Photoelectrochemical studies on aqueous suspensions of some nanometal oxide/chalcogenide semiconductors for hydrogen production

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Abstract. Photoproduction of hydrogen was achieved by photolysis of aqueous suspensions of mixed $\text{TiO}_2/\text{V}_2\text{O}_5$ or CdS/ZnS semiconductor (SC) nanoparticle in phosphate buffers containing $[\text{Fe}(\text{CN})_6]^{4-}$. Manipulations of the band structure of the SC materials took place by either combining oxides/sulphides in binary mixtures or by modification of the SC surface with an organic semiconductor. Studies show that the bandgap of these mixed materials varied monotonically with the percent composition of the mixture. Furthermore, results show that maximum generation of hydrated electrons by $[\text{Fe}(\text{CN})_6]^{4-}$ occurred at pH 6. Mixtures of CdS/ZnS showed greater photoactivity than metal oxides $\text{TiO}_2/\text{V}_2\text{O}_5$. On the other hand, surface-modified CdS or TiO_2 gave much better photoreduction than the high percentage composite mixtures. The aqueous nanosystems used in these studies sustained their stability as indicated by the reproducibility of their photocatalytic activities.

Keywords. Photoelectrochemical; nanomaterial; suspensions; hydrogen; oxides; chalcogenides.

1. Introduction

Photolysis of water using some semiconductor (SC) mediators for generation of hydrogen and oxygen was reported by several researchers.^{1–8} Nano-sized metal chalcogenides such as sulphides, selenides and tellurides with specific bandgaps that can serve this purpose are being produced following a variety of procedures.^{9–15} The photocurrent obtained using such nano-sized assemblies is often low because fast charge recombination limits photocurrent generation. When composite semiconductors are used it is possible to improve the efficiency of charge separation through charge rectification. This can take place by modifying either the surface of the base semiconductor or its composition with either inorganic or organic semiconductors.

In some studies, nano-size semiconductors were used because of their larger surface area and their ability to carry out all the reactions that were previously associated with semiconductor electrodes. TiO_2 (Titania) is known as a photocatalysis agent for a wide range of substances.¹⁶ Nano-sized TiO_2 possesses enhanced photocatalytic activity and solar energy conversion.^{17,18} However, some disadvantages limit the efficient use of TiO_2 . For example, the high bandgap energy (3.2 eV) requires UV radiation for photoactivation, limiting its application in the visible light range, and charge carrier recombination (e^-/h^+) occurs within nanoseconds limiting its photocatalytic activity.¹⁹ The spatial separation between oxidative and reductive sites is very small and increases the occurrence of back reactions.

Charge separation and exchange at the interface between semiconductor/electrolytes interface can be enhanced by doping the metal oxide or chalcogenides with another metal. Such doping or mixing alters the energy band structure of the doped oxides or chalcogenides, and consequently alters the donor/acceptor character of the assemblies. Recent studies show that binary oxides can provide more efficient charge separation, increased lifetime of charge carriers and enhanced interfacial charge transfer to absorbed substrates.²⁰ Studies have been conducted on the photocatalytic activity using the binary semiconductor oxide system such as $\text{TiO}_2/\text{SnO}_2$, $\text{TiO}_2/\text{ZrO}_2$, $\text{TiO}_2/\text{MoO}_3$, TiO_2/CdS , $\text{TiO}_2/\text{Fe}_2\text{O}_3$, TiO_2/WO_3 , CdS/ZnO , CdS/AgI and ZnO/ZnS .^{20,21} The effects of doping metal oxides with another metal oxide was explained in some systems by the creation of oxygen vacancies in the lattice of the studied assembly structures.²²

CdS has been intensively studied as a model for widely used metal chalcogenides due to several advantages such as its bandgap energy in the visible region $E_g = 2.5$ eV and its relatively simple fabrication process. CdS nanoparticles often present novel properties and have been widely used in solar cells, optoelectronics and microelectronics. CdS particles form a group of direct bandgap materials suitable for light-emitting applications, and their luminescent properties have been studied extensively.²³ The small size of nanoparticles leads to their larger surface area. This will increase the number of surface-specific active sites for both chemical reactions and photon absorption. When particle size decreases below the Bohr radius of the first excitation state, quantum size effects can occur due to the confinement of the charge carriers.²⁴

