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Pt-free solar driven photoelectrochemical hydrogen fuel generation using 1T MoS₂ co-catalyst assembled CdS QDs/TiO₂ photoelectrode


The solar to hydrogen generation from TiO₂-CdS-ZnS-MoS₂ (TCZM) heterointerface was demonstrated. We found that Pt free CdS quantum dot sensitized TiO₂ mesoporous electrode with metallic-type 1T MoS₂ co-catalyst resulted 0.11 ml/cm²h⁻¹ H₂ fuel generation under unassisted potential mode, which was strikingly promoted to 1.47 ml/cm²h⁻¹ upon 1 V applied potential.

The energy generation from fossil fuel sources having foremost issues on existing undesirable CO₂ emission in atmosphere and depletion of their resource from earth also predicts a huge demand in energy consumption. Therefore, generating inexpensive, pollution-free fuels (hydrogen and oxygen) is a challenging task to mankind. Hydrogen (H₂) is the easiest and multisource component in view of gaseous fuel or electron-rich precursor to liquid transportation fuel. Though the hydrogen fuel generation from water using solar energy through ‘artificial photosynthesis’ process was demonstrated four decades ago, the recent energy demand fosters ‘solar fuel conversion’ as an emerging technology. The photo electrochemical (PEC) cells are also considered as powerful tool in transforming solar light into hydrogen fuel with appropriate electrolyte and semiconductor electrodes. However, the challenging task in PEC process is designing the visible light semiconductors for tracking major fraction of solar energy with effective charge separation (e⁺ and h⁻) at electrode/electrolyte interfaces.

Recently, the combinatorial approach of assembling low-dimensional semiconducting ‘quantum-dot’ (QDs: CdS, CdSe, PbS, etc) with wide band gap metal oxides (TiO₂, ZnO, and WO₃) showed striking PEC H₂ generation performance owing to the unique properties of QDs (high absorbance co-efficient, multiple carrier generation and fast charge separation). In this line, new type of electrode-architectures like ‘quasi artificial leaf’, ‘panchromatic (QD/dye) sensitizer’ and ‘high light reflector’ explored with Pt counter electrodes realize the QDs as futuristic candidate in PEC H₂ generation. Conversely, in view of fabricating low-cost, Pt-free photocatalytic assemblies for hydrogen generation, a broad range of metal sulphides (CdS, CdSe, Cd₁ₓZn₁₋ₓS, Zn₁ₓCd₁₋ₓS, Zn₁ₓInₓS) were explored in the form of solid solution, nevertheless only very few works were reported on electrode architecture. Despite the above mentioned Pt-free metal sulphide photocatalyst systems showed feasible quantum yield, still their performance is inferior to the Pt catalyst systems. One of the prospective approaches is enhancing the catalytic active sites by implementing atomic scale layered co-catalyst on the photocatalyst assemblies. In this context, thin atomic layer of MoS₂ received great attention in graphene analogue layered transition metal dichalcogenide. The striking features of edge controlled MoS₂ catalytic properties render effective performance in electrocatalytic and photocatalytic hydrogen evolution reaction.

The previous studies on CdS/MoS₂ in the form of suspended photocatalyst endorse new pathways in MoS₂ based solar fuel generation. However limited internal surface area for dual functionality of water oxidation (with sacrificial donor) and reduction process on same CdS/MoS₂ solid interfaces limits the solar fuel yield and necessitates the execution as separate counterpart in the form of electrode.
employed to controlling the properties of each layer independently compared with one-pot synthesized powder type sample. To the best of our knowledge, this is the first report that showcases the application of TCZM heterointerfaces in tandem electrode configuration for solar hydrogen fuel generation. For further experimental details of preparing TiO$_2$ mesoporous electrodes, CdS QDs sensitization and coating of chemically exfoliated MoS$_2$ sheets on TiO$_2$/CdS QDs refer supporting information S1 and SEM images in Fig.S2. Under visible light irradiation (>400 nm), the excitons (e/h) were generated at CdS and electrons were transport to the charge collector through TiO$_2$ layer. Conversely, holes were scavenged by electrolyte species and produce H$^+$ carriers in the electrolyte. Concurrently, the fraction of the light illumination transmitted through photoanode will reach TiO$_2$/CdS/MoS$_2$ counter electrode (CE) and perform analogous function with photoanode. Under unassisted bias condition, the photoelectrons collected from anode will be directed to CE side, where they will recombine with the photoholes at TiO$_2$ surface through Z-scheme mechanism (Scheme 1b). The remaining photoelectrons generated at CdS (CE side) will be injected to MoS$_2$ co-catalyst and perform H$^+$ ions reduction into hydrogen fuel. The schematic photocatalytic mechanism is illustrated in Scheme 1b

