

A Novel One-step Hydrothermal Method for the Preparation of Cd_{1-x}Zn_xS/Titanate Nanotubes Composites for Photocatalytic Hydrogen Production

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Study of ZnO-ZnS Composite as Photocatalyst in the Water Splitting Reaction

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The combined influences of global warming and declining oil reserves have meant that alternative energy resources that are much more environmentally friendly and sustainable are being explored. Hydrogen has always been a favoured candidate of green and renewable energy resources as combusting hydrogen produces mainly energy with water as a by-product. Hydrogen can be generated from water in the presence of a photocatalyst, which harnesses solar energy as illustrated in Figure 1. With light of appropriate wavelengths, electrons can be excited from the valence band to the conduction band of a photocatalyst. These excited electrons then migrate to the surface of the catalyst reducing protons to form hydrogen.

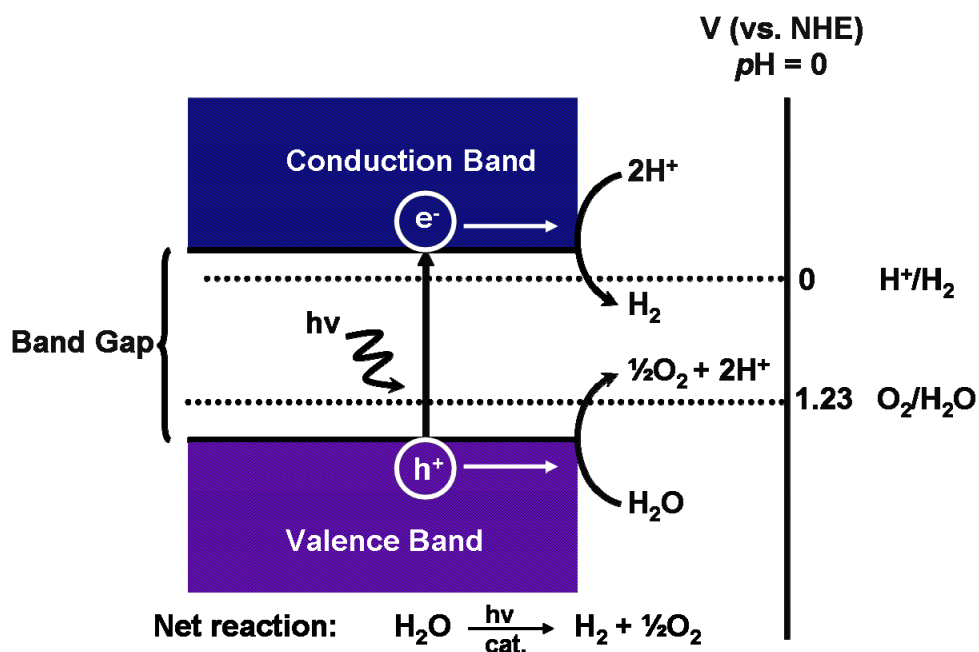


Figure 1: The basic principal of generating hydrogen from water photocatalytically.

Over the last few decades, a large amount of research has been conducted to produce hydrogen photocatalytically from aqueous solution. Recently, investigations have been carried out to utilize a ZnO-ZnS composite as a catalyst for water splitting and organic mineralization [1–3]. Both zinc oxide and zinc sulfide are cheap, widely available and relatively non-toxic to the environment. Even though they are large band gap semiconductors, the band gap of the resulting composites could be smaller and hence absorb a greater fraction of the solar spectrum. The composite materials can be synthesized

by adding aqueous $\text{Zn}(\text{NO}_3)_2$ [2] into a vigorously stirred solution of NaOH and Na_2S . [1] Subsequent heat treatment of the washed white precipitate in nitrogen at 400°C would yield a yellow material. The synthesized composite materials were screened for hydrogen activities using the experimental set-up as illustrated in Figure 2.

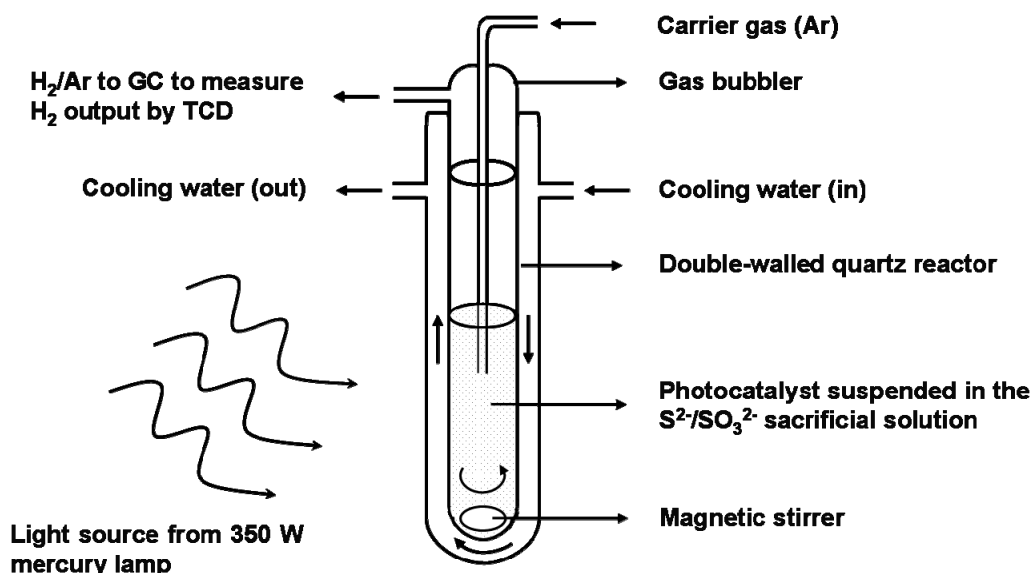


Figure 2: Schematic diagram of the photolysis set-up.