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Although the stability conditions are not met by CdS, because its decomposition potential ($E_{p,d}$) is less than the oxidation potential of water (E_{O_2/H_2O}), its reduction potential is more negative than that of H^+ . Mixing CdS and ZnS by co-deposition may push the limits of the CdS/ZnS band structure to the level where the decomposition potential is greater than that of the decomposition of water. Mixtures of CdS/ZnS and Zr phosphates were used for photolysis of water for hydrogen production.^{25,26}

Effective conversion of solar energy to hydrogen content requires an inexpensive source that contains hydrogen and has a large surface area. Aqueous colloidal nanoparticle suspensions meet these requirements. The suspension media are equally as important as the suspension particles in generating an efficient photolysis process. Previous studies used semiconductor particles as major producers of photonic outcome through heterogeneous charge transfer processes at the particle/electrolyte interface.^{27,28} Hydrated electrons can play an important role in the photodissociation of water through these reactions:

The molecular orbital structure of hexacyanoiron iron (II) $[Fe(CN)_6]^{4-}$ allows electronic transitions under the photoexcitation condition and produces hydrated electrons that react according to the above reaction. $[Fe(CN)_6]^{4-}$ undergoes oxidation to $[Fe(CN)_6]^{3-}$. The disadvantage of a homogeneous process for hydrated electron production is its irreversibility. However, this disadvantage can be overcome by the use of a semiconductor system, which acts as an electron donor and reduces $[Fe(CN)_6]^{3-}$ back to $[Fe(CN)_6]^{4-}$. Achieving such a goal will create the conditions of reversible ergo-dynamics. The CdS bandgap can be expanded for efficient capture of UV-visible radiation by mixing it with ZnS, which possesses a greater bandgap than CdS. Furthermore, TiO_2 bandgap can be altered to absorb a lower energy light wavelength by mixing it with lower bandgap V_2O_5 because V_2O_5 and CdS have a closer bandgap value of 2.4 eV, while TiO_2 and ZnS have a comparable bandgap value of 3.1 eV. Mixing the two chalcogenides ZnS and CdS or the two oxides TiO_2 and V_2O_5 would create either straddling or staggered gaps alignment of the energy band at the interface. This is due to the fact that both V_2O_5 and CdS have smaller bandgaps than either TiO_2 or ZnS. Furthermore, the conduction band of either TiO_2 or ZnS is at more a negative potential than those of V_2O_5 and CdS, respectively. With these similarities in band structure of assemblies, we expect that the oxide mixtures may give better photoactivities than chalcogenides mixture. In this paper we investigated the effects of adding ZnS to CdS in the mixed CdS/ZnS composites, and adding of V_2O_5 to TiO_2 in a

mixture of TiO_2/V_2O_5 on the photocatalytic behaviour of these mixture suspensions towards generation of hydrogen during the photolysis of buffered aqueous ferrocyanide solutions as hydrated electron suppliers.

2. Experimental

2.1 Reagents

All reagents were of analytical grade. All solutions were prepared using deionized water unless otherwise stated. CdS/ZnS and TiO_2/V_2O_5 composites were prepared as described elsewhere.²⁹

2.2 Instrumentation

All electrochemical experiments were carried out using a conventional three-electrode cell consisting of Pt wire as a counter electrode, Ag/AgCl as a reference electrode, and Pt gauze as an electron collector. A BAS 100-W electrochemical analyzer (Bioanalytical Co.) was used to carry out the electrochemical studies. Steady-state reflectance spectra were recorded using a Shimadzu UV-2101 PC.