**Figure 1.** TEM images of exfoliated MoS$_2$ sheets (inset: photography of MoS$_2$ exfoliated solution and SAED pattern); (b) HRTEM image of MoS$_2$ nanosheet (inset: distance between lattice fringes at 1T MoS$_2$ phase); (c) and (d) HRTEM images of TiO$_2$-CdS-MoS$_2$ at different locations (inset: SAED pattern); (e) EDS mapping of Ti,O,Cd, Mo and S.

The TEM image of chemically exfoliated MoS$_2$ is presented in Fig. 1(a), and it seems to have two dimensional (2-D) few layer stacked sheet-like morphology with lateral dimension of ~500-700 nm. At high magnification (2nm) scale (Fig.1b), a single layer of 2-D MoS$_2$ exhibit biphase crystallite structure with clear grain boundary (See supporting information S3). In accord to Eda et al.,$^{11}$ the honeycomb lattice structure (Fig.S3) indicates the trigonal prismatic (2H) and hexagonal lattice corresponding to the octahedral geometry (1T). This clearly demonstrates that exfoliated 2-D sheets can produce atomically thin layers of (002) crystallite facet of MoS$_2$. The lattice space values of 2H and 1T layers were estimated using FFT transform and found to be 0.30 and 0.26 nm, respectively (Fig. S3). Further, the (002) crystallite facet of exfoliated MoS$_2$ is ensured from the predominant peak exhibit at 2θ=14.4° from XRD spectra and no other crystallite orientations were noticed compared with bulk MoS$_2$ (See supporting information S4.a). The Figs. 1(c) and 1(d) shows the HRTEM images of CdS QDs and 2D-MoS$_2$ coated TiO$_2$ at two different locations. It clearly infers that TiO$_2$ exhibited anatase phase with (101) and (004) crystallite orientations and was confirmed through lattice space values of 0.35 and 0.23 nm, respectively. The crystallite structures of TiO$_2$ and TiO$_2$/CdS QDs composite electrodes were further examined with XRD (See supporting information S4.b). Among two crystallite phases (2H and 1T) of MoS$_2$ observed from Fig.1b, only 1T MoS$_2$ layer was noticed from TiO$_2$/CdS QDs interface (Fig.1c and 1d). Lin et al explored the phase transformation of 2H to 1T MoS$_2$ by gliding atomic planes during high temperature treatment, however to confirm the same in the present work more investigation is needed. Recent reports corroborate that 1T MoS$_2$ phase has best performance on electrocatalytic hydrogen production with substantial stability in water medium compare to 2H MoS$_2$.\textsuperscript{12} Therefore, from Figs. 1(c) and 1(d), it is expected that 1T MoS$_2$ layer coated TiO$_2$/CdS QDs interfaces may perform efficient photoelectrocatalytic hydrogen generation. The elemental mapping at TiO$_2$/CdS/MoS$_2$ was recorded (Fig. 1(e)), which confirms the presence of Ti, O, Cd, Mo and S elements with uniform distribution.

