

Enhancement of CdSe film electrode PEC characteristics by metalloporphyrin/polysiloxane matrices



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ABSTRACT

A facile and low-cost strategy to improve stability and conversion efficiency of CdSe film electrodes prepared by chemical bath deposition (CBD) onto FTO/glass substrates, is described. The naked CdSe film electrodes, with band gap value 1.8 eV, photo-corroded under the photoelectrochemical (PEC) working conditions and exhibited no photocurrent. The CdSe film peeled out in short times. Attempts made to enhance stability and efficiency of naked CdSe electrodes, by chemical etching or pre-scratching the FTO surface with fine sand-paper, failed to improve film PEC characteristics. Annealing the glass/FTO/CdSe film also failed to improve its PEC stability or efficiency. When coated with the electro-active species Tetra(-4-pyridyl)porphyrinatomanganese^{III/II} sulfate embedded inside polysiloxane films (MnPyP/Polysil) the CdSe films did not peel out under the PEC conditions. The coated electrode (glass/FTO/CdSe/MnPyP/Polysil) clearly exhibited photocurrents. Pre-annealing the naked CdSe film at 350 °C, followed by coating with MnPyP/Polysil further enhanced the electrode PEC characteristics. Additional heating of the prepared glass/FTO/CdSe/MnPyP/Polysil electrode at 120 °C also enhanced its PEC characteristics. The mode of action of the MnPyP/Polysil coating has been attributed to its ability to behave as a charge transfer catalyst at the solid/liquid interface. The new technique described here could also be potentially valuable for other types of thin film electrode materials.

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1. Introduction

Monolithic semiconductor (SC) electrodes have been effectively used in PEC and photovoltaic (PV) processes [1]. Due to the rising cost of monolithic SC materials, conventionally used as p-n junction grids, scientists are keen to develop new SC thin film electrodes. Such systems are in the nano-/micro-thickness scale which minimizes material amount, cost and pollution [2–6]. Research has been active in preparing different types of SC thin films based on different compounds, such as metal chalcogenides (MX, where X = S, Se or Te) by different methods. Despite the advantages of using such electrodes in PEC systems, they normally lack stability [7] and exhibit low PEC conversion efficiency.

CdSe films were prepared by different techniques such as PVD, CVD, electrochemical (ECD) and chemical bath deposition CBD. The CBD technique is widely used [8]. The CBD-prepared CdSe films were widely studied from different points of view including optical properties, luminescence and other properties [9–15]. CdSe electrodes have been described in PEC study in the bulk system or as films deposited onto different metal substrates [1]. CdSe films combined with other systems have also been described [16,17]. Bulk CdSe has a band gap of 1.7 eV [11,18], whereas thin film CdSe has a wider band gap of ~1.8–1.9 eV [11,19–23].

The CBD-prepared CdSe film on glass/FTO substrates has not been widely investigated in PEC systems in its pristine form in aqueous media, to the best of our knowledge. This is one major reason why pristine CdSe film electrodes, deposited onto FTO substrates, have been chosen in this study. PEC properties of CdSe film electrodes, prepared by CBD, will be assessed here. Simple strategies to stabilize the film and to improve its conversion efficiency will then be studied. Thin film electrodes based on CdSe have reasons

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to be used in PEC, but their instability limits their application. One major reason is the hazardous nature of Cd^{2+} and Se^{2-} ions [24,25]. Therefore, stabilizing such systems is relevant.

In earlier study, monolithic n-GaAs electrode systems modified by anchoring positively charged metalloporphyrin complexes to the SC surface were described [26,27]. By such a technique, the band edge positions were shifted towards positive potentials, and the PEC conversion efficiency was significantly enhanced. Unfortunately, the n-GaAs surface photo-corroded after some time under PEC conditions and the metalloporphyrin species peeled away. In order to simultaneously enhance conversion efficiency and stability of monolithic n-GaAs electrodes, a new method was described [28]. Metalloporphyrinato ions (MnTPyP) were embedded inside inactive polysiloxane (Polyil) matrix, and the MnPyP/Polysil composite was attached to the SC surface. The method was non-costly, easy to achieve and effective in stabilizing n-GaAs monolithic electrodes while enhancing their efficiency. The same method has been utilized here to modify characteristics of CdSe thin film electrodes for the first time. It is assumed that attaching the MnPyP/Polysil composite onto the CdSe film electrode would enhance its PEC conversion efficiency and stability by behaving as charge transfer catalyst between the excited SC film electrode and the electrolyte system. These assumptions will be further tested and discussed here.

2. Experimental

2.1. Materials

Common materials, such as Se, S, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, LiClO_4 , KOH, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_3 , Na_2S , and organic solvents were purchased from Aldrich, Frutarom or Riedel-DeHaën. The tetra(4-pyridyl)porphyrinatomanganese(III)sulfate (MnTPyP) complex solution was prepared by reacting MnSO_4 and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine in DMF as described earlier [5–30]. The characteristic absorption bands at 462, 569 and 620 nm confirmed the formation of the desired complex. The mixture involved complexes of both Mn^{II} and the Mn^{III} , as confirmed by electronic absorption spectra in the visible region, in accordance with literature [29–31].

2.2. CdSe Thin Film Manufacturing

Cadmium selenide thin films were prepared by CBD onto FTO/glass substrates as described earlier [32,33]. To create selenium ions in the form of sodium selenosulfate (Na_2SeSO_3), selenium powder (6.0 g) was mixed with sodium sulfite solution (60 g, in 300 mL DW). The mixture was heated to 90°C for 15 hours, while stirring, and was then filtered.

In another beaker, $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (30.0 g) was added to 300 ml of distilled water, after which 25% NH_3 solution was added to the solution with constant stirring until milky turbid $\text{Cd}(\text{OH})_2$ system resulted. Further addition of excess ammonia dissolved turbidity and converted the system into clear solution. To the solution, 300 ml of the freshly prepared Na_2SeSO_3 were slowly added with constant stirring [30]. The solution was stirred for 10 seconds and then transferred into another beaker containing FTO/glass substrates. The substrates were pre-cleaned and pre-etched with HCl (10% V), and were vertically dipped inside the beaker. The bath solution was heated to 80°C , and film deposition was completed in 4 h time. The soundly uniform red-orange films were then taken, washed with water and stored for further use.