2.3 Photolysis cell

The electrolysis cell was a 120-ml one-compartment Pyrex cell with a quartz window facing the irradiation source. A 10-cm² platinum gauze cylinder was used as the working electrode. A Ag/AgCl/ Cl^- reference electrode was also fitted into this compartment. A 10-cm² platinum counter electrode was housed in a glass cylinder sealed at one end with a fine-porosity glass frit. The pH was adjusted by the

Figure 1. Diffusive reflectance absorption spectra of CdS/ZnS nanoparticle composites.

addition of either 1 M NaOH or 1 M HNO₃. Aqueous suspensions were stirred with a magnetic stirrer during the measurements. Details of the photolysis cell and operation were as described elsewhere.³⁰

3. Results and discussion

3.1 Energy map of CdS/ZnS composite

Figure 1 illustrates the diffusive reflectance absorption spectra of CdS/ZnS nanoparticle composites. Analysis of the data provided by this figure, using Tauc equations,³¹ indicates that the studied CdS/ZnS mixtures possess a direct and an indirect bandgaps. Figure 2 shows that these bandgaps varied monotonically with the percent compositions of ZnS and of CdS. The fact that the absorption of the mixture extended into the

Figure 2. Direct and indirect bandgaps for CdS/ZnS composites.

UV (ca. 380 nm) indicates the conduction band exhibits only small shifts, while the majority of the bandgap change is due to an upward shift of the valence band.

3.2 Energy map of TiO₂/V₂O₅ composite

Figure 3 illustrates the diffusive reflectance absorption spectra of TiO₂/V₂O₅ nanoparticle composites. Analysis of the data in this figure, using Tauc equations, indicates that the studied TiO₂/V₂O₅ mixtures possess both a direct and an indirect bandgaps. Table 1 shows that these bandgaps varied monotonically with the percent compositions of V₂O₅ up to 50%. The fact that the absorption of the mixture extended more into the visible region indicates that the V(V) ions altered the surface states of the mixture.

3.3 Photolysis of aqueous solutions of K₄[Fe(CN)₆]

3.3a Effect of the pH: One of the products of reaction 3 is OH⁻, which makes this reaction pH dependent. This reaction product suggests that an acid pH range would be suitable to shift its equilibrium to favour H₂ production. However, K₄[Fe(CN)₆] as a reactant is pH sensitive. We

Table 1. Bandgap data for TiO₂/V₂O₅ mixtures.

V ₂ O ₅ % in TiO ₂ /V ₂ O ₅ mixtures	Bandgap, eV	Direct band-gap, eV	Indirect band-gap, eV
0.0	3.2	3.2	
10	3.1	2.65	2.9
30	3.0	2.60	2.7
50	2.45	2.45	2.60
90	2.38	2.40	2.55

Figure 3. (A) Steady-state reflectance spectra for TiO₂/V₂O₅ mixtures and (B, C) Tauc plots for indirect and direct bandgap TiO₂/V₂O₅ (50/50) mixture.

Figure 4. Effect of pH change on measured photocurrent.

have found that at pH less than 6, $K_4[Fe(CN)_6]$ will form a green compound known as Berlin green or ferric ferrocyanide, $Fe_3[Fe(CN)_6]_4$. Photolysis of aqueous $K_4[Fe(CN)_6]$ in phosphate buffers at different pH values were performed. The results are displayed in figure 4, from which we can notice a drop in photocurrent at pH greater than 6. For these reasons, photolysis of aqueous $K_4[Fe(CN)_6]$ in the presence of nano-mixture nanoparticles was conducted at pH 6.

3.3b Photolysis of aqueous $K_4[Fe(CN)_6]$ in the presence of CdS/ZnS suspensions: Aqueous suspensions of pure CdS in 0.2 M phosphate buffer at pH 6 containing 10 mmol of $K_4[Fe(CN)_6]$ were subject to the photolysis process. The potential of the Pt collector electrode was kept constant at 0.000 V vs. Ag/AgCl. The results are displayed in figure 5. The recorded photocurrent in figure 5 is due to the electrochemical reduction of $K_3[Fe(CN)_6]$. In the presence of illuminated CdS, reduction of $K_3[Fe(CN)_6]$ can take place by an electrochemical and/or by a photochemical process. The collector electrode records only the electrochemical process. The amount of $K_3[Fe(CN)_6]$ reduced by the photochemical process can be estimated by the difference between the current recorded for the photolysis of $K_4[Fe(CN)_6]$ and at pH 6 in the absence and in the presence of SC according to the following equation:

$$\text{Photoreduction current } I_{\text{photored}} = I_{\text{red}} \text{ in the absence of SC} - I_{\text{red}} \text{ in the presence of SC.} \quad (4)$$

It can be noticed that the recorded I_{red} in the presence of SC (figure 5) is less than that recorded for 10 mmol of

Figure 5. Photoelectrochemical response of working electrode during the photolysis of aqueous suspensions of pure CdS nanoparticles containing 10 mM of $Fe(CN)_6^{4-}$.