The optical absorbance of pristine TiO$_2$, TiO$_2$/CdS and TiO$_2$/CdS/MoS$_2$ electrodes were evaluated from Kubelka-Munk relation ($F(R) = \frac{(1-R)^2}{2R}$) using optical diffused reflectance spectra (Fig. 2a). The optical absorbance edge of TiO$_2$ at 380 nm is extended to ~495 nm upon CdS QDs deposition (4 SILAR cycles). Owing to the high absorbance, CdS QDs enhanced the optical density of TiO$_2$ in this region. For 2 SILAR coated CdS cycles, the absorbance edge is blue shifted to ~450 nm due to the less deposition cycles of CdS. A significant band edge of MoS$_2$ (between 600 to 700 nm) was not observed in Fig. 2a.\textsuperscript{13} This may attribute the less quantity of MoS$_2$ loading on TiO$_2$/CdS QDs or the metallic nature of 1T MoS$_2$ does not exhibit band gap alike exfoliated MoS$_2$ solution (See supporting information S5). It is noteworthy to discuss that the electrode geometry could influence the optical absorbance of back side electrode which depends with the light transmittance allowed by front side electrode (See supporting information S6). In order to decipher the generic mechanism of visible light driven photocatalytic hydrogen fuel generation from TiO$_2$/CdS/ZnS/MoS$_2$ (TCZM) interfaces, we explored the photoelectrochemical property of this structure under dark and light conditions. Here, we used two electrode based PEC configuration (TiO$_2$/CdS(4 cycles)/ZnS as photoanode and TiO$_2$/CdS (2 cycles)/MoS$_2$ as counter electrode (CE) (See Supporting Information S1(d)). The aqueous electrolyte of 0.25 M Na$_2$S with 0.35 M Na$_2$SO$_3$ sacrificial hole scavenger was used.
for PEC experiments. The electrodes were illuminated with artificial solar light (100 mW cm$^{-2}$) from solar simulator with 400 nm UV cut filter.

The resultant PEC performance of TCZM CE is compared with Pt CE in Fig. 2(b). At zero potential, the TCZM showed ~0.8 mA cm$^{-2}$ and is almost comparable to the performance of similar photoanode configuration with Pt as CE. The solar to hydrogen (STH) efficiency of these electrodes was estimated using the relation: \[ STH = \frac{j_{sc} E^0 \eta_F}{P_{total}} \] (1)

where, $j_{sc}$ is the short-circuit current, $E^0$ represents the thermodynamic reaction potential (0.21 V) for oxidation of sacrificial agent (G = 38,600 J/mol), $\eta_F$ is the faradic efficiency of hydrogen generation in standard condition and $P_{total}$ is the incident solar irradiation (Wm$^{-2}$). The STH efficiency of TiO$_2$/CdS/MoS$_2$ CE found to be 0.45% and is comparable to Pt CE based system (STH= 0.44%). Comparing the conversion efficiency of MoS$_2$ catalyst to other previous reports on photocatalytic (PC) hydrogen generation; Zn$_{0.2}$Cd$_{0.8}$S showed the STH efficiency of 0.36% with reduced graphene oxide (RGO) catalyst. This implies that 1T MoS$_2$ had performed as co-catalyst at TiO$_2$/CdS (2 cycles) for generating hydrogen through Z-scheme under unassisted bias condition. Further, by applying electric potential between the two terminals of TiO$_2$/CdS/ZnS and Pt, the resulting photocurrent was found to be enhanced up to 2.2 mA cm$^{-2}$ at 0.2 V vs RHE. It infers that the applied potential facilitate the charge separation process at TiO$_2$/CdS interfaces by extracting the electrons away from CdS conduction band to TiO$_2$, which subsequently reaches CE terminal. In the case of TCZM heterointerface, the applied potential enhances the Z scheme process (Scheme 1b) and generates high photocurrent density of 5.7 mA cm$^{-2}$ at 1 V vs RHE, compare to Pt CE (2.2 mA cm$^{-2}$). It clearly evinces that the photocurrent generation at TCZM heterointerface depends on charge separation process at TiO$_2$/CdS cathode interface and showed competitive photocurrent generation with Pt CE. The photoexcited electron at CdS CB can reduce the H$^+$ ions to hydrogen owing to their negative conduction band position. However, it leads the photocorrosion on CdS surface. This undesired reaction was overwhelmed by the MoS$_2$ co-catalyst layer, which protects the CdS layer from water reduction process through modifying CdS/electrolyte interfaces.

