

Surface analysis of Rh/CdS

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Photodeposition of noble metals on CdS makes it a better photocatalyst and a more stable photoanode for photoelectrochemical (PEC) cells [1-6]. As both photocatalytic activity as well as the photoelectrochemical characteristics of metallized CdS are greatly influenced by its surface and interface properties, surface characterization of metallized CdS is inevitable. Even though, metallized semiconductors are widely used, there are only a few reports on the detailed surface analysis of metallized CdS. X-ray photoelectron spectroscopy (XPS) is most extensively used for the surface characterization of metallized semiconductors. Scanning electron microscopy (SEM) serves as a versatile tool to analyse the surface morphology and the nature of the metal layer on metallized semiconductors. In addition to these conventional surface analysis techniques, we have effectively used photoelectrochemical methods and photocatalytic studies for the characterization of the surface of Rh/CdS and the interface between Rh and CdS. UV-visible diffuse reflectance spectral (DRS) studies on Rh/CdS have been carried out in order to see the effect of deposition of Rh on the light absorption characteristics of CdS.

Rh/CdS was prepared by the photodeposition of Rh on a CdS (Fluka, 99.999%) sintered pellet (4 h at 873 K in nitrogen) from a solution of RhCl₃ (Johnson Matthey Chemical Ltd) in acetic acid (0.25 M) at a pH of 4.5 in nitrogen atmosphere. Photodeposition was carried out by illuminating (1000 W tungsten-halogen lamp) the CdS pellet in RhCl₃ solution. After photodeposition the metallized CdS pellets were washed with triply distilled water and dried at room temperature (303 K). The face of CdS which was exposed to light during the photodeposition was analysed by XPS, SEM, DRS and photoelectrochemical methods [7]. Details of XPS measurements are given elsewhere [8].

Scanning electron micrographs of the CdS pellet were taken before and after photodeposition of

Rh on a Spectroscan-180 (Cambridge Instruments) scanning electron microscope. A Hitachi 150-20 UV-visible spectrophotometer with an integrating sphere was used to record the diffuse reflectance spectra of CdS and Rh/CdS. Details of photocatalytic measurements are described elsewhere [6, 9].

From Fig. 1 and Table I, it can be seen that the binding energies of the Rh 3d electrons of Rh/CdS are higher than those reported for Rh metal, indicating that Rh metal is in a higher oxidation state. Rh is in its +3 oxidation state and is present as Rh₂O₃ on the surface of Rh/CdS. However, from Fig. 1, it is evident that the amount of Rh₂O₃ decreases progressively with argon ion sputtering at 50 μA, indicating the removal of the oxide layer by sputtering. This is further supported by the decrease

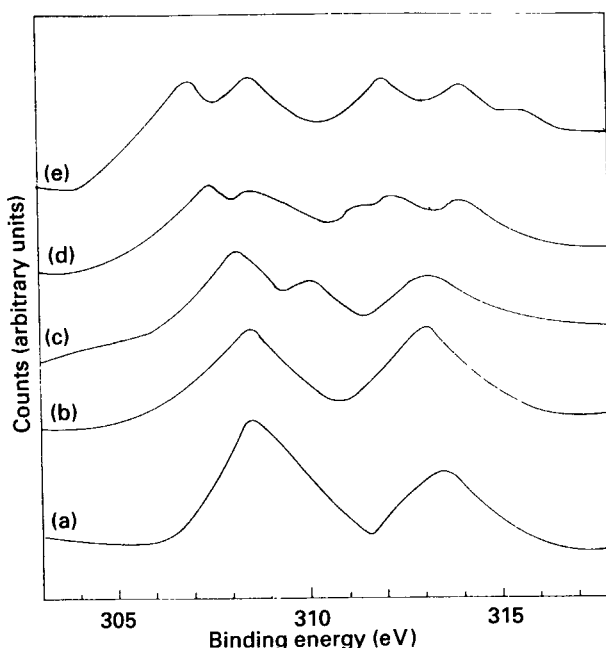


Figure 1 Rh 3d XPS peaks of Rh/CdS (a) before argon-ion sputtering and after sputtering with argon ions at 50 μA for (b) 4.8; (c) 8; (d) 11; and (e) 15 min.