Figure 6. Effect of ZnS percentage on the reduction of $Fe(CN)_6^{3-}$ in pH 6 phosphate buffer.

$K_4[Fe(CN)_6]$ only (figure 4). Furthermore, the recorded current is reproducible at almost constant values, indicating that CdS particles maintained their stability against photodeterioration.

Photolysis of 10 mM of $K_4[Fe(CN)_6]$ containing CdS/ZnS nanocomposites in 0.2 M phosphate buffer at pH 6 took place under conditions similar to those for CdS. The effect of ZnS concentration on the measured photocurrent can be noticed from figure 6. As the percentage of ZnS increases, the reduction of $[Fe(CN)_6]^{3-}$ decreases according to the following equation:

Table 2. Steady-state photocurrent for studied metal oxide nanoparticles at pH 6 in 20 mM $K_4[Fe(CN)_6]$ at -100 mV vs. Ag/AgCl electrode.

% of V_2O_5 in TiO_2	I_{EC} , mA in $[Fe(CN)_6]^{4-}$	I_{EC} , mA in $[Fe(CN)_6]^{4-}$ + oxides	I_{photo} , mA due to oxides	% I_{photo} due to oxides only	Steady-state H_2 production, $mol\ h^{-1}\ m^{-2}$	Bandgap, eV
10	5.76	4.42	1.34	23.6	0.0250	2.9
30	5.39	3.39	2.00	37.1	0.0373	2.7
50	5.85	3.07	2.78	47.5	0.0519	2.6
90	5.65	3.22	2.43	43.0	0.0453	2.55

EC = electrochemical.

Figure 7. Photoelectrochemical response of working electrode during the photolysis of colloidal nanoparticles of TiO_2 doped with V_2O_5 in 20 mM of $K_4[Fe(CN)_6]$ in 0.2 M phosphate buffer (pH = 6). (A) TiO_2 doped with 10% V_2O_5 , (B) TiO_2 doped with 50% V_2O_5 and (C) V_2O_5 doped with 10% TiO_2 , points a and b refer to illumination and dark, respectively.

Such behaviour is expected because the addition of large bandgap material such as ZnS to CdS will expand the bandgap of the resulting mixture. The expanded bandgap will respond only to shorter wavelengths of low intensity.

3.4 Photolysis of aqueous $K_4[Fe(CN)_6]$ in the presence of TiO_2/V_2O_5 suspensions

Photolysis of aqueous suspensions of TiO_2 mixed with 10, 30 and 50% V_2O_5 and V_2O_5 mixed with 10% TiO_2 took place as described in a process similar to that described during the photolysis of CdS/ZnS. The results are recorded in table 2 and figure 7. Table 2 indicates that the photoreduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ caused by the oxide mixture nanoparticles increased with the increase in the percentage of V_2O_5 in the mixture. Such results

are consistent with the decrease of the bandgap of TiO_2 with the increase in the percentage of V_2O_5 . Lowering the bandgap increases the absorption in the visible region of the solar spectrum and consequently increases the photoreduction by the *p*-type semiconductor. When TiO_2 becomes the dopant in V_2O_5 (10% TiO_2 with 90% V_2O_5), the photoreduction drops back slightly to a lower value than that of 50% V_2O_5 .

