Effect of photodeposition of nickel on the photocatalytic, photoelectrochemical and surface properties of CdS

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In situ deposition of ferromagnetic metals (Fe, Co and Ni) increases photocatalytic activity and also avoids the aerial oxidation of the metals. The deposition of sulphides of Fe, Co and Ni also enhances the photocatalytic activity of CdS. Effect of photodeposition of nickel on the photocatalytic activity of CdS for decomposition of aqueous sulphide has also been studied and compared with that of in situ photodeposition of Fe, Co, Rh and Pd. The following order of activity is observed: Rh > Pd > Co > Ni = Fe. Apart from Ni⁰, the various Ni – O species which are formed by the aerial oxidation of Ni⁰ have been identified by XPS studies of the Ni/CdS surface. Photodeposition of Ni increases the photocatalytic activity and the photostability of CdS. A mechanism for the photocatalytic decomposition of aqueous sulphide has been proposed. Photodeposition of Ni decreases the photocorrosion of CdS, photovoltage and photocurrent of the PEC cell and also shifts the photocurrent onset potential to a more positive value.

Deposition of noble metals on CdS increases its photocatalytic activity and photostability¹⁻⁴. However, the use of noble metals is not cost effective either in the conversion and storage of solar energy using metallized CdS as photoanodes in photoelectrochemical (PEC) cells or as photocatalysts for photocatalytic reactions.

The effect of deposition of ferromagnetic metals such as Fe, Co and Ni on the photocatalytic activity of CdS has not been studied in detail. The photocatalytic decomposition of aqueous sulphide¹⁻¹⁰ using CdS as a photocatalyst is an important reaction from the point of view of conversion and storage of solar energy. Further, it has other added advantages like (i) production of hydrogen—a clean fuel and a starting material for many industries, (ii) destruction of a pollutant, viz. H₂S, (iii) production of sulphur—a useful by-product and (iv) recycling the hydrogen used in hydrosulphurization (HDS)—a process widely used in petroleum industries. In the present investigation photocatalytic decomposition of hydrogen sulphide in the presence of metallised CdS has been used to follow the effect of in situ deposition of Fe, Co and Ni on the photocatalytic activity of CdS. Nickel has been selected as one of the representative of this group of metals and detailed X-ray photoelectron spectroscopic (XPS) and photoelectrochemical studies have been carried out on Ni/CdS in order to have a better understanding of the photocatalytic properties of Ni/CdS. Further, no detailed reports are available in literature on the photoelectrochemical and surface properties of Ni/CdS.

Materials and Methods
Iron(III) chloride (FeCl₃·6H₂O; AR, S D Fine Chemicals Pvt Ltd), nickel(II) chloride (NiCl₂·6H₂O; AR, BDH), cobalt(II) chloride (CoCl₂·6H₂O; AR, Glaxo), cadmium sulphide (CdS, 99.999%; Fluka), sodium sulphide (Na₂S·7H₂O; GR, Merck), potassium chloride (AR, Glaxo), glacial acetic acid (100% aldehyde-free; GR, Merck), sodium hydroxide (AR, S D Fine Chemicals Pvt Ltd) were used as such. Triply distilled water was used in all the experiments.

Preparation of Ni/CdS for XPS analysis
Ni/CdS was prepared by illuminating a sintered (4 hr at 873 K in N₂) CdS pellet (8 mm diam) suspended in 2.28 x 10⁻³ M NiCl₂ (20 ml) (acetic acid medium, pH = 4.5, sodium hydroxide solution was used to adjust the pH) for 20 min, deaerating the system and maintaining a nitrogen atmosphere. After washing the CdS pellet with triply distilled water, it was dried at room temperature in air. The illuminated face of Ni/CdS was analyzed by XPS using an ESCA Lab Mk II (VG Scientific Co., UK) at room temperature and at a pressure of 5 x 10⁻⁹ mbar. The XP spectra were taken before and after sputtering Ni/CdS with argon ions at 150 µA for 5 min. The X-ray source used was MgKα with an energy of 1253.6 eV. The carbon 1s XPS peak at 285.0 eV was used as the internal standard.
Photocatalytic studies

