Preparation of Active CdS/RuO$_x$ Particles for the Photogeneration of H$_2$

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Preparation of RuO$_x$ from RuO$_4$, as well as from *in situ* generated 'ruthenium hydroxide' or ruthenate ions, followed by calcination at 400 °C, reproducibly affords active catalysts generally without noxious oxidation of the CdS support, whereas impregnation of RuCl$_3$·3H$_2$O and subsequent annealing yields poor materials; in the latter procedure the CdS is irretrievably damaged.

CdS with a bandgap of 2.4 eV is an attractive material for photoelectrochemical (PEC) targets using solar light, as it absorbs strongly below 520 nm. Systems consisting of CdS particles loaded with a catalyst, *viz.* Pt or RuO$_2$, have been extensively studied in the PEC production of hydrogen from various substrates, *e.g.* water,[1] ethylenediaminetetra-acetic acid (EDTA),[2] and sulphide ions.[3] To date, one of the main problems in studying these systems is the great variation in activity and efficiency of the various CdS/catalyst systems examined by different groups, as well as the poor reproducibility. This is connected with differences in method of preparation and the fact that most of the materials are illcharacterised. Especially in the case of ruthenium dioxide, or more properly $RuO_x(\cdot yH_2O)$, the disparity in reported activities is obvious, not to mention the role of this material as an oxidation or reduction catalyst which is still a matter of uncertainty.

In this paper we present the results of an investigation into the relation between the preparative method of various RuO_x catalysts, the morphology of the resulting CdS/RuO_x powders, and their activity in the PEC production of H_2 from alkaline EDTA and sulphide/sulphite solutions. With regard to the synthesis we have examined the influence of the starting material (RuO_4, $RuCl_3\cdot 3H_2O$, K_2RuCl_6) and of the solvent used. We heated the CdS particles, impregnated with ruthenium chloride to convert the chloride into the oxide under varying conditions (in a stream of air or under vacuum) and various annealing times. The chemical reaction employed as well as the heat-treatment not only determines the appearance and nature of the catalyst thus obtained, but may also affect the properties of the CdS support. Therefore, we have characterised the CdS/RuO_x powders by various techniques [*X*-ray diffraction, elemental analyses, Brunauer–Emmett–Teller (BET) surface area determination, scanning electron microscopy (SEM)]. We outline here that there exists an evident coherence between the method of preparation of RuO_x catalysts on CdS, the appearance of the resulting CdS/RuO_x powders, and the activity in PEC processes.

We prepared the CdS/0.5 wt% RuO_x powders using different starting compounds and different chemical reactions.† Powder (**1**) was obtained by conversion of RuO_4 into RuO_2, for which Graetzel *et al.*[1] have proposed the following equation: $RuO_4 \rightarrow RuO_2 + O_2\uparrow$. According to this equation the CdS support is not oxidised. No subsequent heat-treatment is neccessary to bring the catalyst into the right condition.

Powder (**2**) was prepared starting from $RuCl_3\cdot 3H_2O$. Ru^{III}- or Ru^{IV}-hydroxide or ruthenate is formed *in situ* by addition of NaOH prior to impregnation. Calcination at 400 °C for 6 h in a stream of air completes the synthesis of powder (**2**). Powders (**3**), (**4a**—**c**) have been prepared by impregnation of CdS with $RuCl_3\cdot 3H_2O$ in various solvents, followed by a similar calcination procedure. Finally, powders (**5a**—**c**) have been synthesised from K_2RuCl_6 by means of impregnation of ruthenium hydroxide or ruthenate, as for powder (**2**), with application of different drying or heating methods. We have also applied heat-treatment to CdS to examine the effect of calcination [powder (**6**)].

We have characterised the powders (**1**)—(**6**), and we have determined their activities in the PEC production of hydrogen from alkaline EDTA and from alkaline sulphide/sulphite solutions. The main conclusions from the *X*-ray diffractograms as well as the results from the PEC experiments are presented in Table 1.