Pre-annealing of the CdSe films was conducted, before coating with $\text{MnTPyP/Polysiloxane}$ films, using a thermostated tube furnace. The prepared CdSe film samples were placed in the middle of

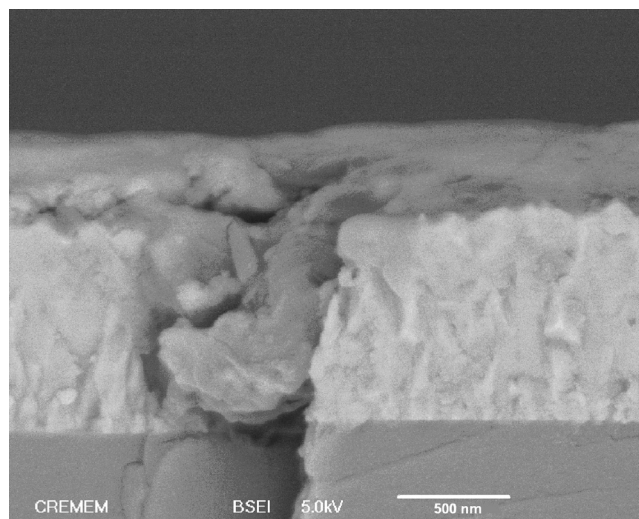


Fig. 1. A cross-sectional SEM micrograph showing thickness values for pre-annealed CdSe film (950–1100 nm) and for MnPy/Polysil layer (400–500 nm).

a 30 cm long Pyrex cylinder. The temperature was raised to the desired setting under nitrogen. Pre-annealing was conducted at different temperatures in the range $100\text{--}450^\circ\text{C}$. The 350°C temperature showed highest PEC characteristics for coated electrodes. Therefore, this temperature was used throughout this work unless otherwise stated. The samples were kept at 350°C for 20 min before cooling was started. The furnace was switched off, and the heated system (Pyrex cylinder and film substrate together) was taken out of the furnace and left to cool to room temperature in ~ 3 min. The film thickness, measured by SEM, was in the range (950–1100 nm). Gravimetric measurements showed (750–850 nm) thickness. Measured film thickness values are higher than that reported for CdSe films prepared similarly at 20°C in literature [33]. The difference in thickness is due to difference in preparation temperature.

2.3. Coating with $\text{MnTPyP/Polysiloxane}$ matrix:

The CdSe electrodes were coated with MnPyP-Polysil as described earlier [28]. A dilute solution, of commercial RTV made polysiloxane paste in acetic acid, was prepared by dissolving the paste (0.01 mg) in dichloromethane (20.0 ml). The MnPyP solution was prepared by dissolving MnPyP (0.01 mg, 1.38×10^{-5} mol) in methanol (10.00 mL). The $\text{MnPyP/polysiloxane}$ stock solution was prepared by adding the MnPyP solution to the polysiloxane solution in a 1:4 (V/V) ratio, respectively. The solid state electronic absorption spectrum measured for MnTPyP species embedded inside polysiloxane film, on glass substrate, resembled that measured in methanol solution with a red shift in the former. The absorption spectra confirmed the existence of mixed Mn^{II} and Mn^{III} species, as reported earlier [28].

The MnPy/polysiloxane stock solution (0.10 ml, containing 4.0×10^{-5} g polysiloxane and 2.0×10^{-4} g MnPy) were then uniformly placed onto pre-polished CdSe films. The glass/FTO/CdSe film was immersed in the stock solution for 4 seconds. After removal from the solution, the organic solvents, dichloromethane and methanol, were then allowed to evaporate off, leaving a uniform thin layer of MnPy/polymer matrix on the surface of electrode. The conditions described in the coating procedure herein were intentionally chosen so as to yield an optimum MnPy/Polysil film thickness of 400–500 nm, as measured by cross-sectional SEM images, Fig. 1. Thicker films exhibited insulator characteristics and passed no measurable current. Therefore, unless otherwise stated,

this thickness was used in coating procedures throughout all this work.

The modified electrode was further annealed, after fabrication, at 125 °C for 30 min under nitrogen. This temperature is known to give MnTPyP/Polysil films with high uniformity and clarity as reported in coating mono-lithic semiconductor electrodes [28]. The system was then left to cool at room temperature under N₂. In control experiments, CdSe surfaces were modified with a polysiloxane film with no MnP.

Coating the pre-annealed CdSe film with the MnPyP/Polysil matrix enhanced its surface uniformity, as evidenced from AFM study. The AFM profile data indicate that the coated film exhibited narrower surface elevation profile range (80% showing depth values 50–170 nm, with average surface elevation height 120 nm) than the naked pre-annealed film (80% showing depth values 70–210 nm, with average surface elevation height 150 nm).

2.4. Equipment

Solid and solution electronic absorption spectra for CdSe films were measured on a Shimadzu UV-1601 spectrophotometer, using FTO/glass as base line reference. Solid state PL emission spectra were measured on a Perkin Elmer LS50B Luminescence spectrometer, using excitation wavelength 250 nm. The CdSe films were thick enough to screen the FTO/glass materials which showed no impact on the measured spectra.

X-Ray Diffraction (XRD) patterns were measured on a Philips XRD X'PERT PRO diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) as a source, available at ICMCB, University of Bordeaux. Field Emission-Scanning Electron Micrographs (FE-SEM) were measured on a Jeol model JSM-6700F microscope, at CREMEM–University of Bordeaux.

Atomic Force Microscopy (AFM) morphology was studied using a tapping mode-AFM system (Quds University, Abu Dees) and WSxM software designed by Nanotec Electronica (Madrid, Spain). Soft, non-conductive, rectangular commercial Si₃N₄ cantilevers (NSG 10, NT MDT Co., Ltd.) with spring constants of 5.5–22.5 Nm⁻¹ and resonance frequencies in the range 190 to 325 kHz were used.

Current–voltage (I–V) plots were measured on a computer-controlled Princeton Applied Research (PAR) Model 263A potentiostat. Current density–voltage (J–V) plots were obtained from values of measured current divided by area of CdSe electrode immersed in solution.