Photocatalytic decomposition of aqueous sulphide was carried out under deaerated condition (deaeration was done by freeze-pump-thaw procedure) in a double walled pyrex glass reactor with water circulation in the outer jacket to prevent heating during irradiation. The gas evolved during illumination was analyzed using a Toshniwal gas chromatograph using thermal conductivity detector molecular sieve-5Å column and nitrogen as the carrier gas. The gas evolved was identified as hydrogen. For subsequent studies the pressure of hydrogen formed was monitored using an in-built manometer. In all the experiments the photocatalyst (100 mg) and 0.25 M aqueous solution (20 ml) of Na$_2$S (pH 13) as the reactant were used. The amount of sulphide was estimated iodimetrically. The dead volume of the reactor was determined and using the pressure of the gas inside the reactor, the volume of hydrogen at STP was calculated. The reaction was carried out at room temperature (303 K). The reaction mixture was stirred during irradiation by a magnetic stirrer. Before starting the illumination, the reaction mixture was stirred for 1 hr in the dark for equilibration. The metal ions (Fe$^{3+}$, Co$^{2+}$ and Ni$^{2+}$) were added to the reaction mixture ($S_2^-$ + CdS) for in situ metalization.

Photoelectrochemical studies

The photoelectrochemical studies were performed in a single compartment PEC cell with the standard three-electrode configuration (photoanode: CdS or Ni/CdS; counter electrode: Pt-foil; reference electrode: saturated calomel electrode SCE and electrolyte: 0.1 M KCl). The PEC cell was provided with a flat quartz window for illuminating the photoanode. The photovoltage and photocurrent of the PEC cell were measured before and after deposition of Ni on CdS. All the photoelectrochemical and electrochemical studies were made using a Wenking POS 73 potentiostan coupled with an Ominigraphic 2000 X - Y - t recorder. The current versus the applied potential (I-V) curves were recorded before and after deposition of Ni on CdS both in the dark and under illumination.

Photocorrosion studies

The photoanodes (CdS and Ni/CdS) were illuminated for 30 min at a bias of +1 V (vs SCE) in 0.5 M KCl (ref. 12). After irradiation, the amount of Cd$^{2+}$ present in the electrolyte was determined by cyclic voltammetry.

Light source

A Philips (India) 1000W tungsten-halogen lamp was used as the light source for both photocatalytic and photoelectrochemical studies.

Results and Discussion

XPS studies on Ni/CdS

The Ni/CdS was analyzed by XPS to know the extent and oxidation state of photodeposited Ni. The feeble Ni 2p$_{3/2}$ XPS peak shows that the amount of photodeposited Ni is very small. The several XPS peaks in the Ni 2p$_{3/2}$ region and in the O 1s region suggest that in addition to Ni$^0$, various types of Ni – O species are also present on the surface of Ni/ CdS. The different oxides of Ni identified are given in Table 1. Sputtering with argon ions considerably decreases the intensity of the O is XPS peaks, implying the removal of oxide layers. However, even after argon ion sputtering, small amount of different types of Ni – O species remain on the surface of Ni/ CdS. Thus the XPS studies on Ni/CdS surface shows that very small quantity of Ni is photodeposited on CdS. Further, several kinds of nickel species like Ni$^0$, NiO, NiO$_{ads}$, NiO$_x$ ($x < 1$), Ni$_2$O$_3$ and Ni(OH)$_2$ are present on the surface of Ni/CdS (Table 1). These oxides could have been formed by the aerial oxidation of Ni during exposure of Ni/ CdS to atmosphere. On n-type semiconductors like CdS the reduction reactions occur on the dark side. But the photodeposition of Ni on the illuminated face of CdS indicates that the photoreduction of Ni$^{2+}$ is mediated by surface states.