The modification of electrochemical TiO$_2$/CdS QDs interfaces by MoS$_2$ coating were analyzed with Mott-Schottky plots (See supporting information Fig. S7). The flat band potential ($V_{fb}$) position of TiO$_2$/CdS interface was found to be slightly modified from 0.05±0.03 V vs RHE to 0.09±0.03 V vs RHE by MoS$_2$. More positive values of $V_{fb}$ position by MoS$_2$ coating indicates that the large band bending at MoS$_2$/CdS interfaces (depletion layer) facilitates the photoelectrons flow from CB of CdS to electrolyte for catalytic reduction of H$^+$ ions on MoS$_2$ sites. Further, to examine the influence of MoS$_2$ coating on TiO$_2$/CdS interfaces the PL spectra was recorded (Fig. 2c). The emission band shoulder around 530 nm was noticed from TiO$_2$/CdS interface, which can be attributed to the band-band PL phenomenon of CdS surface. This PL emission mostly originates from the sulphur vacancies of CdS which act as recombination centres to the photoelectrons. Under identical excitation power, the MoS$_2$ coated TiO$_2$/CdS interface showed higher PL emission. One of the plausible reasons for the enhanced PL emission is reduced surface states at the CdS grain boundaries by occupying MoS$_2$. This infers that the MoS$_2$ can effectively passivate the CdS surface.

The output gas product from PEC experiments were collected for one hour and examined through gas chromatogram (GC). The output product was found to be hydrogen gas from the TiO$_2$/CdS heterointerface and the quantity varies (Fig.2d) with counter electrodes and applied potential condition (See supporting information S8). Under unassisted potential condition, the Pt CE showed almost similar quantity of hydrogen gas (0.13 ml hr$^{-1}$ cm$^{-2}$) than TCZM heterointerface (0.15 ml hr$^{-1}$ cm$^{-2}$). In striking contrast under identical conditions, the TCZM heterointerface exhibited 1.47 ml hr$^{-1}$ cm$^{-2}$ of hydrogen gas at 1 V vs RHE applied potential, which is 150% higher than the hydrogen generated using Pt as CE (0.97 ml hr$^{-1}$ cm$^{-2}$). This is in line with $J-V$ results discussed from Fig. 2b, which ensured applied potential dependent hydrogen generation at TCZM heterointerface. Another significant observation is that the electrode based TCZM heterointerface maximises the fuel generation even with less material consumption (MoS$_2$ coated CdS QDs) compare to the earlier reports on solid state suspended photocatalysis. These results have significant implications in designing the MoS$_2$ co-catalyst based visible light semiconductor electrode architectures for hydrogen fuel generation with the aid of external bias from renewable sources (solar cells or solar batteries). The synergetic composition of 1-T MoS$_2$ with previously reported CuS or CuO...
based electrodes will be futuristic Pt-free cathodes to QDs-
sensitized metal oxide photoanodes in search of effective
photoelectrodes in quasai-artificial photosynthetic leaf.5, 16

Conclusions

In summary, the 1-T metallic type MoS2 nano-sheets were
successfully assembled on TiO2-CdSe electrode. Under visible
light irradiation, TiO2-CdSe-MoS2 electrode exhibit efficient co-
catalytic performance on hydrogen generation in configuration
with TiO2-CdSe-ZnS photoanode. This tandem electrode
configuration (TCZM) showed higher hydrogen fuel generation
of 1.47 ml h⁻¹ cm⁻² at 1 V vs RHE applied potential, which is 150
% higher than that of using Pt as CE. In addition, 1-T MoS2
sheets passivation at the TiO2-CdSe interface beneficially reduced
the charge recombination through uncovered CdS sites on TiO2 to
electrolyte. Improving the photoanode counterpart with high
porous network based electron transport framework (fibers, in-verse opal) in association with narrow band gap semiconductor
as co-sensitizers is anticipated to enhance the hydrogen fuel
generation. Different temperature processed 1-T MoS2 is also
futuristic to promote hydrogen generation through fine-tuning
their catalytic activity through modifying their edges.

