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,11,13,18–19 niobates,20–24 and tantalates25–28) 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 (λ < 385 nm or Eg 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 (λ = 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 carbon38,39).

CdS, n-type semiconductor with Eg = 2.4 eV, has been shown to have photocatalytic activity for H2 production under visible light irradiation, although, sacrificial electron donors such as C2H5OH,35,38 HS−,40,41 or SO3− 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-workers8,42 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 K2Nb6O17,50 or K2Ti4O951,52) 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.45

In this study, we synthesized nanocomposites of potassium niobate (KNbO3) and CdS by solid-state reactions and investigated their properties and photocactivity for H2 production under visible light irradiation (λ > 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 (ΔEg = 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 K2Nb6O17). Moreover, the efficiency of H2 production is significantly enhanced by loading Ni on KNbO3.
Experimental

Sample preparation

Stoichiometric K Nb O 3 was synthesized from Nb 2 O 5 (Aldrich) and K 2 CO 3 (Aldrich) in a standard solid-state reaction. K 2 CO 3 and Nb 2 O 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 ±200 °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 K 4 Nb 6 O 17 is obtained. Synthesis of K 4 Nb 6 O 17 was carried out for comparison using K 2 CO 3 and Nb 2 O 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 × 10⁻³ M Cd(CH 3 COO) 2·2H 2 O for 1 day, followed by sulfurization with 20 mL of ethanol of 2 × 10⁻² M Na 2 S 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 23,33,54 reported. KNbO 3 samples were suspended in a Ni(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 Ni/NiO/KNbO 3/CdS catalyst preparation.](image)

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 Cu-Kα 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 Al-Kα radiation.

Photocatalytic reaction

Photocatalytic reactions for hydrogen production were carried out in an air-tight reactor vessel under visible light irradiation (λ > 400 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 × 0.32 mm × 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 (K 7 Nb 6 O 17). K 7 Nb 6 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.
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 m$^2$ 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 $\lambda > 400$ 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.  

The synthesized KNbO$_3$ samples were suspended in an aqueous Ni(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 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$_3$. 

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**Fig. 2** X-Ray diffraction patterns for (a) KNbO$_3$ powder sample synthesized from 1 : 1 mole ratio of K$_2$CO$_3$ and Nb$_2$O$_5$ at 925 °C and (b) KNbO$_3$ powder sample synthesized from 1 : 1.1 mole ratio of K$_2$CO$_3$ and Nb$_2$O$_5$ at 1025 °C. (●) KNbO$_3$, (○) K$_2$Nb$_5$O$_{17}$.

**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.
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 (λ > 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 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 (K₄Nb₂O₁₇) for comparison because K₄Nb₂O₁₇ is known as a good photocatalyst for H₂ production under UV light irradiation. However, the result shows that KNbO₃/CdS nanocomposite produces more H₂ than K₄Nb₂O₁₇/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.²⁷ 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.²⁸ 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 Nb₂₇O₁₁₆ that involve partial oxygen loss coupled with the formation of Nb(IV). Therefore, the longer lifetimes (τₑ > 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., LiNbO₃⁷ and KNbO₃⁸), 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, pHₑₐₛ, of KNbO₃ was measured as pH ~ 3.2, thus the KNbO₃ surface may be dominated by

<table>
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<tr>
<th>Sample</th>
<th>Weight% of Ni</th>
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<tr>
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<td>37</td>
</tr>
<tr>
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<td>925</td>
<td>50</td>
</tr>
<tr>
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<td>80</td>
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*a* Catalyst, 0.2 g; volume, 50 ml; light source, Hg–Xe lamp (500 W) with λ > 400 nm, 30 v/v% isopropanol.
sized both on KNbO₃ surface and in solution (Fig. 6(a)). As quite small (20–30%) compared to samples having CdS synthesized by external mixing with KNbO₃, Q-size CdS only shows reasonable photoactivity even though the amounts of CdS are (Fig. 6(c)). The CdS surface adsorption sample (Fig. 6(c)) shows reactions that may result in H₂ production on KNbO₃ surface.

In addition, we compared three different procedures for attachment of CdS particles on the KNbO₃ surface as shown in Fig. 6. To form KNbO₃/CdS nanocomposites, we first added Cd²⁺ ions in KNbO₃ suspension, and then we added sulfide (HS⁻/S²⁻) 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 attached of CdS particles on the KNbO₃ surface as shown in Fig. 6(b) and another sample has only CdS adsorbed on the KNbO₃ surface by removing free Cd²⁺ ions in suspension before adding S²⁻ 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 KNbO₃ surface and in solution (Fig. 6(a)). As a consequence, we conclude that direct CdS contact with the KNbO₃ surface plays an important role for effective charge separation with increased H₂ production rates. Although, the externally mixed sample (Fig. 6(b)) also has measurable H₂ production rates. From these results, we can infer that Q-CdS particles are attached to the surface of KNbO₃ under our experimental conditions (pH ~ 8) even though CdS was synthesized initially in solution phase.

