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Surfactant Controlled Metal Oxide Shell Layer Deposition for Enhanced Photocatalytic Solar Hydrogen Generation: CdSe/TiO₂ Nanocomposite a Case Study

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Abstract

The present work demonstrates the effect of cationic, anionic and nonionic surfactants on synthesizing nanoscale thin TiO₂ shell layer deposited on to pre-synthesized CdSe capsule-like nanoparticles. We benchmark a suitable surfactant for synthesizing homogenous, controlled TiO₂ post-deposition onto host 1-D CdSe surface without any complex research tools. Also, we examine the inter-dependence material property and photocatalytic performance in solar hydrogen generation. The generic synthesis of surfactant controlled nanoscale deposition route can transfer to a wide range of semiconductor materials where the surface functional property plays a crucial role.

Keywords: Photocatalysis; CdSe, TiO₂, Nanocomposite; Surfactants; Solar; Hydrogen.

1. Introduction

Hydrogen generation through solar-driven photocatalysts is a cleaner and renewable energy process having great potential for partial fulfilment of electricity for domestic and automobile applications [1]. Though several photocatalysts have been reported with improved efficiency industrial development of solar hydrogen fuel is still limited due to: (a) efficiency of the process is much lower than the benchmark (10%) (b) photocatalyst becomes unstable for continuous usage especially in an aqueous medium. There is a necessity for improving solar-to-hydrogen fuel conversion efficiency and photocatalyst stability to overcome the above-said issues. The TiO₂ is well-reported for its visible-light transparency up to 15 nm thickness, excellent charge transfer (electron and hole) characteristics and reinforce the catalyst stability for prolonged usage [2, 3]. Owing to its chemical stability at a wide pH range, it is preferable to use it as a protecting layer to different photocatalysts. Among the coating routes for synthesizing nanoscale TiO₂, a wet chemical approach is economical and avoids complicated synthesis steps. But controlling the particle size and thickness of the film by chemical approach is challenging to manage. An uncontrolled agglomerated TiO₂ deposition might lower the optical transparency, blocking the light irradiation to host the photocatalyst surface and charge trapping, which affects the photocatalytic performance [4]. In this context, surfactant-assisted wet chemical synthesis can maintain the nanoscale materials coating on the host substrate [5]. But, keeping the compatibility of surface charge between the surfactant and guest layer precursor is an important pre-requisite.

CdSe is a promising photoactive material due to its flexibility in tuning the bandgap energy concerning particle size [6]. Though CdSe exhibits effective photocatalytic hydrogen

generation, a photo corrosion process under extended light irradiation and photo charge carriers trapping at surface states affect photocatalytic performance. Therefore, protecting the CdSe surface, and accelerating the charge transfer is a challenge. This work explores the advantages of surfactants assisted shell layer in protecting the CdSe surface and enhancing the photocatalytic hydrogen fuel generation performance.

2. Experimental

The synthesis protocol of 1-D CdSe nanoparticles was reported in our recent work [2]. The pre-synthesized 1-D CdSe powder (0.1 g) was dispersed into ethyl alcohol (50 mL) for 15 minutes. One of the surfactants, trisodium citrate dihydrate (TSC), cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP), N-tri butyl ammonium bromide (NTAB), and sodium (SOA) was dissolved followed by slow addition of TTIB (0.8 mL, 10 mL) under magnetic stirring at 30°C for 2 h. The resulting precipitate (after washing with water and ethyl alcohol) was dispersed in ethyl alcohol, and acetonitrile (1:3 M, 25:75 mL) and the mixture was placed in the hydrothermal reactor. The hydrothermal reactor was kept in a furnace at 160°C for 20 h. The final product (after washing with water and ethyl alcohol) was dried at 80°C for 12 hours. The experimental details of X-ray diffraction (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscopy, optical absorbance, and photoluminescence are provided in the supplementary information. The pristine CdSe and TiO₂ coated CdSe for different surfactants were tested for solar to hydrogen generation. Typically, 5 mg of powder was taken for photocatalysis experiments. The aqueous mixture consists of Na₂S and Na₂SO₄ (300 mM) was used as a scavenger. A 300 W Xe-lamp fitted with solar simulator used as a light source, and experiments were performed under visible light with UV cut off filter ($\lambda > 420$ nm). The recyclability experiments were carried out under identical conditions.