A 50 Watt Xenon lamp, with housing and concentrating lens, having a 450–800 nm spectral range, was used as a light source. The lamp was placed at a fixed distance from the working electrode. The illumination power on the electrode was $\sim 0.02 \text{ W/cm}^2$ (slightly less than AM10 solar spectrum). Light intensity was measured with Lutron–LX 102 light meter, which was pre-calibrated against a Kipp and Zonen CM11 Pyranometer.

2.5. PEC experiment

PEC measurements were conducted in a three-electrode one-compartment cell. The prepared CdSe film electrode was employed as a working electrode, with a platinum counter electrode and a reference saturated calomel electrode, SCE. Two types of redox couple systems were examined. The first involved 0.10 M of LiClO₄, 0.05 M of K₃Fe(CN)₆ and 0.05 M of K₄Fe(CN)₆, while the second involved 0.10 M of (Na₂S, S, KOH), all in distilled water. In each case high purity nitrogen (99.999%) was bubbled through the solution for at least 5 minutes before each experiment, and was kept to bubble above the solution during the experiment to minimize contamination with air.

The photo J–V plots were measured under illumination with the Xenon lamp as described above. The dark J–V plots were measured under complete dark using a thick blanket cover.

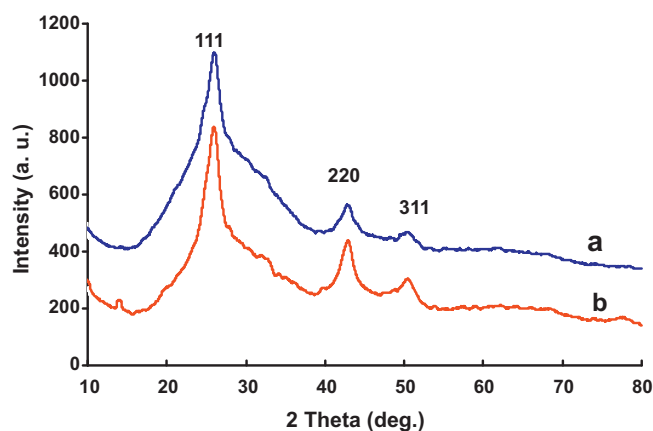


Fig. 2. XRD patterns measured for naked CdSe thin film a) non-annealed and b) after annealing at 350 °C.

Stability experiments were performed by keeping the working electrode under constant illumination (0.02 W/cm^2) at 0.00 V bias (vs. SCE reference), at room temperature.

3. Results and discussion

With a band gap less than 1.9 eV ($\sim 652 \text{ nm}$), CdSe film electrodes are not expected to be highly stable to photodegradation. Their PEC activity may thus not be easily observed. Therefore, stabilizing them was one major objective in this work. Attempts to stabilize the films and enhance their PEC conversion efficiencies are discussed herein.

3.1. Naked film electrodes (glass/FTO/CdSe system)

Glass/FTO/CdSe electrodes were first prepared in the naked form. Different techniques were used to characterize the resulting CdSe films. XRD pattern, Fig. 2a, measured for the pre-annealed film confirmed its CdSe nature with a hexagonal phase (Wurtzite structure). This was based on comparison with earlier reports [8,34–36]. Annealing the film at 350 °C enhanced the XRD peaks, in terms of peak height and width, Fig. 2b. Using the Scherrer equation using the (220) plane, the calculated particle size values were 4.5 and 5.5 nm for the non-annealed and the pre-annealed films, respectively. The XRD patterns thus indicate that annealing affected crystallinity and particle sizes of the CdSe film, by sintering.

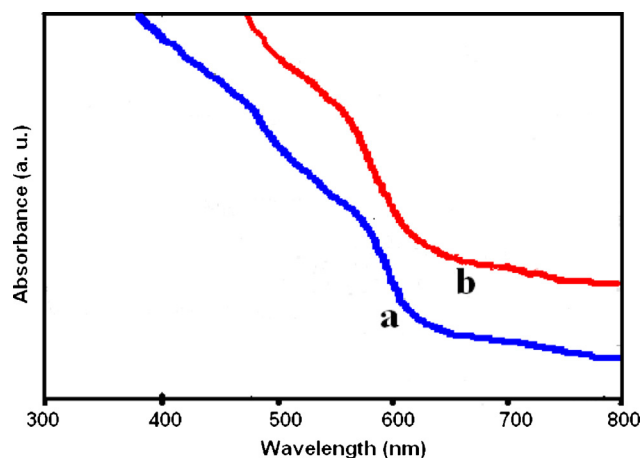


Fig. 3. Solid state electronic absorption spectra for CdSe films (a) non-annealed and (b) after annealing at 350 °C.

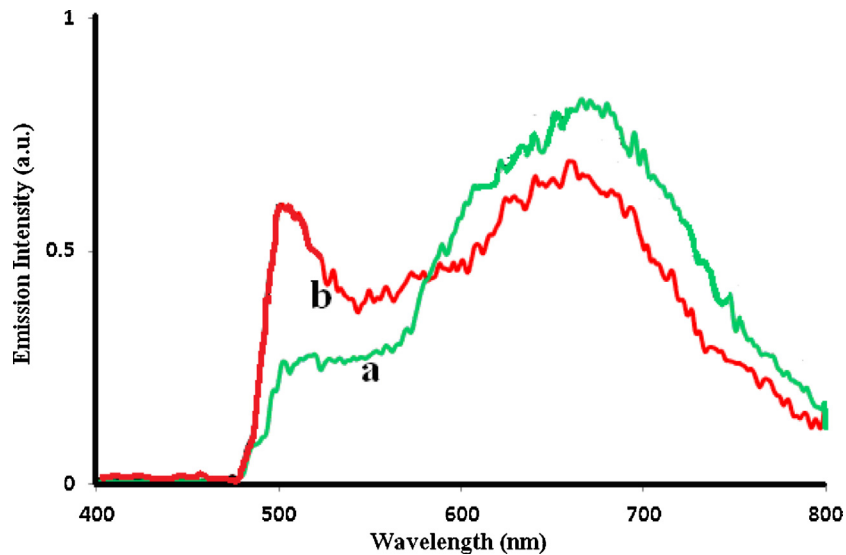


Fig. 4. Photoluminescence emission spectra for CdSe films, (a) non-annealed, and (b) after annealing at 350 °C.