The KNbO₃ surface is negatively charged under the pH conditions of our experiments since the pHₚₑᵥ of KNbO₃ is measured as pH ~ 3.2. The actual determination of pHₚₑᵥ of the nanoparticulate CdS colloids is more difficult. Park and Huang reported a pHₚₑᵥ of 7.5 for colloidal CdS based on electrophoretic mobility measurements and acid–base titrations. At an ionic strength of μ = 0.05 M, they determined that pKₐ₁ = 6.1 and pKₐ₂ = 9.0 for [Cd²⁺] = 2.5 μM and σ₀ = 20 mC cm⁻². Liu and Huang subsequently reported a pHₚₑᵥ for cubic CdS of 7.0 and pHₚₑᵥ = 7.5 for hexagonal CdS. In contrast, other researchers have reported substantially lower values for the pHₚₑᵥ for CdS in aqueous suspensions. Under experimental conditions that were quite different from those employed by Park and Huang, Nicolau and Menard determined a pHₚₑᵥ = 1.8 for 0.01 M Na₂SO₄ and KC1 as background electrolytes based on electrophoretic mobility measurements. Guindo et al. found even lower values of pHₚₑᵥ 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 pHₚₑᵥ 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 KNbO₃ particles under our experimental pH conditions.

The rates of H₂ production on the four-component composite, Ni/NiO/KNbO₃/CdS, are compared to the three-component composite containing only Ni or NiO. The data presented in Fig. 7 show that elemental Ni on KNbO₃ is a more active species than NiO on KNbO₃ to improve H₂ production although its external surface is partially oxidized to NiO. However, the H₂ production rates are not greatly enhanced in the three-component composite containing only NiO. This tendency is consistent

![Fig. 6](image6.png) Effect of CdS loading on KNbO₃ surface on photocatalytic activities for H₂ production: (a) CdS synthesized both on KNbO₃ surface and in solution, (b) CdS synthesized by external mixing with KNbO₃, (c) CdS adsorbed on KNbO₃, (d) Q-size CdS only.

![Fig. 7](image7.png) Effect of oxidation states of Ni deposited KNbO₃ (0.1 wt% loading as Ni₄) on photocatalytic H₂ production from water-isopropanol mixed solution.
with previous results obtained for Ni/NiO loaded onto SrTiO3 as reported by Domen et al.\textsuperscript{53} They reported that Ni/NiO/SrTiO3 produced substantially more H\textsubscript{2} 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 H\textsubscript{2} production activity. Domen et al.\textsuperscript{64} also found small amounts of H\textsubscript{2} evolved under the band gap irradiation of Ni/SrTiO3. They attributed their low activity to loss of Ni by release of Ni\textsuperscript{2+} 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/KNbO\textsubscript{3}/CdS, composite can produce a comparable amount of H\textsubscript{2} compared to the four-component, Ni/NiO/KNbO\textsubscript{3}/CdS, composite. In both the 3- and 4-component catalysts, the primary absorption occurs at \(\lambda > 400\) nm (compared to SrTiO\textsubscript{3} with \(\lambda < 400\) nm) with CdS as a chromophore. Thus, elemental nickel deposited on KNbO\textsubscript{3} is unlikely to be directly oxidized by holes in our composite material.

As shown in Table 1, the highest H\textsubscript{2} production rates were obtained with a Ni-deposition level of 0.1 wt% as Ni\textsubscript{2} (Ni + NiO), and above this level enhancement due to nickel deposition was marginal. However, we observed the enhanced H\textsubscript{2} production with higher wt\% of Ni deposition on KNbO\textsubscript{3} samples prepared at low calcination temperatures. The increase of photoactivities with 0.5–1.0 wt\% Ni-loaded on KNbO\textsubscript{3} prepared at low calcination temperatures may be only due to simply an increase in the total reactive surface area. It is noted that a KNbO\textsubscript{3} sample mixed with the K\textsubscript{2}Nb\textsubscript{6}O\textsubscript{17} structure which was calcined at 1025 °C produces comparable amounts of H\textsubscript{2} to KNbO\textsubscript{3} 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, H\textsubscript{2} 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 S\textsubscript{2} \(\rightarrow \) S\textsubscript{0} in the CdS matrix is also oxidized partially by trapped valence band holes to form S(0) and eventually polysulfide ion (S\textsubscript{2} \(\rightarrow \)). 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, \(\phi\), for H\textsubscript{2} production, were determined as follows:

\[
\phi = \frac{dN_{H_2}/dt}{P_{abs} \times 2}
\]

where \(dN_{H_2}/dt\) is the initial production rate of H\textsubscript{2} (mol s\textsuperscript{-1}) and \(P_{abs}\) is the photon absorption rate in units of Einstein s\textsuperscript{-1} (mol e\textsuperscript{-} \textsuperscript{-1} s\textsuperscript{-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 \(\times\) 10\textsuperscript{17} photons s\textsuperscript{-1} as determined by ferrioxalate actinometry with an apparent quantum yield for H\textsubscript{2} production of 4.4% for \(\lambda > 400\) nm. It should be noted that the amount of light scattered from the nanocomposite suspension was not considered here and therefore the actual quantum yield may be higher.

