Charge-transfer regulated visible light driven photocatalytic H_2 production and CO_2 reduction in tetrathiafulvalene based coordination polymer gel

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Abstract

The much-needed renewable alternatives to fossil fuel can be achieved efficiently and sustainably by converting solar energy to fuels via hydrogen generation from water or CO_2 reduction. In this regard, a soft processable metal-organic hybrid semiconducting material has been developed and studied for photocatalytic activity towards H_2 production and CO_2 reduction to CO and CH_4 under visible light and direct sunlight irradiation. A tetrapodal low molecular weight gelator (LMWG) has been synthesized by integrating tetrathiafulvalene and terpyridine moieties through amide linkages (TPY-TTF). The TPY-TTF LMWG acts as a linker, and self-assembly with ZnII results in a charge-transfer (CT) coordination polymer gel (CPG); Zn-TPY-TTF. The Zn-TPY-TTF CPG shows high photocatalytic activity towards H_2 production (rate = 530 µmol $g^{-1}h^{-1}$) and CO_2 reduction to CO (rate = 438 µmol $g^{-1}h^{-1}$, selectivity >99%) regulated by charge-transfer interactions. Furthermore, in situ stabilization of Pt nanoparticles on CPG (Pt@Zn-TPY-TTF) exhibits remarkably enhanced H_2 evolution (rate = 14727 µmol $g^{-1}h^{-1}$). Importantly, Pt@Zn-TPY-TTF CPG produces CH_4 (rate = 292 µmol $g^{-1}h^{-1}$, selectivity >97%) as CO_2 reduction product instead of CO. In situ DRIFT study monitors the real-time CO_2 reduction reaction, and the plausible mechanism is derived computationally.

Image

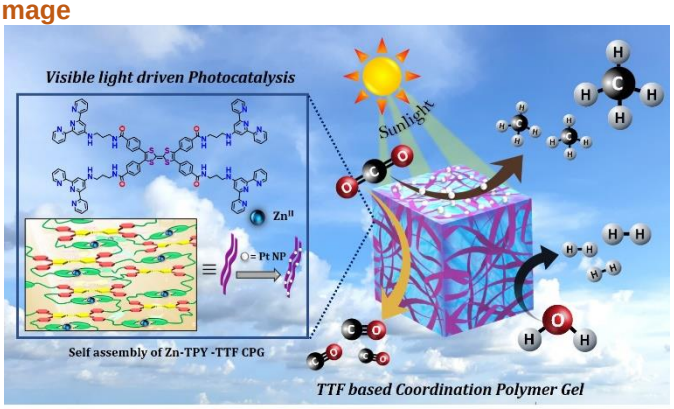


Fig. 1 Schematic presentation of visible/sunlight driven photocatalysis in TTF-based coordination polymer gel towards H_2 evolution and CO_2 reduction.

Recent Publications (minimum 5)

1. Verma P; Singh A; Rahimi F A; Maji T K (2021) Colocalization of Light Harvesting and Catalytic Units in 'Soft' Coordination Polymer Hydrogel toward Visible-Light Driven Photocatalytic Hydrogen Production. J. Mater. Chem. A, 9: 13608-13614.
2. Verma P; Singh A; Maji T K, (2021) Photo-Modulated Wide-Spectrum Chromism in Eu^{3+} and Eu^{3+}/Tb^{3+} Photochromic Coordination Polymer Gels: Application in Decoding Secret Information. Chem. Sci., 12: 2674-2682.
3. Verma P; Singh A; Samanta D; Dey A; Dey J; Maji T K, (2021) Stabilization of Ultra-Small Gold Nanoparticles in a Photochromic Organic Cage: Modulating Photocatalytic CO2 Reduction by Tuning Light Irradiation. J. Mater. Chem. A, 9: 5780-5786.
4. Singh A; Verma P; Samanta D; Singh T; Maji T K, (2020) Bimodal Heterogeneous Functionality in Redox-Active Conjugated Microporous Polymer toward Electrocatalytic Oxygen Reduction and Photocatalytic Hydrogen Evolution. Chem. Eur. J., 26: 3810-3817.
5. Singh A; Verma P; Laha S; Samanta D; Roy S; Maji T K, (2020) Photochromic Conjugated Microporous Polymer Manifesting Bio-Inspired pcFRET and Logic Gate Functioning. ACS Appl. Mater. Interfaces, 12: 20991-20997.



Biography

Ms. Parul Verma obtained her bachelor's degree (B.Sc. Hons. Chemistry) and master's degree (M.Sc. specialization in Organic Chemistry) from the Department of Chemistry, Institute of Science, Banaras Hindu University (BHU), Varanasi, Uttar Pradesh, in 2012 and 2014, respectively. After completing post-graduation, she joined the Thermal System Group of ISRO Satellite Center (ISAC, Bangalore) as a research scholar and worked on 'development of polymer nanocomposite's coating for thermo-optical properties' till Dec 2016. After that, she joined the Chemistry and Physics of Materials Unit (CPMU), Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, as a Junior Research Fellow (JRF) for Ph.D. degree from Jan 2017-August 2021 under the supervision of Prof. Tapas K. Maji in Molecular Materials Laboratory, JNCASR. Presently, she is research associate in the same laboratory. Her research focuses on "organic and metal-organic hybrid soft materials towards H_2 production, CO_2 reduction, and optoelectronic applications."

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