Solid state electronic absorption spectra confirmed the formation of the CdSe film. The spectra resembled literature values for CdSe nano-particles dispersed in toluene [37]. Fig. 3 shows effect of annealing (at 350 °C) on the spectra. The results were consistent with earlier spectra reported for CdSe films [36]. While the non-annealed electrode exhibited absorption at 620 nm, corresponding to 2.0 eV band gap, the electrodes annealed at 350 °C exhibited longer wavelengths of absorption in the range 650–680 nm. In congruence with XRD results discussed above, the spectra indicate that annealing the CdSe films caused sintering and growth in the

film grains. Such behavior is known for different particle systems [38,39]. Rate of cooling (quenching and slow cooling) did not show systematic influence on values of band gap.

PL spectra, Fig. 4, confirmed CdSe film formation with a band gap of 680 nm, in agreement with earlier reports [37]. Annealing showed only slight effect on the PL spectra. Cooling rate did not show significant effect. The PL spectra showed no presence for FTO bands due to the relatively thick CdSe films present.

Effect of annealing on naked CdSe films was studied by AFM, as shown in Fig. 5. The non-annealed film showed particles spread

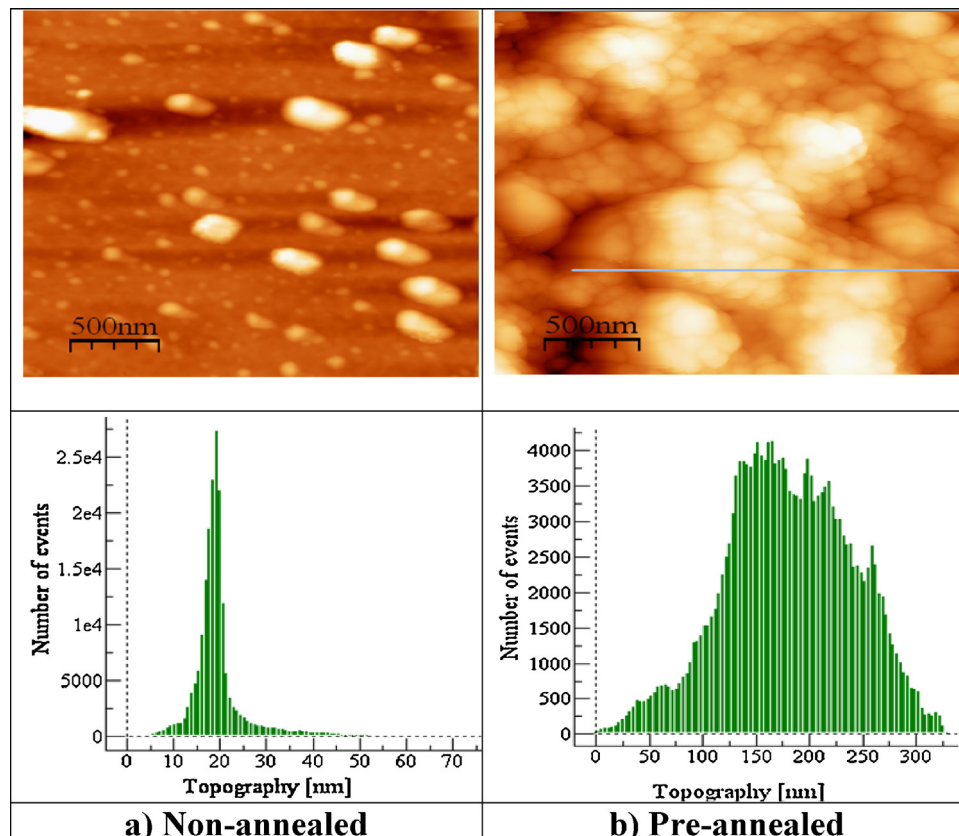


Fig. 5. AFM images and depth profiling for CdSe films deposited onto FTO/glass substrates, a) Non-annealed, and b) Annealed.

in more uniform pattern than the annealed films, while the latter showed tightly bound coagulate formation. Annealing caused more variation in film depth profiling; as a result of coagulate formation. Coagulate formation is believed to enhance carrier mobility in the film, which is a reason for enhanced PEC characteristics observed for pre-annealed coated CdSe electrodes as described later.

The naked glass/FTO/CdSe electrodes were examined in PEC study. The electrodes failed to exhibit any dark- or photo-current characteristics under the working conditions. Changing the electrolyte system, using $\text{LiClO}_4/\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ at one time and $\text{S}/\text{Na}_2\text{S}/\text{KOH}$ at another time, did not make things any better. In each case the electrode exhibited normal conductor behavior with Ohmic contact due to the instability of the CdSe film. The film degraded readily and peeled out of the glass/FTO surface leaving wide areas of FTO in direct contact with the electrolyte. Ohmic contact occurred between the electrode and the electrolyte without showing any dark- or photo-current behaviors in the PEC cell. Pre-annealing the glass/FTO/CdSe electrode did not improve its stability or PEC characteristics, and the CdSe film continued to peel out. The leaching was confirmed by analyzing the Cd^{2+} ions that occurred in the solution during the PEC experiment.

Different attempts were made to stabilize the CdSe and prevent its peeling out. Prolonged chemical etching (by HCl solution) or physical abrasion (with fine sand paper) of the FTO prior to deposition of CdSe layer did not significantly improve stability under PEC conditions. The results indicate that the glass/FTO/CdSe electrodes are unstable to corrosion under PEC conditions used here. This justifies the need for new techniques to stabilize CdSe film-based electrodes.

3.2. Coated film electrodes (glass/FTO/CdSe/MnPyP-Polysil systems)

The glass/FTO/CdSe/MnPyP-Polysil electrode stability under PEC conditions using the $\text{S}/\text{Na}_2\text{S}/\text{NaOH}$ redox couple system was clearly observed. This was manifested firstly from resistance to peel out. Fig. 6 shows pictures for naked and coated CdSe electrodes immediately after removal from the PEC experiments. While the naked electrode showed wide areas of exposed FTO, the coated electrode retained its uniform red color during the PEC experiments. This behavior was observed in all coated electrodes, even those prepared with non-annealed CdSe films.

The coated electrode showed negative dark current under only negative bias, as shown in Fig. 7. Such behavior is typical for n-type semiconducting materials. Therefore, coating with MnPyP-Polysil is responsible for enhanced dark current behavior of the CdSe electrode. Further enhancement in dark-current plots was achievable by pre-annealing CdSe at 350°C before coating. Value of dark-current density measured at -0.5V applied bias was taken as a criterion for electrode dark current activity.