Effect of in situ deposition of Fe, Co and Ni on the photocatalytic activity of CdS

The photocatalytic decomposition of aqueous

| Table 1—Various species present on Ni/CdS surface |
| Ni 2p$_{3/2}$ XPS peak binding energy in eV | Species assigned |
| Before | After 5 min | Reported$^{11}$ |
| Ar$^+$ sputtering | (Ar$^+$ sputtering at 150 mA) | |
| 852.4 | 852.6 | 852.6, 852.4 | Ni (ref. 14) |
| 859.0 | 858.7 | 858.8$^a$ | Ni |
| 853.5 | 853.5 | 853.5 | NiO$_{ads}$ |
| 854.9 | 854.3 | 854.5 (ref. 4-16) | NiO |
| 856.5 | 856.3$^a$ | NiO |
| 861.4 | 861.7$^a$ | NiO |
| 855.7 | 855.4 | 855.8 | Ni$_2$O$_3$ |
| 861.2 | 861.7 | 861.4$^a$ | Ni$_2$O$_3$ |
| 857.0 | 856.5 | 856.6 | Ni(OH)$_2$ |
| 862.4$^a$ | Ni(OH)$_2$ |

$p$—energy loss peak, $q$—multiplet splitting and $r$—electron shake-up satellite peak.
sulphide\(^1\)\(^-\)\(^10\) has been used as a test reaction to follow the effect of \textit{in situ} deposition of Fe, Co and Ni on the photocatalytic activity of CdS. The reduction potentials of Fe\(^{3+}\)/Fe \((-0.278\) V), Co\(^{2+}\)/Co \((-0.519\) V) and Ni\(^{2+}\)/Ni \((-0.492\) V) are negative indicating that the reduction of these metal ions is thermodynamically unfavourable. As these values lie below the conduction band level of CdS \((-0.952\) V vs SCE), the conduction band electrons of CdS can reduce these metal ions. It is evident from the XPS studies on Ni/CdS that the amount of photodeposited Ni is very small. Even though the reduction potential of Ni\(^{2+}\)/Ni couple lies below the conduction band edge of CdS, as the difference between them is very small and as this reaction is thermodynamically unfavourable, the extent of reduction is also small, resulting in the deposit of only a small quantity of Ni. For the same reasons the amounts of photodeposited Fe and Co are also expected to be low. So in the case of \textit{in situ} deposition of Fe, Co and Ni on CdS, the enhancement in the photocatalytic activity of CdS (Table 2) could be mainly due to the deposition of sulphides of the Fe, Co and Ni which are formed during the addition of these metal ions to the reaction mixture (S\(^2-\) + CdS). The sulphides of Fe, Co and Ni which are known to be active for HDS\(^9\) could serve as the site for the oxidation of sulphide ions. The naked CdS and the metal sites (very small amount) could act as reduction centers, as these are better sinks for the photoelectrons than the sulphides of Fe, Co and Ni. 

In the case of Ni/CdS, the rate of hydrogen evolution observed is almost the same as that in the case of \textit{in situ} deposition of Ni (Table 2). This shows that the enhanced activity observed is largely due to deposition of NiS. This further supports the fact that the increased photocatalytic activity observed in the case of \textit{in situ} deposition of Fe, Co and Ni is mainly due to the deposition of the sulphides of Fe, Co and Ni. The sulphides of these metals by themselves do not act as photocatalysts (Table 2). The following order of activity is observed in the case of \textit{in situ} metallization of CdS: Co > Ni = Fe. In the case of noble metals like Pd and Rh\(^3\)^\(^,\)\(^4\) the conduction band electrons can be easily transferred to the noble metals and further the hydrogen evolution overvoltages of noble metals are lower than those of the ferromagnetic metals considered here. So noble metals act as better reduction centers than the ferromagnetic metals like Fe, Co and Ni. This is obvious from the higher hydrogen evolution rates observed in the case of Pd/CdS and Rh/CdS (Table 2).

**Mechanism of photocatalytic decomposition of aqueous sulphide**

Based on the experimental findings the mechanism shown in Scheme 1 is proposed for the photocatalytic decomposition of aqueous sulphide:

\[ S^{2-} + 2H^+ \rightarrow SH^- + H^+ \]  \(\text{(1)}\)

\[ \text{MS} - M - \text{CdS} \xrightarrow{h_v} \text{e}_{CB} (\text{MS} - M - \text{CdS}) \]

\[ + h_v^+ (\text{MS} - M - \text{CdS}) \]  \(\text{(2)}\)

\[ 2\text{e}_{CB} (\text{MS} - M - \text{CdS}) + 2H^+ \rightarrow H_2 \]

\[ + 2\text{MS} - M - \text{CdS} \]  \(\text{(3)}\)

\[ 2h_v^+ (\text{MS} - M - \text{CdS}) + SH^- \rightarrow S + H^+ \]

\[ + 2\text{MS} - M - \text{CdS} \]  \(\text{(4)}\)

overall reaction,

\[ \ldots (5) \]