TABLE I Different species present on the surface of Rh/CdS

Energy level of the element probed	Binding energy (eV)		Species assigned
	Observed	Reported	
Rh 3d _{5/2}	Before argon ion sputtering		Rh ₂ O ₃
	308.4	308.4 [10]	
Rh 3d _{5/2}	After argon ion sputtering for 15 min at 50 μA		Rh Rh ₂ O ₃
	307.0	307.0 [11]	
	308.4	308.4 [10]	

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TABLE II X-ray photoelectron spectroscopic data on Rh/CdS

Energy levels of the elements probed	Before Ar ⁺ sputtering		After Ar ⁺ sputtering	
	B E ^a (eV)	Peak height (mm)	B E ^a (eV)	Peak height (mm)
Cd				
3d _{5/2}	405.5	119	405.3 (405.0)	700
3d _{3/2}	412.9	81	412.0 (411.7)	540
4d	11.6	18	11.2 (11.0)	32
S				
2p _{3/2}	161.1	16	161.5 (161.3)	22
2p _{1/2}	162.2	15	162.3 (162.0)	18
O				
1s	530.4 (530, Rh ₂ O ₃)	8	531.0	5
	531.5	12	532.0	5
	532.4	11	532.5	4

^aBinding energy. The binding energy values reported for Cd 3d, 4d and O 1s reported in [12–16] for CdS are given in parenthesis.

in the O 1s peak height (Table II). The increase in the Cd 3d, 4d and S 2p XPS peak heights on argon ion sputtering also implies the removal of oxide layer (Table II). When the oxide layer is removed by argon ion sputtering for 15 min, the Rh metal peak appears (Fig. 1 and Table I), indicating that the photodeposited metal is in the zero oxidation state, but, it is prone to aerial oxidation. Even after 15 min of argon ion sputtering, some oxide still remains on the surface. In general, on n-type semiconductors like n-CdS, reduction reactions ($\text{Rh}^{3+} + 3\text{e}^- \rightleftharpoons \text{Rh}$), take place on the dark side of the semiconductor [17]. But XPS analysis (Fig. 1 and Table I) shows that the photodeposition of Rh takes place on the face of the CdS pellet which was illuminated during the photodeposition of Rh, indicating that the photoreduction of Rh^{3+} is mediated by surface states. Photodeposition of Rh does not affect the binding energies of the Cd 3d, 4d and S 2p electrons (Table II), implying that RhCl_3 does not react with CdS and that there is no charge transfer between Rh and CdS. When a metal forms a Schottky barrier with CdS, the Cd 4d level shifts towards lower binding energy [12], but in the present case, as there is no negative shift in the binding energy of the Cd 4d electrons of CdS due to photodeposition of Rh, there is no barrier between Rh and CdS.

To learn more about the Rh/CdS interface, photocatalytic studies have been carried out. From Table III, it is clear that photodeposition of Rh on CdS increases the rate of hydrogen evolution from an aqueous sulphide solution, indicating that Rh serves as a good proton reduction centre or a sink for electrons. For metals to act as efficient reduction centres, the contact between the metal and the n-type semiconductor should be ohmic, as a Schottky barrier would drive the electrons away from the metal [18]. Thus the photocatalytic studies on Rh/CdS also support the formation of an ohmic contact between Rh and CdS.

TABLE III Effect of photodeposition of Rh on the photocatalytic activity of CdS (weight of photocatalyst: 100 mg; temperature: 303 K; reactant: 0.25 M aqueous Na₂S; light source: 1000 W tungsten-halogen lamp)

Photocatalyst	Initial H ₂ evolution rate $\mu\text{l/h}$
CdS	31
Rh/CdS (1.37 wt %)	253

The diffuse reflectance spectrum of Rh/CdS (Fig. 3) shows that photodeposition of Rh extends the light absorption of CdS to wavelengths longer than the characteristic absorption edge of CdS (517 nm). Photodeposition of Rh on CdS does not affect the

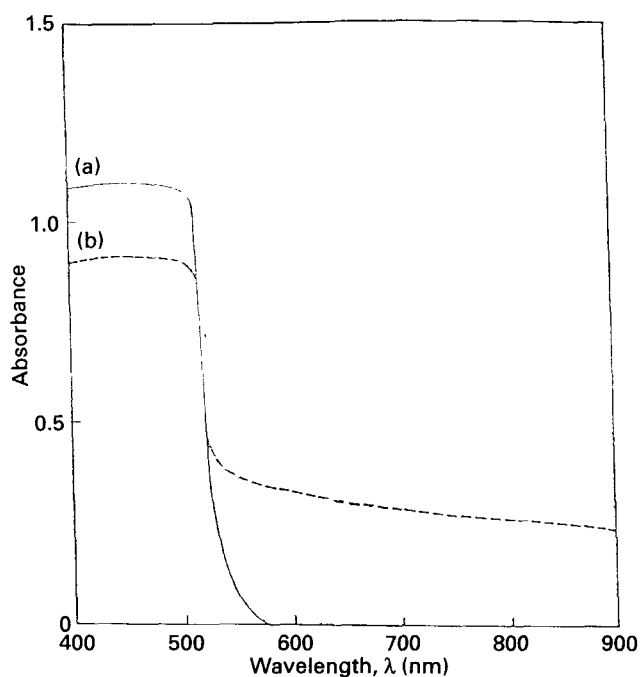


Figure 2 Diffuse reflectance spectra of (a) CdS; and (b) Rh/CdS (1.37 wt %).