3 Results and discussion

The X-ray diffraction results of CdSe and CdSe/TiO₂ composite prepared using different surfactants are presented in **Figure S1 (a-f)** and **S2** (See supplementary information). **Figure 1 (a-f)** reveals the surface morphology of the pristine CdSe and surfactant mediated TiO₂ coated CdSe. It is found that the surfactants significantly influences the pre-synthesized CdSe shape and assembly of post-deposited TiO₂. Among the surfactants, nonionic surfactants (PVP) assisted CdSe/TiO₂ composites showed (**Figure 1b**) homogenous TiO₂ shell layer coating onto CdSe surface compared to uncoated CdSe (**Figure 1a**). The cationic and anionic

surfactants either deforms the CdSe shape or results in uncontrolled agglomeration deposition of TiO₂ nanoparticles. It might be due to incompatibility between the surface charge of CdSe and surfactants. For instance, CdSe possesses a negative surface charge which electrostatically attracts cationic surfactants CTAB (Figure 1c) and NTAB (Figure 1d) and repels the anionic surfactants TSC (Figure 1e) and SOA (Figure 1f). As a result, the anionic surfactant electrostatically repelled by CdSe tends to form aggregation (micelle), which is favorable for TiO₂ particles growth randomly on the CdSe surface. Based on the TEM images, we propose a possible mechanism (Figure 1g) illustrating surfactants' role (chemical structure of surfactants presented in Figure S3) on TiO₂ post-deposition layer on CdSe. Briefly, nonionic surfactant balances to attach their hydrophilic head with CdSe and hydrophobic tail with TTIB. As a result, the TTIB has homogeneously covered CdSe in the presence of nonionic surfactant (PVP) resulting in a thin layer on TiO₂ coating onto CdSe capsules. This is the reason for CdSe/TiO₂ core-shell formation (Figure 1b). On the other hand, the TTIB species have CH₃ nonpolar groups with a strong affinity towards the surfactant's hydrophobic tails, which implies that irrespective of the surfactant's surface charge TTIB likes to attach with surfactant's tail, but without TTIB CdSe allows only cationic and nonionic surfactants.

The quantity of hydrogen gas evolution per hour per gram catalyst using pristine CdSe and CdSe/TiO₂ nanocomposite powders was measured under visible light illumination. The results are summarized in Figure 2(a), and corresponding solar to hydrogen generation (STH) is estimated and presented in Figure 2(b). The mechanism of photocatalytic hydrogen generation is explained in the supplementary information (Figure S4). Among the various surfactants, the nonionic surfactant PVP mediated CdSe/TiO₂ core-shell type nanocapsule results in higher photocatalytic solar hydrogen generation activity 23.1 mmol.h⁻¹.g⁻¹_{cat}, which is approximately eight times higher than that of pristine CdSe (3.07mmol.h⁻¹.g⁻¹_{cat}). This enhanced photocatalytic performance due to the conformally coated TiO₂ layer by PVP surfactant which protects the CdSe layer from the photo corrosion issue and facilitate the photo charge carrier (electron and holes) transfer from CdSe the electrolyte. A sufficient thickness of the TiO₂ layer on CdSe is necessary to protect against the photo corrosion issue. However, overloading or thicker TiO₂ layer hinders the light penetration to the CdSe layer. The anionic surfactants TSC and SOA mediated TiO₂ have non-homogenous and inadequate coverage on CdSe which results in low STH efficiency. The optical transmittance estimated from Kubelka-Munk studies (Figure 2c) showed PVP mediated TiO₂ samples balancing the optical transmittance at the

visible light region. In other surfactants, the uncontrolled TiO₂ growth reduces the light transmittance to CdSe and lower the absorbance at visible wavelength region.

