

Hydrogen Production by Photosplit Reaction of Water with the Composite of Modified TiO₂ Hosting Q-sized CdS under irradiation of Visible Light

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ABSTRACT: The visible light responding, modified TiO₂ hosting Q-sized CdS was utilized for hydrogen production by photosplitting of water. Powder type of modified TiO₂ was prepared without heat treatment (NS) and with heat treatment at 400°C (NP400), respectively. Nanowires of NP400 and NS were synthesized without heat treatment (NPW, NSW) and heat treated again at 400°C (NPW400, NSW400). These NPW400 and NSW400 were employed as host materials of CdS (CdS/NP400, CdS/NPW400, CdS/NSW400) to utilize visible light. These modified photocatalysts have shown about 5 times higher hydrogen production efficiency compared to that of bare TiO₂ or CdS. The nanowire shape of TiO₂ shows higher efficiency than spherical shape of TiO₂, and crystalline states with heat treatment also contributes to enhance hydrogen production.

Keywords: hydrogen production, visible light, CdS, TiO₂, nanowire

1. INTRODUCTION

Hydrogen production via photocatalytic water splitting has attracted considerable interest due to the potential of hydrogen as a clean-energy source. Since the initial work of Fujishima and Honda with TiO₂-photoanode,¹ many different metal oxide semiconductors²⁻⁸ and metal sulfides⁹⁻¹¹ have been reported to be active for water splitting. While initial efforts involved large bandgap ($E_g > 3.0\text{eV}$, $\lambda < 400\text{nm}$) semiconductors including TiO₂ that utilize only UV light, recent efforts have focused on using visible light ($\lambda = 400\text{-}700\text{nm}$) as the ultimate goal is to use solar energy to produce hydrogen fuel. One candidate is CdS, which is an n-type semiconductor with a bandgap energy of 2.4eV. It is known to show relatively high photocatalytic activity for H₂ production even under visible light

irradiation, but its drawback is photocorrosion. The activity of CdS can be enhanced by nanocomposite materials, which combine CdS with mesoporous or microporous materials having different energy levels such as TiO₂/CdS,¹² ZnO/CdS, ZnS/CdS,^{13,14} K₄Nb₆O₁₇/CdS,¹⁵ and K₂Ti₄O₉/CdS^{16,17} composites. The prevailing theory is that in composite systems photogenerated electrons move to an attached semiconductor, i.e., CdS to TiO₂, while photogenerated holes remain in CdS. This charge carrier separation can prevent charge recombination, thus improving the photocatalytic activity of CdS. The energy levels of the CdS can be tuned by changing the particle size without changing the chemical composition. The pore sizes of the mesoporous and microporous host support material control the resulting particle size of the supported semiconductor prepared in

situ. Decreasing particle size has revealed higher catalyst efficiency.^{18,19} More importantly, the use of meso- or microporous support material leads to suppression of photocorrosion by encapsulating the catalyst that limits the exposed surface area. It has been observed a competition between photocorrosion of CdS and electron transfer to and from the substrates depending on the nature of the support/semiconductor contact.

Since our home-made modified TiO₂ has 30Å of pore size and 300m²/g of BET surface area,²⁰ this TiO₂ and its nanowire could be appropriate host material of CdS. Photocatalytic behaviour of Nanotube or nanowire shape of materials have been studied by several scientists exploring the highway effect.²¹⁻²⁵ In this paper, the synthesis of home-made TiO₂, its nanowire with their characterizations and then the synthesis of quantum sized CdS (Q-CdS)/TiO₂ nanocomposites are introduced. Even though the ability of CdS and related hybrid systems have been known to produce molecular hydrogen in the presence of sacrificial electron donors and light for many years, our goal was to gain a better understanding of the relationship between Q-CdS and crystal structure of TiO₂ under our experimental conditions.

