalytic H₂ production

Without the addition of acid or base, the pH of the KNbO₃/CdS suspensions in ROH–H₂O is between pH 8 and 9. The pH-dependent production of H₂ from aqueous isopropanol solution under visible light is shown in Fig. 10. The highest production rates of H₂ were obtained in circumneutral pH region, while the rates of H₂ production decreased at higher and lower pH.

The relative attachment of Q-CdS on the KNbO₃ particles should be influenced by the KNbO₃ and CdS surface charges. Since the pH_{zpc} value of KNbO₃ was determined to be 3.2, the KNbO₃ surface is negatively charged at both neutral and alkaline pH (*i.e.*, $\text{pH} > \text{pH}_{\text{zpc}}$) and is positively charged at very acidic pH (*i.e.* $\text{pH} < \text{pH}_{\text{zpc}}$). In case of Q-CdS, the pH_{zpc} value varies from pH 1 to 7, according to the structure and surface characteristics of CdS, types and concentrations of background electrolytes. However, we assume that the pH_{zpc} of CdS is more likely to be high under our conditions to possibly account for the rapid attachment of CdS colloids to the larger KNbO₃ particles

Fig. 10 pH-Dependent H₂ production from water–isopropanol mixed solution. The pH was adjusted with 0.1–1 M NaOH and HCl.

(Fig. 6(c)). Therefore, at circumneutral pH, positively charged CdS can be adsorbed onto the negatively charged KNbO₃ surface. At low pH, the surface charges of CdS and KNbO₃ would be positive, and at high pH, both particles are negatively charged so that effective contact and charge transfer from CdS to KNbO₃ is less likely to occur at extreme pH. Furthermore, proton ion-exchange also occurs for KNbO₃ samples under acidic conditions. K⁺ ions in the framework of KNbO₃ may be ion-exchanged with H⁺ ions, and the proton-exchanged form, K_{1-x}H_xNbO₃, may have different structure and physicochemical properties from original KNbO₃ materials. We prepared K_{1-x}H_xNbO₃ samples by stirring in 0.5 N H₂SO₄ solutions for several days followed by washing, filtration, and drying and tested the photoactivity of K_{1-x}H_xNbO₃/CdS nanocomposites for H₂ production. In the circumneutral pH region, K_{1-x}H_xNbO₃/CdS nanocomposites shows extremely low H₂ production rate ($\sim 2.8 \text{ μmol h}^{-1} \text{ g}^{-1}$). Therefore, we conclude that proton-exchanged KNbO₃ can be formed in low pH and it may cause low photoactivity of KNbO₃ for H₂ production in acidic pH.

Conclusions

Efficient H₂ production was obtained with Ni/NiO/KNbO₃/CdS composites with visible light irradiation ($\lambda > 400$ nm). H₂ production rates were higher than for TiO₂/CdS or K₄Nb₆O₁₇/CdS composites. Partially reduced states of niobium (*e.g.*, Nb(IV) and Nb(III)), which are generated during Ni formation under H₂ and by photoreduction, may contribute to the enhanced reactivity of the KNbO₃ composites. Aliphatic alcohols (methanol, ethanol, isopropanol, *etc.*) serve as alternative electron donors and modified the near-surface environment *via* electrical double layer compression. The solution pH also influences the rate of photocatalytic H₂ production; highest H₂ production rates were obtained at circumneutral pH. In addition, the 4-component nanocomposite (Ni/NiO/KNbO₃/CdS) produces H₂ rapidly under natural sunlight. Our findings suggest that use of solar energy for photocatalytic water splitting with this developed photocatalyst system may give a promising source for hydrogen fuel.

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