The influence of MnPy/Polysil coating on electrode photo-current activity was pronounced. Unlike the naked electrode, the glass/FTO/CdSe/MnPyP-Polysil electrode showed a clear photoactivity, even without pre-annealing the CdSe film. The J-V plots show that, unlike the naked CdSe film electrodes, the coated electrode exhibited measurable PEC characteristics, Fig. 8.

Further enhancement in photo J-V plots has been achieved by pre-annealing the CdSe film before coating with MnPyP/Polysil. Fig. 8 shows how pre-annealing affected photo J-V plots of the coated electrodes.

Results of Fig. 8 are summarized in Table 1. Contrary to the naked CdSe electrodes discussed above, the Table shows that the coated electrode exhibited PEC characteristics in terms of V_{OC} , J_{SC} , conversion efficiency ($\eta\%$) and fill factor (FF). Such parameters were not observable for the naked electrode under the working conditions here. Moreover, the Table shows that pre-annealing the CdSe

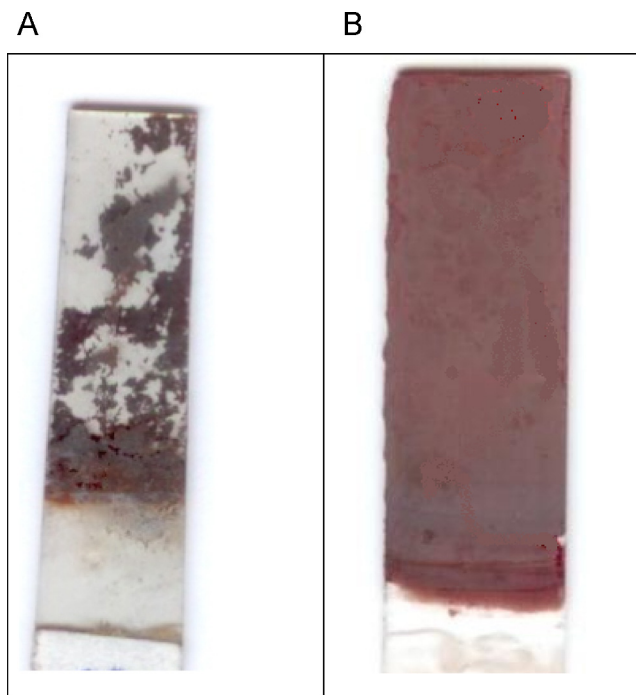


Fig. 6. Pictures for pre-annealed CdSe film electrodes after recovery from PEC experiments, showing tendency of the film to peel out (a) naked electrode, and (b) coated electrode.

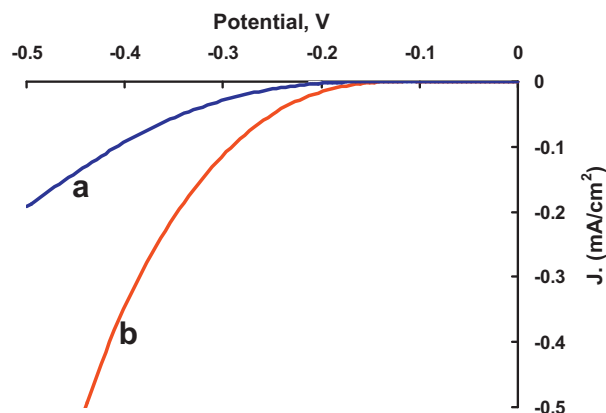


Fig. 7. Effect of pre-annealing the coated CdSe films on dark J-V plots (a) coated without pre-annealing (b) coated after pre-annealing at 350°C .

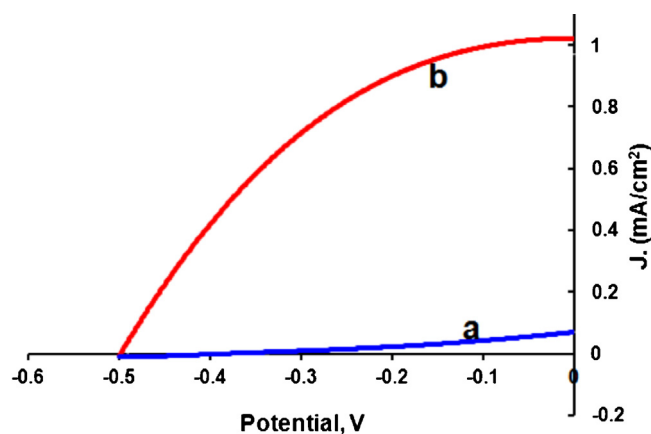


Fig. 8. Effect of pre-annealing the coated CdSe films on photo J-V plots (a) coated without pre-annealing (b) coated after pre-annealing at 350°C .

Table 1
Effect of pre-annealing and method of cooling on PEC characteristics for glass/FTO/CdSe-MnPyP-Polysil electrodes.

Pre-annealing temperature (°C)	Cooling method	V_{OC} value (V)	J_{SC} value mA/cm ²	$\eta\%$	FF%
Room Temperature	-	-0.34	0.58	0.26	30
350	Quenched	-0.46	0.28	0.28	35
350	Slowly cooled	-0.46	0.28	0.27	44

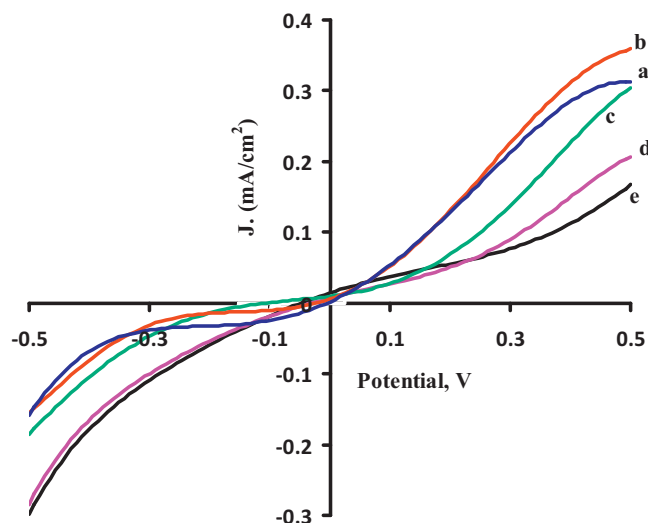


Fig. 9. J-V plots under light illumination for control electrodes a) naked FTO, b) FTO treated with Mn(TPyP) solution, c) FTO/MnPyP/Polysil (with no CdSe layer), d) FTO/CdSe/Mn(TPyP) e) FTO/CdSe/Polymer.