2. EXPERIMENTALS

2.1 Preparation and characterization of materials

The visible light responding modified TiO₂ colloidal solution (NS) was prepared by hydrolyzing TiCl₄ in water containing ammonium ion. Its pore size was 30 Å, and BET surface area was 300m²/g. These properties imply to be an appropriate hosting substrate to incorporate with Q-CdS (< 10nm). Two different powders were further obtained by drying NS at 80°C (NP), and heat treat NS at 400°C (NP400)²⁰. These NS and NP were treated hydrothermally in 10M NaOH solution at 150°C for 72 hours to produce nanowires, NPW and NSW,

respectively. NPW (made from powder) and NSW (made from sol) were also heat treated at 400°C (NPW400, NSW400), respectively. Q-CdS/TiO₂ nanocomposites were prepared by utilizing Cd(NO₃)₂ 4H₂O and Na₂S 9H₂O solutions with each host substrate. FE-SEM/EDAX (JSM-6700F) was used to analyze shape and component of TiO₂-modified photocatalysts and XRD (D/MAX-2500/PC) was employed to identify their crystal structures.

2.2 Hydrogen production

Photocatalytic water splitting for hydrogen production was carried out in an air-tight reactor vessel under visible light irradiation (> 400nm). 0.2g of each prepared material was suspended in 40mL of a water/isopropanol mixture (50v/v %) in a Pyrex glass reactor. This mixed solution was purged with Ar gas for 30min prior to photoreaction to get rid of dissolved O₂ for the anoxic condition. A high-pressure 300W Xe arc lamp (Oriel Instruments) with a 400nm cut-off filter and a water filter was used as the primary light source. The amount of H₂ evolved during photocatalysis was analyzed by GC/TCD (Young Lin Instrument, Acme 6000 GC) with a molecular sieve column (30m × 0.32mm × 12.00μm).

3. RESULTS AND DISCUSSION

3.1 Characteristic of materials

Figure 1(a) shows microstructure of NP400 is of typical sphere shapes with primary particle size of 5~10 nm. Both NPW400 and NSW400, synthesized from NP and NW, respectively, have wire shaped structure with 60nm and 30nm in diameter, and few ten to hundred nm in length as shown in Figure 1(b) and (c).

The crystal structure of NP has been identified by XRD as shown in Figure 2 (a) indicating a typical TiO₂ crystal structure. The sphere shaped NP 400 and wire shaped

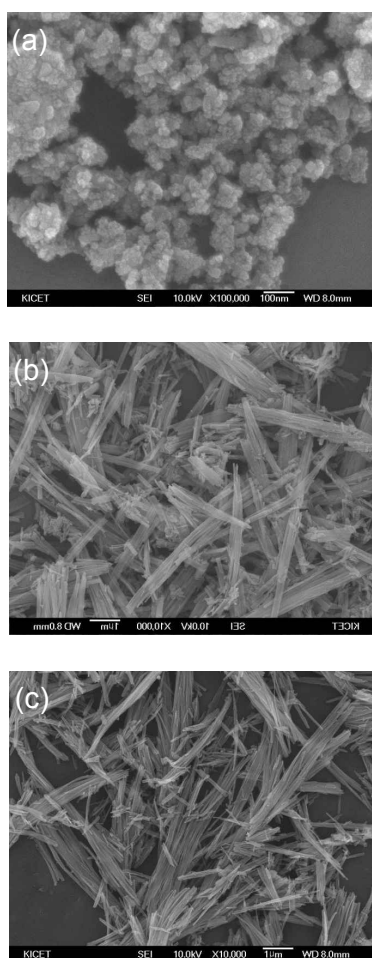


Figure 1: SEM image of NP400(a), NPW400(b), NSW400(c).

NPW400 show similar crystallinity, mixture of anatase and rutile, while NP shows less degree of crystalline of only anatase, and NSW400 has a very low degree of crystallinity as shown in the figure. The XRD of synthesized Q-CdS²⁶ is shown in Figure 2(b). The crystal structure of CdS changed from cubic to hexagonal with lower degree of crystallinity when it was heat treated at 400°C. FT-IR analysis for CdS400 shows a peak at 1150cm⁻¹ (S=O bond stretching), indicating CdS undergoes partial thermal oxidation to CdSO₄.

