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Designing of cobalt doped pyridine based covalent organic frameworks for efficient visible light driven CO_2 reduction

H. Shanavaz [a], K. Yogesh Kumar [a], M.K. Prashanth [b], Gaurav Jhaa [c], L. Parashuram [d], Fahd Alharethy [e], M.S. Raghu [f,*], Byong-Hun Jeon [g,**]

[a] Department of Chemistry, Faculty of Engineering and Technology, Jain University, Bangalore, 562112, India
[b] Department of Chemistry, BNM Institute of Technology, Banashankari, Bangalore, 560070, India
[c] Chemical Information Sciences Laboratory, Department of Chemistry, Pondicherry University, Puducherry, 605014, India
[d] Department of Chemistry, Nitte Meenakshi Institute of Technology, Yelahanka, Bangalore, 560064, India
[e] Department of Chemistry, College of Science, King Saud University, Riyadh, 11451, Saudi Arabia
[f] Department of Chemistry, New Horizon College of Engineering, Outer Ring Road, Bangalore, 560103, India
[g] Department of Earth Resources and Environmental Engineering, Hanyang University, 222, Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea

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ABSTRACT

Covalent organic frameworks (COF) are the class of compounds that impulses the boundaries of organic/polymer chemistry and materials science to achieve the exceptional control of predesigned long-range ordered structures. The present work deals with one-pot reaction of pyridine-2,6-diamine and terephthalaldehyde in pyrex tube at slightly elevated temperature and resulted in the formation of PDT/COF. The obtained PDT/COF was then functionalized using cobalt (Co@PDT/COF). The formation of COF and metal incorporation is confirmed by Fourier transform Infrared spectroscopy (FTIR). The simulated AB staggered stacking model for both PDT/COF and Co@PDT/COF correlate well with the observed PXRD pattern than AA eclipsed stacking. The theoretical findings using materials studio software showed increase in the porosity and interlayer spacing after the addition of Co to PDT/COF. The superior photocatalytic CO_2 reduction activity is observed in Co@PDT/COF compared to PDT/COF. Co@PDT/COF was able to produce 13, 24 and 45 μmol $g^{-1}h^{-1}$ of H_2, CH_4 and CO, respectively. The obtained experimental optical properties were correlated well with Density functional theory (DFT) studies. Based on the characterization results, mechanism of photocatalysis has been discussed. Good stability and efficiency towards photocatalytic reduction CO_2 in presence of the Co@PDT/COF shows its suitability for further research on pyridine based COFs for different applications.

1. Introduction

Massive use of fossil fuel by human beings and social development has led to global environmental problems and energy crisis. As a result of global industrialization and urbanization, there has been an ongoing increase in the demand for energy sources [1,2]. Reducing environmental pollution and simultaneously producing value added fuels offered a glimmer of hope for maintaining the ecological balance [3,4]. Photosynthesis in plants utilizes solar energy for transforming carbon dioxide and water through enzyme catalysis in to carbohydrates and oxygen. This natural phenomena encouraged the researchers worldwide to convert CO_2 in to useful carbonaceous products through artificial photosynthesis [5,6]. Light driven CO_2 reduction in presence of catalyst is having plenty of advantages since it utilizes renewable energy, production of alternate energy sources and thereby reduces the global warming [7]. So, designing the photocatalyst that is stable, selective and can efficiently reduce the CO_2 is on high demand.

A series of novel porous, carbonaceous materials like hydrogen-bonded organic frameworks (HOFs), metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have been used for photochemical applications [8–11]. In spite of many advantages of all these organic frameworks, MOFs and HOFS exhibit some drawbacks like low conductivity, stability, density and low porosity hinders their practical applications [12,13]. COFs are the crystalline, predesigned

* Corresponding author.
** Corresponding author.
E-mail addresses: raghuhassan2009@gmail.com, dr.msraghu@newhorizonindia.edu (M.S. Raghu), bhjeon@hanyang.ac.kr (B.-H. Jeon).

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