Further, the surfactant mediated TiO₂ layer's recyclability to protect the CdSe surface was tested for the optimized photocatalyst (PVP) for four cycles under simulated solar light irradiation (**Figure 2d**). Each process consists of 6h continuous light irradiation, and it is noticed that the PVP mediated photocatalyst showed almost constant hydrogen evolution for the first and second cycles, which was slightly decreased after the third and fourth cycles, this may be due to the decrease in sacrificial ions in the reaction solution. Owing to high light absorbance, and protecting the photo corrosion issue PVP mediated CdSe/TiO₂ composite exhibits STH=14.0% (See **supplementary information**). The adequate bonding of the TiO₂ shell layer on the CdSe surface was studied by X-ray photoelectron spectroscopy. The core spectra of Cd2p, Se2p, Ti2p and O1s presented in **Figures 3(a)–(d)**, respectively ensure the presence of CdSe and TiO₂ and effective interaction between them. More detailed explanation can be found in the supplementary information.

4. Conclusion

In summary, the role of surfactant on post-deposition of metal oxide (TiO₂) on host CdSe surface was demonstrated. A nonionic surfactant PVP balances both Ti precursor and CdSe surface's surface charge and results in good growth of the TiO₂ seed layer, which further forms the conformal shell around CdSe host. Anionic surfactants produce uncontrollable agglomerated TiO₂ growth on CdSe and infers that surface charge of the host layer is a crucial parameter for making core-shell composites in surfactant mediated synthesis routes. Also, more optimization (pH and concentration) is required for cationic based surfactants. This protocol can be adopted for similar negative surface charge based host, and any types of polar groups attached metal oxide precursors. Overall, this work emphasizes that a simple chemical route derived metal oxide coatings enhances solar to hydrogen generation eight times than pristine CdSe photocatalyst.

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Figure captions

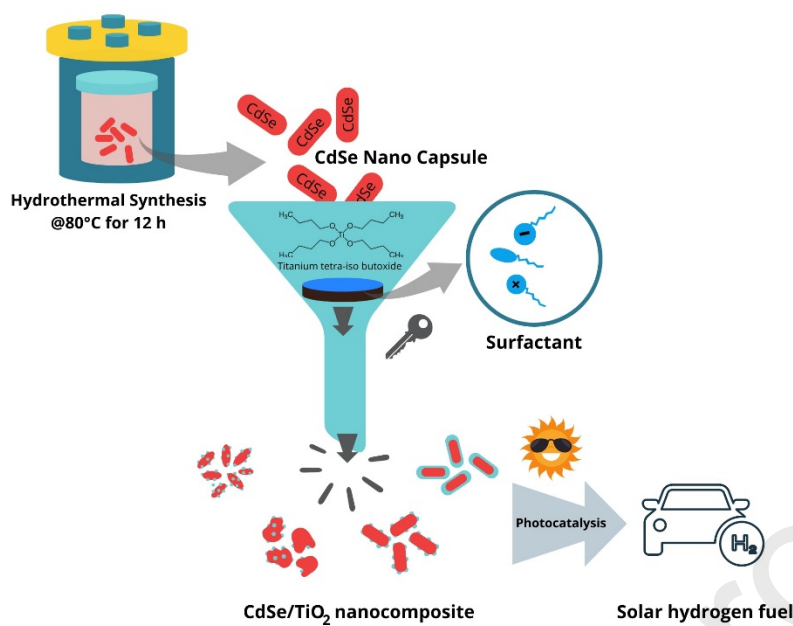
Figure 1. HRTEM images of (a) pristine CdSe and, surfactant assisted CdSe/TiO₂ composites using (b) PVP, (c) CTAB, (d) NTAB, (e) TSC and (f) SOA; proposed mechanism of surfactant role on TiO₂ deposition on CdSe surface.