The results displayed in figure 7 can be explained on the basis of V(V) effects on the band structure of the oxide mixtures. Briefly, two important observations that were reported in this work demonstrate the major effect of V_2O_5 : (1) a more efficient photoresponse was reported when nanoparticles of TiO_2 doped with V_2O_5 were suspended in buffered $[Fe(CN)_6]^{4-}$ (see figure 7C); (2) the reproducible reactivity of these aqueous suspensions for a longtime without deactivation reflects their stability against photocorrosion. Our studies³⁰ indicated that TiO_2 doped with 5% V_2O_5 gives the greatest effect in phosphate buffer. Vanadium (V^{5+}) facilitates the transfer of charge carriers at the interface because of alteration of the flat-band potential, and increases the absorption of incident light energy as a result of the increase in depletion layer width at the junction.³² V^{5+} also supplied a high density of states that lower the bandgap of TiO_2 and changed its bandgap transition from direct to indirect transitions.

3.5 Hydrogen production in the photolysis process

The results displayed in tables 2 and 3, and in figure 5 indicate that $[Fe(CN)_6]^{4-}$ is an excellent supplier of hydrated electrons, which produce hydrogen according to reaction 3. The continuous presence of $[Fe(CN)_6]^{4-}$ will insure the generation of hydrated electrons and, consequently, hydrogen. Rates of hydrogen production via regeneration of $[Fe(CN)_6]^{4-}$ by photochemical reduction of $[Fe(CN)_6]^{3-}$ at semiconductor surfaces are listed in tables 2 and 3. The data listed in table 2 indicate that increasing the percentage of V_2O_5 the photoreduction rate (and also hydrogen production rate) increases. On the other hand, the data listed in table 3 indicate that pure CdS generated the greatest rate among the studied mixtures. As the percentage of ZnS increases, the rate of hydrogen production decreases.

Table 3. Hydrogen production rate during the photolysis process of $[\text{Fe}(\text{CN})_6]^{4-}$ in the aqueous suspensions of the studied nanoparticles.

Semiconductor composition	I_{EC} , mA in $[\text{Fe}(\text{CN})_6]^{4-}$	I_{EC} , mA in $[\text{Fe}(\text{CN})_6]^{4-}$ + sulphides	I_{photo} , mA due to sulphides	% I_{photo} due to sulphides only	Steady-state H_2 production, $\text{mol h}^{-1} \text{m}^{-2}$	Bandgap, eV
Pure CdS	6.09	2.664	3.431	56.2	0.0676	2.20
CdS/ZnS 9:1	6.09	3.092	2.765	45.3	0.0546	2.25
CdS/ZnS 7:3	6.09	3.426	2.669	43.8	0.0341	2.40
CdS/ZnS 5:5	6.09	3.521	2.097	34.4	0.0316	2.55

4. Conclusion

Mixed CdS/ZnS or $\text{TiO}_2/\text{V}_2\text{O}_5$ semiconductor materials were prepared and subjected to spectroscopic, electrochemical and photochemical characterization. Studies show that the direct bandgap of mixed nanomaterials varied monotonically with the percent of either ZnS or V_2O_5 in the mixture. Photolysis of $[\text{Fe}(\text{CN})_6]^{4-}$ in aqueous suspensions of nanoparticles is more efficient at pH 6. At higher pHs the electrochemical reduction process for $[\text{Fe}(\text{CN})_6]^{3-}$ decreases noticeably, while at lower pH, formation of Berlins–Green complex was observed. The amount of $[\text{Fe}(\text{CN})_6]^{3-}$ reduced via the photochemical process decreased by increasing ZnS content in the CdS/ZnS mixture (table 3), and increases with increasing V_2O_5 (upto 50%) in $\text{TiO}_2/\text{V}_2\text{O}_5$ (table 2) mixtures. Pure CdS generated the greatest photochemical production of hydrogen, compared with its mixtures with ZnS. The data listed in tables 2 and 3 indicate that the sulphide mixtures were more effective in the hydrogen production than the oxides. Such results cannot be interpreted on the basis of the bandgap value, but rather on the efficient band alignments for each of the mixture components. The reproducibility of the photocatalytic activities of the studied nanoparticle mixtures is an indication that these systems retained their stability under illumination conditions. Other than stability factors, our results indicate that bandgap manipulations were an important factor in the photochemical activities of the tested composites of mixed chalcogenide and oxide nanoparticles.

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