From the solid state UV-Vis analysis, the absorption band edges of the resulting composite materials are shifted to longer wavelengths as compared to both ZnO and ZnS . Characterising the materials using XRD revealed that the synthesized material exists as a mixture of two different phases, which can be assigned as wurtzite ZnO and cubic ZnS . At present, it is suggested the observed red shift in the absorption band edges is due to the presence of defects in the material. This suggestion will be tested by other characterisation techniques such as Photoluminescence.

As for the hydrogen activities, it is found that the composite materials photocorrode, possibly because of the instability of ZnO upon UV illumination. Preliminary results showed that ZnO barely produced any hydrogen in the presence of the $\text{S}^{2-}/\text{SO}_3^{2-}$ sacrificial solution. However, an increase of hydrogen activities was observed with prolonged exposure of UV light. The XRD patterns of the photolysed ZnO sample exhibited an increase in intensity with photolysis duration of impurity peaks that can be attributed to elemental Zn and cubic ZnS . An intense S K_α peak observed in the EDX spectrum of the photolyzed ZnO sample further supported the XRD result. It is therefore suggested that during photolysis, ZnO photocorroded to form Zn^{2+} , which either reacted with S^{2-} from the sacrificial solution to form ZnS with a concomitant increase in hydrogen evolution, or was reduced to elemental Zn .

Both XRD and EDX-FESEM techniques were employed to examine a series of the composite materials with different molar ratios of ZnO to ZnS , before and after photolysis. Overall, no distinct peaks of wurtzite ZnO were observed from the XRD patterns of the photolyzed composite materials, except the sample with the most ZnO . As mentioned earlier,

ZnO is not stable under the given experimental condition, and thus it is reasonable that no wurtzite ZnO XRD pattern was detected from the photolyzed samples. Generally, all of the photolyzed composite materials exhibited more of the crystalline phase of cubic ZnS by comparison with non-photolyzed samples.

A change of surface morphology of the composite material is apparent after photolysis as illustrated in the FESEM images in Figure 3. The composite material lost its dendritic features after the photocatalysis reaction. The observation implied that the dendritic feature consists of mostly ZnO. And since ZnO photocorrodes, it is reasonable that the dendritic feature is not being observed from the photolyzed samples anymore. In addition, the observed decrease in the intensity of the Zn K_{α} peak relative to that of the S K_{α} from the EDX spectrum suggests an increase in S content in the composite material after photolysis. The analysis result implied that excess ZnS was formed during photolysis which complemented the XRD result.

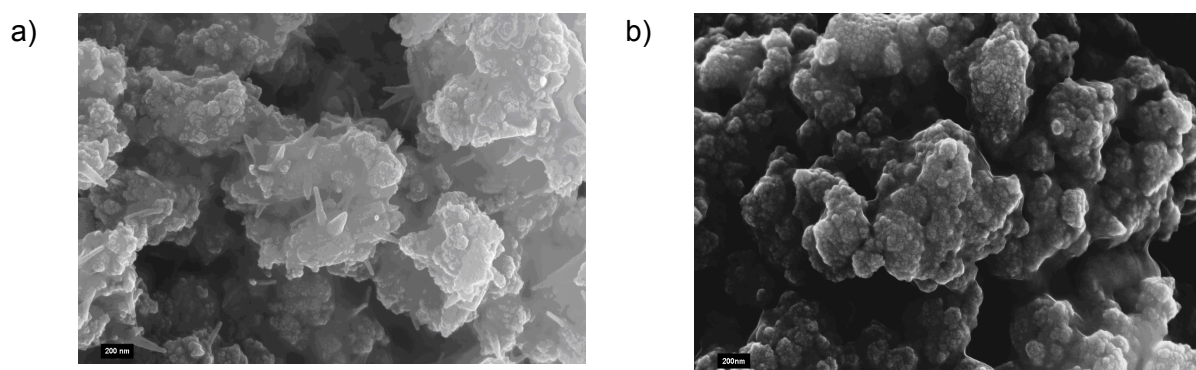


Figure 3: FESEM images of the composite material with ZnO(75):ZnS(25) (a) before and (b) after photolysis.

In conclusion, the composite materials are active in generate hydrogen generation, using light mainly in the UV region. With the insertion of a 395nm cut-off filter, there is no activity observed from ZnS whereas there is still traceable activity from the composite materials. This is most likely due to the effective shifting of the band edge towards longer wavelength that can be attributable to the presence of defects in the materials. Further investigations are to be carried out to explore the reason behind the extended absorption band edge of the composite materials to the region of longer wavelengths, as well as correlating the physical properties and activities of the composite materials with different synthetic conditions.

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