**Photocatalytic H\textsubscript{2} 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, H\textsubscript{2} is readily produced from aqueous isopropanol solutions under natural sunlight; however, the amount of H\textsubscript{2} 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/KNbO\textsubscript{3}/CdS nanocomposite for H\textsubscript{2} production with sunlight.

**Influence of solvent composition on photocatalytic H\textsubscript{2} production**

The relative effects of a variation of solvent–water mixtures on H\textsubscript{2} production for KNbO\textsubscript{3}/CdS at \(\lambda > 400\) nm are illustrated as shown in Fig. 9. 30 \textsuperscript{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., \(\varepsilon\)\text{IPA} = 19 < \(\varepsilon\)\text{EtOH} = 24.3 < \(\varepsilon\)\text{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 H\textsubscript{2} production, since little H\textsubscript{2} 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 H\textsubscript{2}O (\(\varepsilon = 80.4\)). As a consequence, we predict that the relative thickness of the electrical double layer (EDL) should decrease when alcohols are
added. The EDL thickness should decrease in the order of dielectric constants, as given by the Debye equation:

$$\kappa = \left(\frac{2F^2 \mu}{\varepsilon_0 RT}\right)^{0.5}$$  \hspace{1cm} (8)

where $\varepsilon$ is the dielectric constant of the solvent or mixed solvent system, $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$), $\mu$ is the ionic strength of the background electrolyte (mol m$^{-1}$), $R$ 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 ($96485 \text{ C} \text{ mol}^{-1}$). 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 $\text{H}_2$ production rates.

We note that $\text{SO}_3^{2-}$ and $\text{S}_2^{2-}$ are also frequently used as sacrificial donors to prevent the photocorrosion of metal sulfide semiconductors; however, the $\text{H}_2$ production rate of KNbO$_3$/CdS nanocomposites with the addition of $0.01 \text{ M SO}_3^{2-}$ and $0.1 \text{ M S}_2^{2-}$ was very low relative to those with the addition of alcohols as electron donors.

**Influence of $\text{pH}$ on photocatalytic $\text{H}_2$ production**

Without the addition of acid or base, the $\text{pH}$ of the KNbO$_3$/CdS suspensions in ROH–H$_2$O is between $\text{pH}$ 8 and 9. The $\text{pH}$-dependent production of $\text{H}_2$ from aqueous isopropanol solution under visible light is shown in Fig. 10. The highest production rates of $\text{H}_2$ were obtained in circumneutral $\text{pH}$ region, while the rates of $\text{H}_2$ production decreased at higher and lower $\text{pH}$.

The relative attachment of Q-CdS on the KNbO$_3$ particles should be influenced by the KNbO$_3$ and CdS surface charges. Since the $\text{pH}_{\text{zpc}}$ value of KNbO$_3$ was determined to be 3.2, the KNbO$_3$ surface is negatively charged at both neutral and alkaline $\text{pH}$ (i.e., $\text{pH} > \text{pH}_{\text{zpc}}$) and is positively charged at very acidic $\text{pH}$ (i.e., $\text{pH} < \text{pH}_{\text{zpc}}$). In case of Q-CdS, the $\text{pH}_{\text{zpc}}$ value varies from $\text{pH}$ 1 to 7, according to the structure and surface characteristics of CdS, types and concentrations of background electrolytes. However, we assume that the $\text{pH}_{\text{zpc}}$ of CdS is more likely to be high under our conditions to possibly account for the rapid attachment of CdS colloids to the larger KNbO$_3$ particles.

**Conclusions**

Efficient $\text{H}_2$ production was obtained with Ni/NiO/KNbO$_3$/CdS composites with visible light irradiation ($\lambda > 400$ nm). $\text{H}_2$ production rates were higher than for TiO$_2$/CdS or K$_4$Nb$_6$O$_{17}$/CdS composites. Partially reduced states of niobium (e.g., Nb(IV) and Nb(ni)), which are generated during Ni formation under $\text{H}_2$ and by photoreduction, may contribute to the enhanced reactivity of the KNbO$_3$ 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 $\text{pH}$ also influences the rate of photocatalytic $\text{H}_2$ production; highest $\text{H}_2$ production rates were obtained at circumneutral $\text{pH}$. In addition, the 4-component nanocomposite (Ni/NiO/KNbO$_3$/CdS) produces $\text{H}_2$ 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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