**Scheme 1**

In alkaline medium:

\[ S + S^{2-} \rightarrow S_2^{2-} \]  \(\text{(6)}\)

In the presence of sulphite:

\[ S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-} \]  \(\text{(7)}\)

The band gap illumination of the photocatalyst (MS - M - CdS, M = Fe, Co, Ni; MS, the corresponding metal sulphide) results in the excitation of electron from the valence band to the conduction band leading to the formation of valence band holes (Eq. 2). The electrons migrate to the photocatalyst/
aqueous sulphide interface, where the reduction of protons takes place (Eq. 3) and the holes react with the \( \text{SH}^- \) ions (pH 13) leading to the formation of sulphur (Eq. 4). In alkaline medium, the sulphur formed reacts with the sulphide ions to give disulphide ions (Eq. 6), which in turn reacts with sulphur to give polysulphide ions (\( \text{S}^{2-} \)) and they being yellow in colour reduce the light available for absorption by CdS. Hence the reaction slows down after prolonged irradiation. The colourless sulphide solution turns into yellow after the reaction, indicating the formation of polysulphide ions. The formation of yellow disulphide and hence that of polysulphide can be avoided by the addition of sulphite ions to the reaction mixture, which react with the disulphide ions to give colourless thiosulphate ions (Eq. 7) (see ref. 1). As the in situ metallization and photocatalytic reaction are carried out in vacuo, therefore is no possibility of formation of metal oxides on the surface of the metallized CdS.

**Photoelectrochemical studies on Ni/CdS**

Illumination of CdS photoanode in NiCl\(_2\) solution for longer periods of time brings about significant changes in the photoelectrochemical characteristics of CdS (Table 3 and Fig. 1). Photodeposition of Ni on CdS photoanode decreases both the photovoltage and the photocurrent of the PEC cell (Table 3) and shifts the photocurrent on-set potential towards a more positive value. The surface coverage\(^{20} \), \( \Theta_{\text{Ni}} \), increases with the time of deposition (Table 3). Conductivity of Ni (metal) is more than that of CdS—a semiconductor. Thus the deposition of Ni over CdS photoanode decreases the cell resistance \( R_{\text{cell(dark)}} \). The \( R_{\text{cell(dark)}} \) decreases with the increase in the amount of Ni deposited (Table 3). In the present case, only the photoanode is being coated with nickel and all other elements of the PEC cell like, the electrolyte, the counter electrode and the reference electrode remain unchanged. Hence the change in \( R_{\text{cell(dark)}} \) is mainly due to change in the photoanode.

![Current-voltage curves of the PEC cell with (a) CdS photoanode in the dark, (b) Ni/CdS (\( \Theta_{\text{Ni}} = 0.10 \)) and (c) CdS during illumination](image_url)

**Fig. 1**—Current-voltage curves of the PEC cell with (a) CdS photoanode in the dark, (b) Ni/CdS (\( \Theta_{\text{Ni}} = 0.10 \)) and (c) CdS during illumination

<table>
<thead>
<tr>
<th>Time of photodeposition of Ni/min</th>
<th>( V_{\text{OC}} ) (mV)</th>
<th>( I_{\text{SC}} ) (mA)</th>
<th>( R_{\text{cell(dark)}} = V/I ) (k ohm)</th>
<th>Net Photo ( V_{\text{OC}} ) (mV)</th>
<th>( I_{\text{SC}} ) (mA)</th>
<th>( R_{\text{cell(photo)}} = V/I ) (k ohm)</th>
<th>( \Theta_{\text{Ni}} = I^0 - I^1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>140</td>
<td>0.001</td>
<td>140</td>
<td>370</td>
<td>0.154</td>
<td>2.4</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>125</td>
<td>0.001</td>
<td>125</td>
<td>365</td>
<td>0.154</td>
<td>2.4</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>92</td>
<td>0.001</td>
<td>92</td>
<td>358</td>
<td>0.149</td>
<td>2.4</td>
<td>0.03</td>
</tr>
<tr>
<td>15</td>
<td>74</td>
<td>0.001</td>
<td>74</td>
<td>338</td>
<td>0.144</td>
<td>2.4</td>
<td>0.07</td>
</tr>
<tr>
<td>16*</td>
<td>44</td>
<td>0.001</td>
<td>44</td>
<td>346</td>
<td>0.138</td>
<td>2.5</td>
<td>0.10</td>
</tr>
</tbody>
</table>