band gap of CdS. The extra allowed wavefunctions generated out of the perturbation of the CdS lattice by Rh yield allowed energy states which can participate in the excitation and de-excitation processes. Hence, in addition to band gap excitation, excitation of electrons from the valence band of CdS to these allowed energy levels is feasible [19–22].

Photoelectrochemical techniques are utilized to further probe the interface between Rh and CdS. Table IV shows that photodeposition of Rh on a CdS photoanode decreases the $R_{\text{cell(Dark)}}$ of the PEC cell as Rh is a metal, which is a better conductor than CdS which is a semiconductor. A decrease in R_{cell} will normally increase the photocurrent, whereas photodeposition of Rh on a CdS photoanode decreases the photocurrent and $R_{\text{cell(Photo)}}$, indicating that part of the conduction band electrons of CdS can be transferred to Rh [17, 19, 23]. This implies that Rh forms an ohmic contact with CdS. Further, the electrons from the valence band of CdS can be excited to the extra allowed energy states generated by the perturbation of the CdS lattice by Rh [19–21]. $R_{\text{cell(Photo)}}$ is lower than $R_{\text{cell(Dark)}}$ as the charge carriers produced during the illumination of CdS and Rh/CdS aid effective electrical transport. Photodeposition of Rh on CdS shifts the photocurrent onset potential to a more positive value (Table IV), indicating the deposition of a neutral or positively charged species on the surface of CdS. However, XPS studies show the deposition of a neutral species, Rh^0 . The photocurrent at a bias of +1 V versus saturated calomel electrode (SCE) is mainly due to the photocorrosion of CdS ($\text{CdS} + 2 h_{\text{VB}}^+ \rightleftharpoons \text{Cd}^{2+} + \text{S}$) [22, 24]. Hence the decrease in the photocurrent at a bias of +1 V versus SCE on photodeposition of Rh on CdS (Table IV) indicates that photodeposition of Rh decreases the photocorrosion of CdS.

Scanning electron microscopic (SEM) examination of Rh/CdS (not shown) reveals that photodeposition of Rh results in the formation of discontinuous metal layers on CdS. Photodeposition of metals on semiconductors normally results in the formation of ohmic contacts [25, 26]. Nakato and Tsubomura [21] observed discontinuous metal layers when the contact between the metal and the semiconductor is ohmic. In the present study a discontinuous Rh layer

is observed, implying that the contact between Rh and CdS could be ohmic.

Photodeposited Rh is in the zero oxidation state, however, it is prone to aerial oxidation. Photodeposited Rh forms an ohmic contact with CdS. Besides the conventional surface analysis techniques such as XPS, SEM and DRS, photocatalytic as well as photoelectrochemical methods can be effectively used to characterize both the surface and the interface of metallized semiconductors.

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TABLE IV Effect of photodeposition of Rh on the photoelectrochemical properties of CdS (reference electrode: saturated calomel electrode (SCE); counter electrode: Pt-foil; electrolyte: 0.1 M KCl)

Photoanode	Dark		$R_{\text{cell(dark)}}$	Net photo		$R_{\text{cell(photo)}}$	Photocurrent onset potential V vs SCE	Photocurrent at bias of +1 V vs SCE (μA)
	V_{OC} (mV)	I_{SC} (mA)	V/l (k Ω)	V_{OC} (mV)	I_{SC} (mA)	V/l (k Ω)		
CdS	150	0.002	75	300	0.108	2.8	-0.64	245
Rh/CdS $\theta = 0.18$	6	0.001	6	394	0.089	4.2	-0.56	170

θ – fraction of the surface of CdS covered by Rh

$R_{\text{cell(dark)}}$ – internal resistance of the PEC cell in the dark

$R_{\text{cell(photo)}}$ – internal resistance of the PEC cell under illumination

V_{OC} – open-circuit voltage

I_{SC} – short-circuit current

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