Acknowledgements

One of the corresponding authors P.S appreciate the JSPS for
provide the post-doctoral fellowship. R.R. thanks National
Institute for Materials Science (NIMS), Japan and Anna
University, India for the NIMS internship award.

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† Electronic Supplementary Information (ESI) available: [Experimental,
Characterization, XRD, SEM, TEM, PL, Chronoamperometry, OCVD].
See DOI: 10.1039/b000000x/

4(a) J. Hensel, G. Wang, Y. Li and J. Z. Zhang, Nano Letters, 2010, 10, 478; (b) P. Rodenas, T. Song, P. Sudhagar, G.
Marzari, H. Han, L. Badia-Bou, S. Gimenez, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, U. Paik and Y. S. Kang,
Advanced Energy Materials, 2013, 3, 176; (c) Y. Jinnouchi, T. Hattori, Y. Sumida, M. Fujishima and H. Tada,
ChemPhysChem, 2010, 11, 3592; (d) P. Sudhagar, E.
Juárez-Pérez, Y. Kang and I. Mora-Seró, in Low-cost Nanomaterials, eds. Z. Lin and J. Wang, Springer London,
2014, pp. 89-136.
5(a) R. Trevisan, P. Rodenas, V. Gonzalez-Pedro, C. Sima, R. S.
Sanchez, E. M. Barea, I. Mora-Sero, F. Fabregat-Santiago and
Fabregat-Santiago, E. de la Rosa, I. Mora-Seró and S. Giménez, The Journal of Physical Chemistry C, 2013, 118,
891; (c) K. Kim, M.-J. Kim, S.-I. Kim and J.-H. Jang, Sci.
7 M. Antoniadou, S. Sfaelou and P. Lianos, Chemical Engineering
8(a) S. Das, M. Kim, J.-w. Lee and W. Choi, Critical Reviews in
Solid State and Materials Sciences, 2014, 39, 231; (b) K. F.
Mak, C. Lee, J. Hone, J. Shan and T. F. Heinz, Physical Review
Letters, 2010, 105, 136805; (c) U. Maitra, U. Gupta, M. De, R. Datta, A. Govindaraj and C. N. R. Rao,
9(a) T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S.
Horch and I. Chorkendorff, Science, 2007, 317, 100; (b) Y.
Li, Y.-L. Li, C. M. Araujo, W. Luo and R. Ahuja, Catalysis Science & Technology, 2013, 3, 2214; (c) D.
10(a) T. Jia, A. Kolpin, C. Ma, R.-C.-T. Chan, W.-M. Kwok and S.
C. E. Tsang, Chemical Communications, 2014, 50, 1185; (b) Y.
Min, G. He, Q. Xu and Y. Chen, Journal of Materials Chemistry A, 2014, 2, 2578; (c) X. Zong, H. Yan,
G. Wu, G. Ma, F. Wen, L. Wang and C. Li, Journal of the American Chemical Society, 2008, 130, 7176; (d) X.
11 G. Eda, T. Fujita, H. Yamaguchi, D. Voiry, M. Chen and M.
12 M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S.
Jin, Journal of the American Chemical Society, 2013, 135,
10274.
13(a) G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen and M.
Chhowalla, Nano Letters, 2011, 11, 5111; (b) A. P.
S. Gaur, S. Sahoo, M. Ahmadi, M. J. F. Guinel, S. K. Gupta,
Physical Chemistry C, 2013, 117, 26262.
Gana, Journal of Physics and Chemistry of Solids, 2000, 61,
829; (b) P. V. Kamat, N. M. Dimitrijevic and R. W.
16(a) C. G. Morales-Guiño, S. D. Tilley, H. Vrabel, M. Gratzel and
X. Hu, Nat Commun., 2014, 5; (b) A. Devadoss, P.
Sudhagar, C. Ravidhas, R. Hishinuma, C. Terashima, K.
Nakata, T. Kondo, I. Shitanda, M. Yuasa and A. Fujishima,
Physical Chemistry Chemical Physics, 2014.