Figure 2. (a) Quantity of hydrogen evolution and (b) solar to hydrogen generation efficiency of photocatalysis process using pristine CdSe and, surfactant-assisted CdSe/TiO₂ composites; (c) optical transmittance of CdSe and CdSe/TiO₂ composites and (d) stability analysis for PVP surfactant-assisted CdSe/TiO₂ under simulated solar irradiation.

Figure 3. XPS results of (a) Cd2p, (b) Se2p, (c) Ti2p and (d) O1s measured from PVP surfactant-assisted CdSe/TiO₂.

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Highlights

- Exploring the role of surfactants on nanoscale metal oxide synthesis
- A nonionic surfactant (Polyvinyl pyrrolidone) based TiO₂ effectively wrap CdSe
- Cationic and anionic surfactants deform CdSe host or result in agglomerated TiO₂
- CdSe/TiO₂ composite results in 8 times enhancement in H₂ production than CdSe
- Benchmarking TiO₂ shell coated CdSe exhibits 23.1 h⁻¹.g⁻¹.cat of hydrogen gas

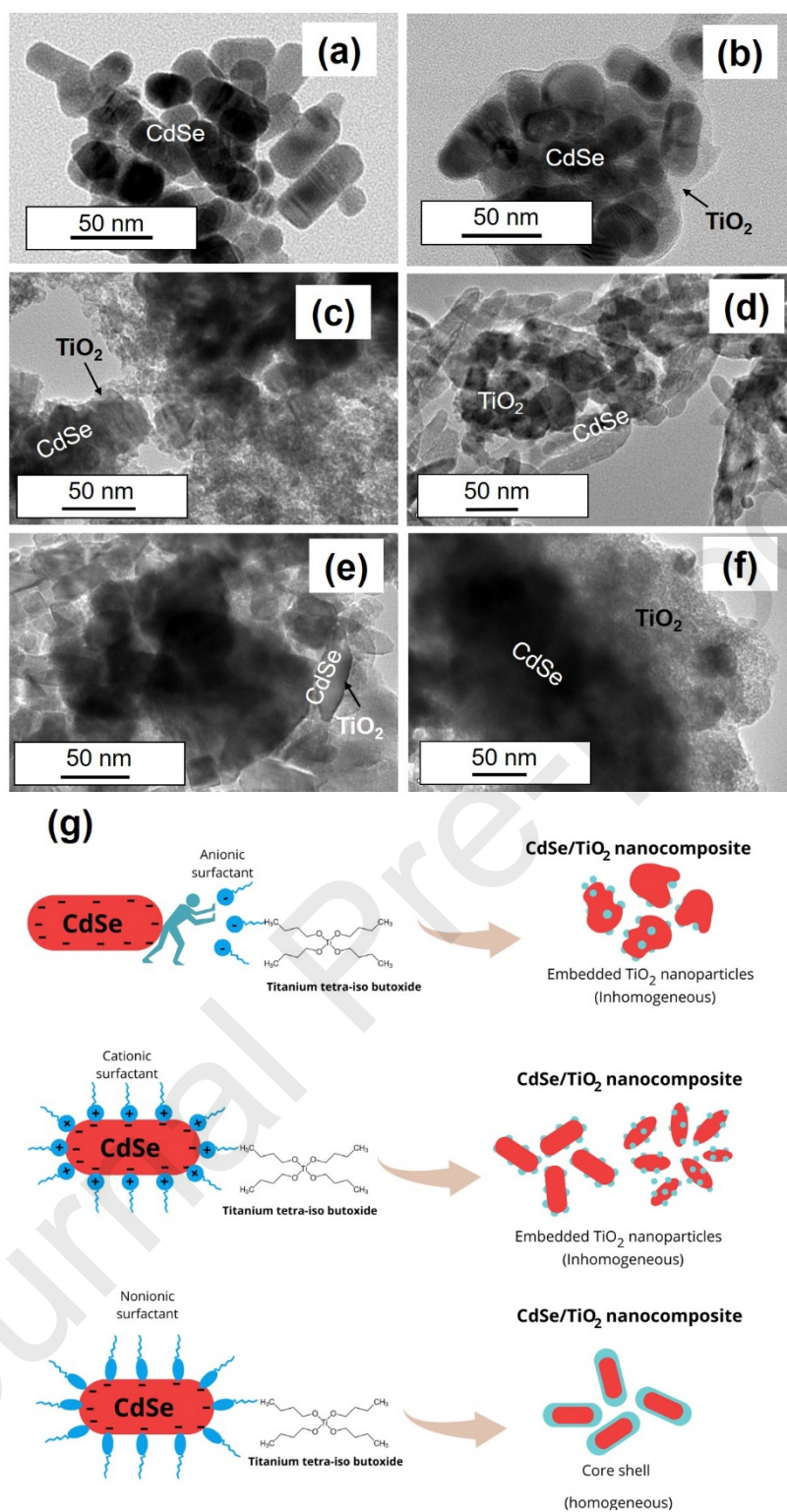


Figure 1

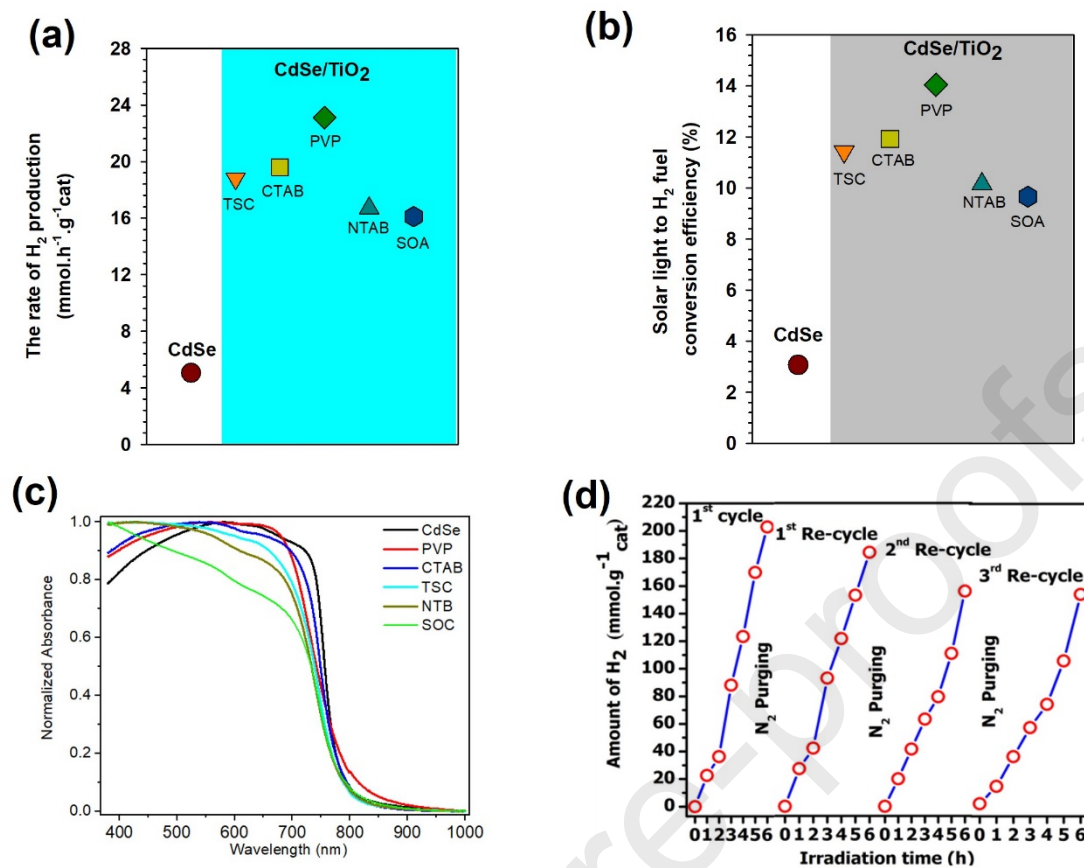


Figure 2

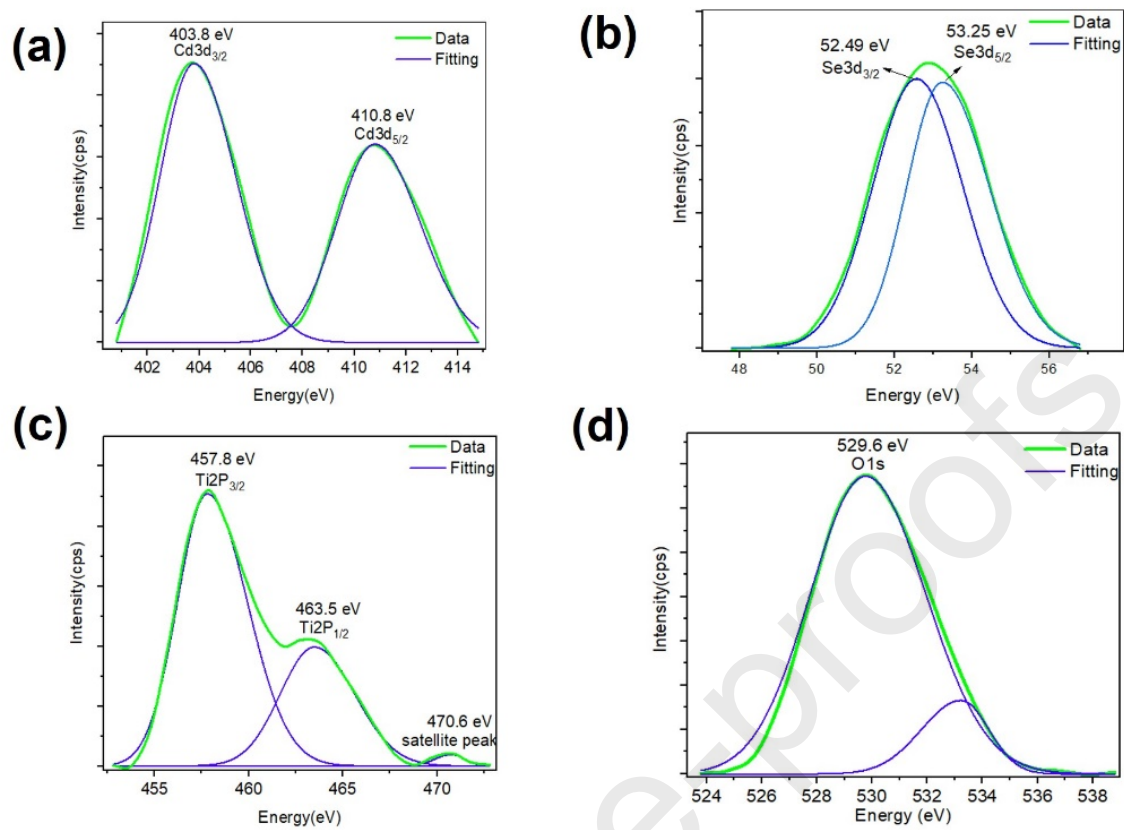


Figure 3

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Muthukonda Venkatakrishnan Shankar and **Sudhagar Pitchamurtu**: Involved in conceptualization, Methodology and funding. **Vempuluru Navakoteswara Rao, Urupalli Bharagav, Ashish Kumar**: Carried out all the experiments, Writing- Original draft preparation. **Venkata Krishnan, and Marappan Sathish**: Supervision, funding and analysis. **Parnapalli Ravi, Jayaraman Velusamy, Murikinati Mamatha Kumaria**: X-ray diffraction measurements, SEM, Optical analysis, Investigation. **All authors equally contributed for:** Writing- Reviewing and Editing