electrode at 350 °C significantly enhanced all PEC characteristics of the coated electrode. While the non-annealed coated electrode showed V_{OC} , J_{SC} , $\eta\%$ and FF values of -0.34 V, 0.07 mA/cm², 0.24 and 0.22, respectively, the 350 °C annealed electrode showed corresponding values of -0.50 V, 1.1 mA/cm², 1.1 and 0.41, respectively. As discussed above in Fig. 5, such enhancement is presumably due to better sintering among coagulates by pre-annealing. Sintering should enhance carrier mobility and short-circuit current density.

In order to confirm the role of MnTPyP/Polysil coating in PEC activity enhancement of the modified CdSe electrodes, experiments were conducted using different control electrodes. Naked FTO, FTO/Polysil, FTO dipped in Mn(TPyP) solution, FTO/MnPyP/Polysil (with no CdSe layer), FTO/CdSe/Mn(TPyP) and FTO/CdSe/Polymer electrodes were all prepared and tested for PEC activity as control electrodes. None of the electrodes showed any measurable photocurrent, with all exhibiting zero value for short circuit current density (J_{SC}). Fig. 9 shows photo J-V plots observed from control electrodes. The results indicate that photoactivity exhibited by the glass/FTO/CdSe/MnTPyP/Polysil electrode is due to the CdSe film itself. The coating matrix by is not responsible for photoactivity, but is responsible for enhancement of the CdSe efficiency and stability to peeling.

PEC stability of the coated CdSe electrodes was studied under continuous illumination with light at zero bias (SCE). Values of J_{SC} were plotted vs. time, as shown in Fig. 10. Contrary to the naked electrode system, all coated CdSe electrodes exhibited constant values with time, showing stability under PEC conditions. The lower values of the J_{SC} observed in the Figure at the beginning of the PEC experiment are understandable. At the beginning, the surface of the coated electrode may have different forms of contaminants which inhibit charge transfer at the solid/liquid interface. With time such contaminants are washed away and the electrode shows stable J_{SC} values. Similar behaviors have been encountered in earlier reports [28]. This was confirmed here by repeating the stability experiment on same electrode for five times, by switching off the circuit,

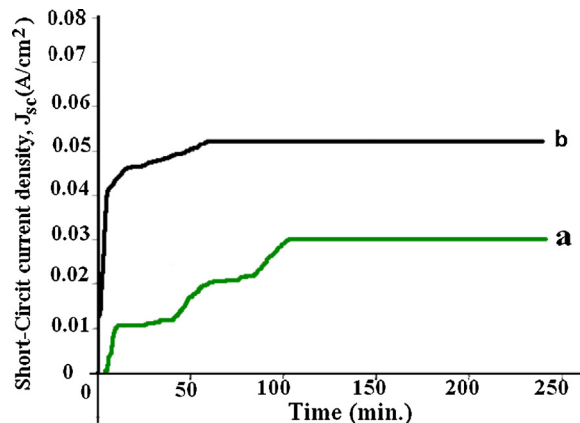


Fig. 10. Effect of pre-annealing on plots of J_{SC} vs. time measured for MnP/polysiloxane coated CdSe thin film electrodes (a) non-annealed (b) pre-annealed at 350 °C.

shutting off the light, and immediately measuring the value for the resulting J_{SC} under resumed illumination. The value was consistent with the corresponding J_{SC} constant value shown in the Figure. While all coated electrodes exhibited steady values for J_{SC} with time, showing acceptable stabilities, pre-annealing the CdSe electrode affects the values of J_{SC} , as discussed in photo J-V plots above. The Figure shows that pre-annealing further enhanced the value for J_{SC} , in agreement with dark- and photo- J-V plots and efficiency results presented above.

Collectively, the results showed that coating the CdSe electrodes with MnPyP-Polysil films prevented their tendency to leach out, enhanced their dark- and photo- J-V plots, and enhanced their stability under PEC conditions. The mode of action of the MnPyP-Polysil film is understandable based on a model proposed in earlier reports for monolithic n-GaAs electrodes using $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ redox couple [26–28]. The model described the Mn^{II}/Mn^{III} redox couple as an extra charge transfer mediator system that lowered the flat band edges and consequently facilitated hole transfer across the solid/redox couple interface. By doing so, the Mn^{II}/Mn^{III} system enhanced monolithic semiconductor electrode efficiency and stability at the same time. The earlier model can similarly explain effect of the MnTPyP/Polysil coating on CdSe film electrode PEC characteristics. The matrix includes both Mn^{II} and Mn^{III} ions, as evidenced from electronic absorption spectra of the solid matrix as discussed above. While the band at 470 nm confirms the presence of the Mn^{III} porphyrin species, the bands at shorter wavelengths (400–420 nm) are attributed to the Mn^{II} porphyrin species [27]. The Mn^{II}/Mn^{III} mixed species may undergo oxidation and reduction reactions at -0.15 and -0.2 V (vs. SCE) respectively as reported earlier [26,40]. Moreover the reported valence and conduction band gap edge values for CdSe are +1.256 V and -0.694 V with respect to SCE, respectively, keeping in mind that the values may vary with particle size [37]. The CdSe conduction band edge potential is thus lower (more positive) than the potential for the $Mn^{II/III}PyP$ species. Therefore, the holes created in the CdSe valence band upon excitation can readily be transferred to the Mn^{II}/Mn^{III} species. The $Mn^{II/III}$ species in turn facilitates the transfer of the holes to the redox couple. The Mn^{II}/Mn^{III} system thus

behaves as a charge transfer catalyst at the solid/liquid interface. Such mediation enhances short circuit current value and, consequently, the conversion efficiency. Similar discussions have been made in earlier reports [26–28]. Naked CdSe electrodes did not exhibit PEC characteristics as they peeled out with no activity. The coated CdSe showed enhanced stability under PEC conditions. Stability enhancement under PEC conditions is due to the ability of the MnTPyP/Polysil matrix to behave as charge transfer mediator. Under PEC conditions, the holes may accumulate in the space charge layer, and then oxidize the SC surface causing photodegradation. By quickly transferring the holes to the redox couple, the Mn^{II}/Mn^{III} species can help stabilize the SC surface from photodegradation. The mode of action of the MnTPyP species is evidenced by the fact that the electrodes covered with polysil layers only (with no MnTPyP) did not exhibit enhancement in PEC characteristics.