\( V_{\text{OC}} \)—open circuit voltage; \( I_{\text{SC}} \)—short circuit current; \( \Theta_{\text{Ni}} \)—fraction of the CdS surface covered by Ni \([20]\); \( I^0 \) and \( I^1 \)—photocurrents observed before and after deposition of Ni on CdS\(^1 \) respectively; \( R_{\text{cell(dark)}} \)—resistance of PEC cell in the dark and \( R_{\text{cell(photo)}} \)—under illumination; \( a \)—after photodeposition of Ni from a \( 2.75 \times 10^{-3} \) M solution of NiCl\(_2\) for 15 min; Ni was photodeposited from a \( 2.75 \times 10^{-2} \) M solution.
With a decrease in $R_{cell(\text{dark})}$, normally an increase in the photocurrent is expected. But the photocurrent decreases (Table 3). Even though the deposition of Ni increases progressively, the $R_{cell(\text{photo})}$ remains constant. When there is a decrease in the intensity of light, the number of charge carriers produced also decrease and hence both photovoltage and photocurrent of the PEC cell decrease. In the present case also, the decrease in the photocurrent and the photovoltage is attributed to the geometrical blocking of the CdS surface by Ni. This is further confirmed by the constancy of $R_{cell(\text{photo})}$ (Table 3). If the conduction band electrons of CdS were to be transferred to Ni, the $R_{cell(\text{photo})}$ would increase with increase in $\Theta_{Ni}$ (ref. 21). Thus the constancy of $R_{cell(\text{photo})}$ indicates that not many of the conduction band electrons of CdS are transferred to Ni. So in Ni/CdS, Ni does not function as a good reduction center due to non-availability of electrons on Ni.

The positive shift in the photocurrent on-set potential (Fig. 1) indicates that a neutral or a positively charged species is being deposited on CdS photoanode. The XPS studies indicate that Ni$^0$ is deposited on CdS. Hence this positive shift in the photocurrent on-set potential could be attributed to the deposition of Ni$^0$. The other Ni – O species detected by XPS are formed from Ni$^0$ only. So initially only Ni$^0$ is deposited on CdS and when Ni/CdS is exposed to the atmosphere, different types of Ni – O species are formed.

The photocorrosion of CdS (Eq. 8) is one of the disadvantages of using CdS as a photocatalyst and as a photoanode for the conversion and storage of solar energy. As the photocorrosion leads to the formation of Cd$^{2+}$,

$$\text{CdS} \rightarrow \text{Cd}^{2+} + \text{S} \quad \ldots \quad (8)$$

the extent of Cd$^{2+}$ dissolved in the electrolyte is a direct measure of the photocorrosion. The concentration of Cd$^{2+}$ present in the electrolyte has been monitored by cyclic voltammetry. It can be seen that the amount of Cd$^{2+}$ present in the electrolyte after the photocorrosion of Ni/CdS is 23% less than that present in the case of CdS (Fig. 2). This shows that the photodeposition of Ni decreases the photocorrosion of CdS. The photocurrent at +1V (vs SCE) (Fig. 1) is mainly due to photocorrosion of CdS (refs 20, 22). Hence a decrease in the photocurrent at +1V (vs SCE) in the case of Ni/CdS also implies a reduction in photocorrosion of CdS. Solvation of Cd$^{2+}$ ions formed (during the photocorrosion) beneath the Ni layer is difficult. Thus decrease in photocorrosion is largely attributed to geometrical blocking of CdS surface by Ni. Even though, photodeposition of Ni on CdS decreases the photovoltage and photocurrent of PEC cell, it has other advantages like stabilization of CdS against photocorrosion.

References