As evidenced by Table 1, the outward colour is a first, important indication of properties. Yellow and yellow–green powders display high activities, whilst brown (just like grey) substances are poor materials. This is substantiated by the *X*-ray diffractograms; for the active powders only, the lines of the hexagonal CdS phase are found. On the other hand, the inactive materials show in their *X*-ray diffractograms the occurrence of considerable amounts of $CdSO_4\cdot 2CdO$, and, in a single case, of $CdSO_4$ [powder (**2**)], or of $CdSO_4\cdot H_2O$ [powder (**5c**)]. Remarkably, the partial oxidation of the semiconductor support has occurred in all those cases in which we used the $RuCl_3$-impregnation method followed by calcination. Obviously, conversion of $RuCl_3$ impregnated on CdS into the oxide does not proceed smoothly, as concomitantly the CdS is affected. We have the impression that materials obtained from this $RuCl_3$-impregnation route all contain chloride to a lesser or higher degree, depending on the annealing conditions. Graetzel *et al.*[3] have reported that heating CdS impregnated with $RuCl_3$ under air may lead to some substitution of S^{2-} in the CdS-lattice by Cl^-. We observe here, that on heating $RuCl_3$-impregnated CdS, the semiconductor itself is also oxidised. Interestingly, preparation from RuO_4 or by means of impregnation of ruthenium hydroxide or ruthenate with subsequent annealing gives satisfying results. Removal of the chloride ions by substitution by OH^- prior to calcination seems an absolute condition to warrant an appreciable activity. In this respect powder (**2**) is somewhat an exception; it is substantially contaminated with $CdSO_4\cdot 2CdO$, yet its activity is high, and its colour is like that of an active powder. Besides, the RuO_4 and the ruthenium hydroxide impregnation method afford reproducibly good and active catalysts, when CdS from the same batch is used. It should be noted again, that the quality and activity of various batches of commercially purchased CdS may differ considerably, a phenomenon which has also been observed by other groups.[4] The use of various batches might obscure the effect of catalyst preparation.

We also observe that there is an effect of heating on the nature of the catalyst. Heating at low temperature (200 °C) under vacuum enhances the photocatalytic activity of the samples [*e.g.* powder (**5b**)] significantly. Calcination at higher temperature (400 °C) under a stream of air has no further improving effect [powder (**5c**)]. By this treatment at 200 °C the water, adsorbed on the surface, is removed and thus a water-free, stable catalyst is obtained. This is in accordance with the findings of Mills *et al.*,[5] who established in an elegant study that the lower the content of water on the catalyst (present as ruthenium dioxide hydrate), the higher the activities and the more stable the catalysts are.

Next to the influence of the employed preparation procedure on the quality of the CdS-support and on the water

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† Powder (**1**). Under vigorous stirring a solution of 31.2 mg of RuO_4 (Alfa Chemicals) in 50 ml of distilled water was added dropwise to an orange–yellow suspension of 5 g of CdS (Fluka, *puriss.*) in 500 ml of distilled water, which had been sonicated for 2 h prior to use. After 1 h the yellow–greenish precipitate was filtered off, evaporated, and dried under vacuum above KOH.

Powder (**2**). Under vigorous stirring a solution of 45.20 mg of NaOH in 25 ml of distilled water was added dropwise in 15 min to a solution of 49.34 mg of $RuCl_3\cdot 3H_2O$ (Drijfhout Chemicals) suspended with 5 g of CdS in 50 ml of distilled water. The solution discoloured. Stirring was continued for 4 h. After evaporation of the solvent, filtration, and drying, the powder was heated at 400 °C for 6 h in a stream of air.

Powder (**3**). A solution of 3.775 ml of 0.05 M of $RuCl_3\cdot 3H_2O$ in 1 M HCl suspended with 5 g of CdS was sonificated for 0.5 h and was then stirred for 0.5 h. After evaporation of the solvent under vacuum and drying, the powder was heated at 400 °C for 6 h in a stream of air.

Powder (**4a**—**c**). A solution of 49.34 mg of $RuCl_3\cdot 3H_2O$ suspended with 5 g of CdS in 50 ml of solvent was sonicated for 15 min and was then stirred for 15 min. After slow evaporation under reduced pressure and drying, the powder was heated at 400 °C for 4 h in a stream of air. Solvents used: distilled water (**4a**), n-butanol (**4b**), ethanol (**4c**).

Powder (**5a**—**c**). Under vigorous stirring a solution of 60.5 mg of NaOH in 25 ml of distilled water was added dropwise over 45 min to a solution of 73.95 mg of K_2RuCl_6 (Ventron) suspended with 5 g of CdS in 50 ml of distilled water. The solution discoloured. Stirring was continued for 4 h. After filtration, washing with distilled water and drying, powder (**5a**) was dried under vacuum above KOH, whereas powders (**5b**) and (**5c**) were heated for 4 h at 200 °C under vacuum, and at 400 °C in a stream of air, respectively.

Powder (**6**). Without further treatment commercially obtained CdS (Fluka *puriss.*) was heated at 400 °C for 6 h in a stream of air.

Table 1. Nature and activity for the photogeneration of H_2 of various CdS/RuO_x powders.