In addition to charge transfer mediation, the Mn^{III} complex ion (which carries a net 1+ charge) may play another additional role. Preliminary AFM study conducted here, on charge concentration distribution, showed that the metalloporphyrin positive ions in the matrix are located in closer proximity to the semiconductor surface. The positive ions in the matrix thus cause shifting (to more positive potential) in values of flat band potentials of the semiconductor, as reported earlier for monolithic SC electrode electrodes [26–28]. Such shifting may affect charge transfer at the solid/liquid interface. In case of coated CdSe electrodes, the holes which accumulate near the SC valence band edge, have higher positive potential and are more able to move to the Mn^{II}/Mn^{III} couple in the solid polymer matrix. This behavior yields higher efficiency and stability in case of coated SC electrode.

Collectively, the results clearly indicate that the MnTPyP/Polysil matrix enhances PEC characteristics for the CdSe film electrode, by facilitating charge transfer across the solid/liquid interface and by lowering bad edge positions of the SC. Based on these encouraging results, work is underway to use the technique described here in other types of thin film electrode systems.

4. Conclusions

CdSe film electrodes were deposited onto glass/FTO substrates by chemical bath deposition. The naked CdSe film electrodes failed to exhibit PEC activity and peeled out of the FTO under PEC conditions. When coated with metalloporphyrin complexes embedded into polysiloxane matrices, the CdSe film electrodes exhibited measurable PEC activity. Both efficiency and stability of the CdSe electrodes were enhanced by coating. The MnTPyP species involves Mn^{II} and Mn^{III} species which combined together may act as charge transfer mediator across the SC/redox couple. The positively charged Mn^{III} species may also lower the flat band edge positions of the CdSe electrode. The technique described here can be a potentially useful strategy to enhance conversion efficiency and stability of the CdSe and other types of film electrodes in future PEC processes.

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References

- [1] H.O. Finklea, *Semiconductor electrodes*, Elsevier Science Ltd, 1988.
- [2] H.S. Hilal, R. Ismail, A. El-Hamouz, A. Zyoud, I. Saadeddin, Effect of cooling rate of pre-annealed CdS thin film electrodes prepared by chemical bath deposition: Enhancement of photoelectrochemical characteristics, *Electrochim. Acta* 54 (2009) 3433–3440.
- [3] A. Zyoud, I. Saadeddin, S. Khudruj, Z.N. Hawwash, D. Park, G. Campet, H.S. Hilal, CdS/FTO thin film electrodes deposited by chemical bath deposition and by electrochemical deposition: A comparative assessment of photoelectrochemical characteristics, *Solid State Sci.* 18 (2013) 83–90.
- [4] G. Hodes, *Chemical solution deposition of semiconductor films*, CRC press, 2002.
- [5] H.S. Hilal, Z. Zainal, M. Yunus, W. Mahmood, Z.A. Talib, N. Sabli, M. Fujii, CuZn-SnS Thin Film Electrodes Prepared by Vacuum Evaporation: Enhancement of Surface Morphology and Photoelectrochemical Characteristics by Argon Gas, *Mater. Sci. Forum*, Trans. Tech. Publ 756 (2013) 273–280.
- [6] N. Sabli, Z.A. Talib, W.M.M. Yunus, Z. Zainal, H.S. Hilal, M. Fujii, Effect of Argon Gas on Photoelectrochemical Characteristics of Film Electrodes Prepared by Thermal Vacuum Evaporation from Synthesized Copper Zinc Tin Selenide, *Int. J. Electrochem. Sci* 8 (2013) 10910–10920.
- [7] J. Portier, H. Hilal, I. Saadeddin, S. Hwang, M. Subramanian, G. Campet, Thermodynamic correlations and band gap calculations in metal oxides, *Progr. Solid State Chem.* 32 (2004) 207–217.
- [8] R. Singh, S. Bhushan, A. Singh, S. Deo, Characterization and optical properties of CdSe nano-crystalline thin films, *Dig. J. Nanomat. Bios.* 6 (2011) 403–412.
- [9] M. Šimurda, P. Němec, P. Formanek, I. Němec, Y. Němcová, P. Malý, Morphology of CdSe films prepared by chemical bath deposition: The role of substrate, *Thin Solid Films* 511 (2006) 71–75.
- [10] M. Behboudnia, Y. Azizianekalandaragh, Synthesis and characterization of CdSe semiconductor nanoparticles by ultrasonic irradiation, *Mater. Sci. Eng.: B* 138 (2007) 65–68.
- [11] S. Kale, C. Lokhande, Thickness-dependent properties of chemically deposited CdSe thin films, *Mater. Chem. Phys.* 62 (2000) 103–108.
- [12] C. Vargas-Hernández, V. Lara, J. Vallejo, J. Jurado, O. Giraldo, XPS, SEM and XRD investigations of CdSe films prepared by chemical bath deposition, *Phys. Status Solidi: B* 242 (2005) 1897–1901.
- [13] C. Lokhande, E.-H. Lee, K.-D. Jung, O.-S. Joo, Ammonia-free chemical bath method for deposition of microcrystalline cadmium selenide films, *Mater. Chem. Phys.* 91 (2005) 200–204.
- [14] E. Lifshitz, I. Dag, I. Litvin, G. Hodes, S. Goror, R. Reisfeld, M. Zelner, H. Minti, Optical properties of CdSe nanoparticle films prepared by chemical deposition and sol-gel methods, *Chem. Phys. Lett.* 288 (1998) 188–196.
- [15] Q. Dai, Y. Song, D. Li, H. Chen, S. Kan, B. Zou, Y. Wang, Y. Deng, Y. Hou, S. Yu, Temperature dependence of band gap in CdSe nanocrystals, *Chem. Phys. Lett.* 439 (2007) 65–68.
- [16] T. Ju, L. Yang, S. Carter, Thickness dependence study of inorganic CdTe/CdSe solar cells fabricated from colloidal nanoparticle solutions, *J. Appl. Phys.* 107 (2010) 104311–104315.
- [17] D. Kim, C. Hangarter, R. Debnath, J. Ha, C. Beauchamp, M. Widstrom, J. Guyer, N. Nguyen, B. Yoo, D. Josell, Backcontact CdSe/CdTe windowless solar cells, *Solar energy materials and solar cells* 109 (2013) 246–253.
- [18] C. Kittel, *Introduction to Solid State Physics*, J. Wiley & Sons, NY, 1986.
- [19] V. Garcia, M. Nair, P. Nair, R. Zingaro, Preparation of highly photosensitive CdSe thin films by a chemical bath deposition technique, *Semicon. Sci. Technol.* 11 (1996) 427.
- [20] P. Němec, D. Mikeš, J. Rohovec, E. Uhlířová, F. Trojánek, P. Malý, Light-controlled growth of CdSe nanocrystalline films prepared by chemical deposition, *Mater. Sci. Eng. B* 69 (2000) 500–504.
- [21] A.K. Singh, S.R. Deo, G.S. Thool, R. Singh, Y. Katre, A. Gupta, Synthesis and Characterization of Chemically Deposited Nanocrystalline CdSe Thin Film, *Syn. React. Inorg. Metal-Org. Nano-Metal Chem.* 41 (2011) 1346–1350.
- [22] C. Mehta, J. Abass, G. Saini, S. Tripathi, Effect of deposition parameters on the optical and electrical properties of nanocrystalline CdSe, *Chalcogenide Lett* 11 (2007) 133–138.
- [23] P. Hankare, S. Delekar, M. Asabe, P. Chate, V. Bhuse, A. Khomane, K. Garadkar, B. Sarwade, Synthesis of Cadmium Selenide thin films at low-temperature by simple chemical route and their characterization, *J. Phys. Chem. Solids* 67 (2006) 2506–2511.
- [24] A.H. Zyoud, N. Zaatar, I. Saadeddin, C. Ali, D. Park, G. Campet, H.S. Hilal, CdS-sensitized TiO₂ in phenazopyridine photo-degradation: Catalyst efficiency, stability and feasibility assessment, *J. Hazard. Mater.* 173 (2010) 318–325.
- [25] A. Zyoud, N. Zaatar, I. Saadeddin, M.H. Helal, G. Campet, M. Hakim, D. Park, H.S. Hilal, Alternative natural dyes in water purification: Anthocyanin as TiO₂-sensitizer in methyl orange photo-degradation, *Solid State Sci.* 13 (2011) 1268–1275.
- [26] H.S. Hilal, J.A. Turner, Controlling charge-transfer processes at semiconductor/liquid junctions, *Electrochim. Acta* 51 (2006) 6487–6497.
- [27] H.S. Hilal, M. Masoud, S. Shakhshir, N. Jisrawi, Metalloporphyrin/polysiloxane modified n-GaAs surfaces: effect on photoelectrochemical efficiency and surface stability, *J. Electroanal. Chem.* 527 (2002) 47–55.
- [28] H.S. Hilal, W.M. Ateereh, T. Al-Tel, R. Shubeita, I. Saadeddin, G. Campet, Enhancement of n-GaAs characteristics by combined heating, cooling rate and metalloporphyrin modification techniques, *Solid State Sci.* 6 (2004) 139–146.