The amount of Q-CdS incorporated with modified TiO₂ hosting materials were analyzed by EDAX as list in Table 1. Cd and S were synthesized stoichiometrically. CdS was incorporated in wire shaped NPW400 and NSW400 more than 10 times

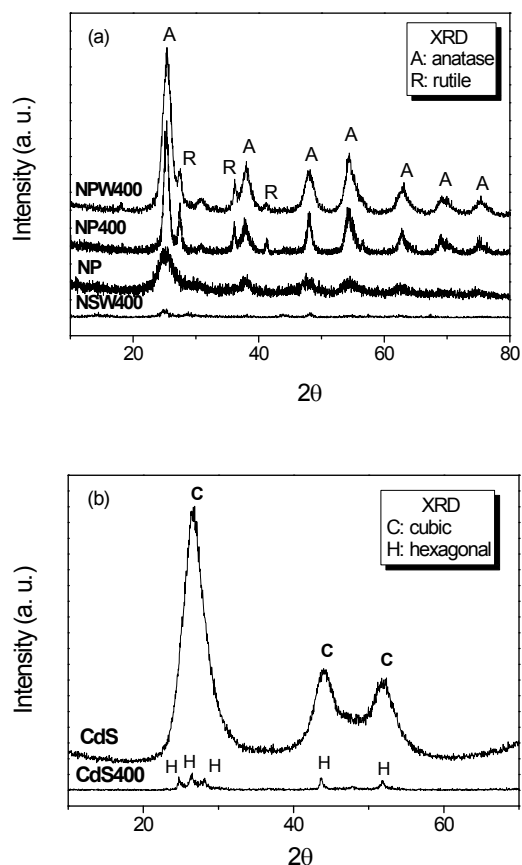


Figure 2: XRD pattern of photocatalysts ; (a) NPW400, NP400, NP, NSW400, (b) CdS, CdS400.

when compared with sphere shaped NP400. The specific surface areas of each host substrate by BET measurement were found to be: NP400(100m²/g)>NSW400(96m²/g)>NPW400(80m²/g). It should be noted that incorporated amount of CdS is not affected by the surface area of the supporting materials. The wire shaped TiO₂ provided better condition for CdS to incorporate in supporting photocatalysts.

Table 1: EDAX of CdS/NP400, CdS/NPW400, CdS/NSW400.

	mol. %		
	Cd	S	Ti
CdS/NP400	0.0126	0.0146	0.8113
CdS/NPW400	0.2038	0.1903	0.4626
CdS/NSW400	0.1470	0.1481	0.4860

3.2 Hydrogen production

Figure 3 displays hydrogen evolution efficiencies for CdS incorporated each different host material. The highest H₂ evolution rate of 73.7 $\mu\text{mol/g h}$ was observed with CdS/NPW400 under the same experimental condition. However, hydrogen evolution rate rather decreased with CdS/NSW400 compared to those with CdS/NPW400 and CdS/NPW400. XRD along with FE-SEM study indicates that the wire shaped photocatalysts provide more efficient water splitting hydrogen evolution than that of sphere shaped photocatalysts with the same crystal structure. The wire shaped host materials could provide unidirectional pathway for electrons, preventing electron from scattering and recombination of electron/hole pairs, thus more efficient transfer of electrons to the surface of photocatalysts for hydrogen evolution^{24,25,27}.

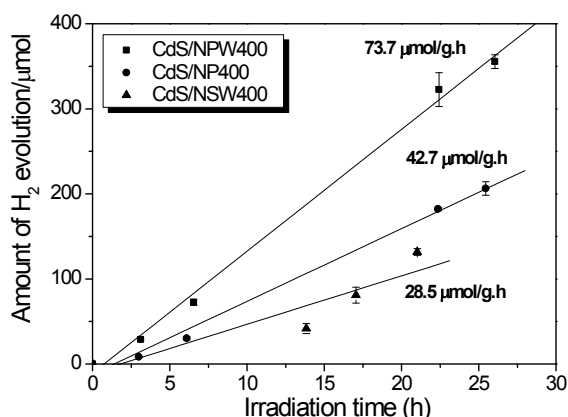


Figure 3: Rate of H₂ evolution under visible light irradiation ($\lambda > 400$ nm) in a mixed IPA water solvent (IPA:H₂O = 1:1V/V, V_T=40mL) for CdS/TiO₂ metal oxide nanocomposite.

The result from EDAX also indicates the wire shaped photocatalysts incorporated more CdS amount than sphere shaped ones. However, wire shaped NSW400 was not appropriate as CdS supporting photocatalyst due to the lower crystallinity. These results lead us to conclude that the shape of supporter as well as the degree of

crystallinity is important factor to hydrogen production from water.

The heat treatment effect on hydrogen evolution rate was studied and depicted in Figure 4.