Powder	Colour	Composition[a]	PEC-H_2 production from EDTA[b,c] /µl h^{-1}	PEC-H_2 production from S^{2-}/SO_3^{2-} [b,d] /µl h^{-1}
(1)	Yellow–green	CdS only	37	671
(2)	Yellow–green	CdS, $CdSO_4$, $CdSO_4 \cdot 2CdO$ (minor)	42	397
(3)	Dark brown	CdS, $CdSO_4 \cdot 2CdO$ (major)	5	35
(4a)	Light brown	CdS, $CdSO_4 \cdot 2CdO$ (major)	10.5	53
(4b)	Light brown	CdS, $CdSO_4 \cdot 2CdO$ (major)	6	35
(4c)	Green–brown	CdS, $CdSO_4 \cdot 2CdO$ (major)	9	35
(5a)	Yellow	CdS only	16	385
(5b)	Yellow–green	CdS only	63	356
(5c)	Yellow–green	CdS, $CdSO_4 \cdot H_2O$ (minor)	63	796
(6)	Dark yellow	CdS only	~0	6
(7)[e]	Yellow	CdS only	~0	8

[a] From X-ray diffraction (Philips, Cu-K_α). [b] Illumination in home-made Rayonet photochemical reactor, fitted with Philips TL55 daylight lamps in closed Pyrex tubes, the gas volume, initially N_2, being 55 ml. Hydrogen production measured by g.c. (see ref. 3b). [c] System 15 mg powder/15 ml 0.1 M EDTA; pH 12.8, 25 °C. [d] System 15 mg powder/15 ml 0.1 M sulphide and 0.1 M sulphite; pH 12.8, 25 °C. [e] Fluka *puriss.*, untreated.

content of the catalyst, we have also studied its impact on the surface area and the particle size. The total surface area, measured according to the BET method, amounts to approximately 1.2 m^2 g^{-1} for the untreated Fluka CdS. Loading with 0.5 wt% of a ruthenium dioxide catalyst without any heat-treatment yields values of 1.7 to 1.9 m^2 g^{-1}. Upon calcination at 400 °C there is a surface area drop to almost 0.8 m^2 g^{-1} for the majority of the samples. Apart from this, there does not seem to be an explicit parallel between BET surface in this range (0.5 to 2.0 m^2 g^{-1}) and activity.

SEM micrographs of the untreated Fluka CdS and of powder (**1**) show that the form and the size of the particles are, at least optically, similar. Closer inspection shows that the ruthenium dioxide is finely dispersed over the CdS particles, which underlines again that the RuO_4 preparation method produces a good and active catalyst.

In conclusion, we have found that preparation of RuO_x from RuO_4 as well as from $RuCl_3 \cdot 3H_2O$ or K_2RuCl_6, assuming that the chlorides are converted into hydroxide or ruthenate before impregnation is performed, followed by calcination, reproducibly yields a well-defined and active catalyst. The CdS support remains almost intact. Calcination of impregnated $RuCl_3 \cdot 3H_2O$ or K_2RuCl_6 without preceding treatment with hydroxide, produces materials which still contain chloride. Simultaneously, the CdS particles are greatly and irreversibly oxidised to $CdSO_4 \cdot 2CdO$ and other compounds as shown by the X-ray diffractograms. Dehydration, attained by heating at fairly low temperature, improves the activity of the catalyst. Variation in BET surface area by treatment does not contribute much to the activity.

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References

1 *E.g.* K. Kalyanasundaram, E. Borgarello, and M. Graetzel, *Helv. Chim. Acta,* 1981, **64**, 362.
2 *E.g.* J. R. Darwent and G. Porter, *J. Chem. Soc., Chem. Commun.,* 1981, 145.
3 *E.g.* (a) E. Borgarello, K. Kalyanasundaram, M. Graetzel, and E. Pelizzetti, *Helv. Chim. Acta,* 1982, **65**, 243; (b) D. H. M. W. Thewissen, A. H. A. Tinnemans, M. Eeuwhorst-Reinten, K. Timmer, and A. Mackor, *Nouv. J. Chim.,* 1983, **7**, 191; (c) D. H. M. W. Thewissen, E. A. van der Zouwen-Assink, K. Timmer, A. H. A. Tinnemans, and A. Mackor, *J. Chem. Soc., Chem. Commun.,* 1984, 941.
4 *E.g.* N. Serpone, E. Borgarello, M. Barbeni, and E. Pelizzetti, *Inorg. Chim. Acta,* 1984, **90**, 191.
5 A. Mills, C. Lawrence, and R. Enos, *J. Chem. Soc., Chem. Commun.,* 1984, 1436.