- [29] H. Hilal, C. Kim, M. Sito, A. Schreiner, Preparation and characterization of tetra (4-pyridyl) porphyrinatomanganese (III) cation supported covalently on poly (siloxane), *J. Mol. Catal.* 64 (1991) 133–142.
- [30] M.L.S.H.S. Hilal, A.F. Schreiner, Preparation and characterization of poly(siloxane)-supported metalloporphyrins: The effect of the support on the electronic absorption spectra, *Inorg. Chim. Acta* 189 (1991) 141–144.
- [31] H. Hilal, C. Kim, A. Schreiner, Investigation of the catalytic activity of poly (siloxane)-supported tetra (4-pyridyl) porphyrinatomanganese (III) in olefin oxidation reactions, *J. Mol. Catal.* 81 (1993) 157–165.
- [32] R. Tenne, G. Hodes, Improved efficiency of CdSe photoanodes by photoelectrochemical etching, *Appl. Phys. Lett.* 37 (1980) 428–430.
- [33] R. Kale, C. Lokhande, Influence of air annealing on the structural, optical and electrical properties of chemically deposited CdSe nano-crystallites, *Appl. Surf. Sci.* 223 (2004) 343–351.
- [34] P. Gupta, M. Ramrakhiani, Influence of the particle size on the optical properties of CdSe nanoparticles, *Open Nanosci. J.* 3 (2009) 15–19.
- [35] P. Srivastava, K. Singh, Synthesis of CdSe nanoparticles by solvothermal route: Structural, optical and spectroscopic properties, *Adv. Mat. Lett.* 3 (2012) 340–344.
- [36] M.R.S. Mahajan, R.B. Dubey, Jagrati Mahajan, Characteristics and properties of CdSe quantum dots, *Int. J. Latest Res. Sci. Tech.* 2 (2013) 457–459.
- [37] K. Rajeshwar, Fundamentals of semiconductor electrochemistry and photoelectrochemistry, in: S. Licht (Ed.), *In Semiconductor Electrodes and Photoelectrochemistry*, 6, Wiley-VCH, Weinheim, 2003, p. 1.
- [38] D. Demirskyi, D. Agrawal, A. Ragulya, Comparisons of grain size-density trajectory during microwave and conventional sintering of titanium nitride, *J. Alloys Comp.* 581 (2013) 498–501.
- [39] S. Dalawai, A. Gadkari, T. Shinde, P. Vasambekar, Effect of sintering temperature on structural and electrical switching properties of cadmium ferrite, *Adv. Mater. Lett.* 4 (2013) 586–590.
- [40] A. Harriman, G. Porter, Photochemistry of manganese porphyrins. Part 1.—Characterisation of some water soluble complexes, *J. Chem. Soc. Faraday Trans. 2* 75 (1979) 1532–1542.