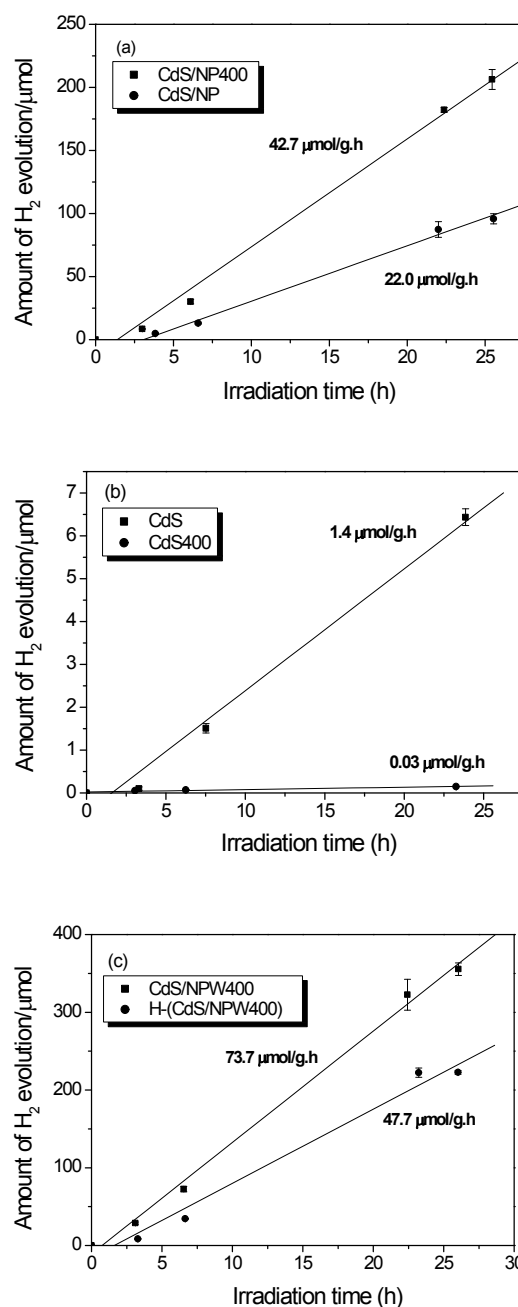


Figure 4: Heat treatment effect of various photocatalysts (a) CdS/NP (b) CdS and (c) CdS/NPW400 on the rate of H₂ evolution under visible light irradiation ($\lambda > 400$ nm) in a mixed IPA water solvent (IPA:H₂O = 1:1 V/V, V_T=40 ml) for heat treatment of photocatalysts.

The H₂ evolution rate for the photocatalysts of NP incorporated with CdS and NP400 is shown in Figure 4(a). As indicated in XRD study, NP400 (heat treated NP at 400°C) shows clear crystallinity and it affects H₂ evolution rate. However, H₂ evolution rate decreased in case of heat treated CdS400 as shown in Figure 4(b). From XRD and FTIR analysis, this is due to the partial oxidation of Q-CdS to CdSO₄, which does not have photocatalytic activity. The effect of heat treatment was carried out further for composite photocatalysts as shown in Figure 4(c). The heat treatment of composite photocatalysts also decreases H₂ evolution rate. Generally, bulk CdS oxidizes to sulfate or oxide at about 800°C²⁸ but Q-CdS undergoes partial oxidation at lower temperature, thus decreases its photocatalytic activity.

4. CONCLUSION

This study compares hydrogen production efficiencies for CdS incorporated each TiO₂-modified photocatalysts. NP400 has typical sphere shaped TiO₂ with primary particle size of 5~10 nm and it was anatase phase TiO₂. Both NPW400 and NSW400 have wire shaped structure with 60nm and 30nm in diameter and few ten to hundred in length. The composite photocatalysts showed higher H₂ evolution rate than pure photocatalysts such as CdS and TiO₂. The wire shaped supporter showed higher photocatalytic activity than sphere shaped supporter due to its higher contents of CdS with the same crystal structure. However, the wire shaped photocatalysts with lower crystallinity displays lower H₂ evolution rate than that of sphere shaped photocatalysts with higher crystallinity. The heat treatment of supporting photocatalysts increase its crystallinity, and thus increases H₂ evolution rate, while H₂ evolution rate decreases tremendously in case of Q-CdS due to the partial oxidation to CdSO₄.

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