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# Facile One-Pot Synthesis of $Cu_xO/TiO_2$ Photocatalysts by Regulating Cu Oxidation State for Efficient Solar $H_2$ Production

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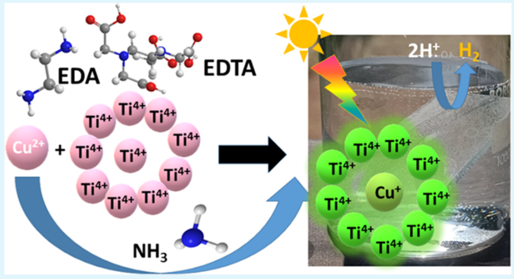
**ABSTRACT:** Development of highly efficient $Cu_xO/TiO_2$ photocatalysts by regulating the oxidation state of Cu exclusively in either single or mixed oxidation state(s) is desirable but difficult to achieve without employing any external reagents. The present work describes a one-pot synthesis strategy to obtain $Cu_xO/TiO_2$ photocatalysts with Cu in +1 and/or +2 by using a suitable combination of ethylene diamine tetra acetic acid (EDTA) and ethylene diamine, carefully varying the Cu content, and heat treatment process. $Cu_xO/TiO_2$ nanocomposite catalysts were characterized thoroughly by physicochemical methods. Textural analysis indicates a high dispersion of $Cu_xO$ on porous $TiO_2$ with p−n heterojunctions between them in $Cu_xO/TiO_2$ catalysts. UV−visible spectral analysis suggests the presence of $Cu_xO$ on $TiO_2$ with significantly extended absorption from the UV to the visible region. X-ray photoelectron spectroscopy (XPS) analysis indicates a strong synergetic interaction between $TiO_2$ and $Cu_xO$ due to the comparable CB potential and p−n heterojunction at the interface among them. Photoelectrochemical studies demonstrate excellent charge-carrier separation efficiency, low charge-transfer resistance, and high double-layer capacitance with $Cu_2O/TiO_2$ photocatalysts. Photocatalytic efficacy of a $Cu_xO/TiO_2$ nanocomposite in thin-film form has been demonstrated for solar hydrogen generation in sunlight. The incorporation of $Cu^+$ in $TiO_2$ largely improves the $H_2$ production, and all of the $Cu_xO/TiO_2$ nanocomposites in thin-film form exhibited higher efficiency compared to their particulate/suspension counterpart. Among the composite catalysts, TiCu-1 in thin-film form, with Cu exclusively in +1 oxidation state, exhibited a high hydrogen production rate of 7.06 mmol/h·g, which is 6 times higher than its suspension counterpart; also catalysts containing mixed Cu-oxidation states exhibited about 60−70% activity as that of TiCu-1. The superior performance of $Cu_2O/TiO_2$ nanocomposites in thin-film form was due to their enhanced light harvesting ability, high mass transfer rate, and easy accessibility of the reactant species to the active sites.




**KEYWORDS:** *titania, photocatalysis, thin film, solar hydrogen, heterojunction*



## 1. INTRODUCTION

Development of sustainable energy resource-based process technology is one of the major focus of researchers worldwide because of the ever increasing energy demands and serious environmental issues such as global warming and climate changes related to the extensive use of nonrenewable fossil fuels.[1−3] Photocatalytic hydrogen production by effectively utilizing the readily available sunlight has gained increasing attention in recent years due to the eco-friendly nature of the process technology. Transition metal oxide-based nanomaterials with favorable structural and optical properties exhibit excellent photocatalytic performance.[2,4] Although $TiO_2$ is known for its advantages in photocatalysis, the inherent characteristics of $TiO_2$, such as large band gap (3.2 eV), rapid electron−hole recombination rate, and poor charge-transfer property, hinder its practical applications in sunlight-driven $H_2$ production.[2,4−6]

In order to overcome the aforementioned issues, numerous modifications such as metal-ion doping,[4,5] composite formation with other metal oxides,[7] and heterojunction with other semiconducting materials have been explored.[8−11] $TiO_2$ when combined with p-type semiconductor metal oxides, such as $Fe_2O_3$, $Co_3O_4$, NiO, and $Cu_xO$,[2,12] extended light absorption to a wider wavelength range which is possible with enhanced charge separation. In the category of transition metal oxides, $Cu_xO$ is a favorable candidate to be used as a cocatalyst with $TiO_2$ in photocatalytic application due to its ability to absorb visible light from the solar spectrum, narrow band gap,[13] and well-matched electronic band structures with $TiO_2$. Besides, $Cu_xO$ ($Cu_2O$ and CuO) possess a more negative conduction band position compared to $TiO_2$, which is more advantageous for the formation of heterojunction between $Cu_2O$ and $TiO_2$.[14] The establishment of the p−n junction at the interface of two semiconductors may generate an internal electric field,[15] which

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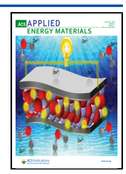





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LET YOUR LIGHT SHINE BEFORE MEN

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To

21st November, 2023

Dr.Chinnakonda S. Gopinath
Outstanding Scientist, Catalysis & Inorganic Chemistry Division
CSIR-National Chemical Laboratory,
Pune - 411008, India

Dear Sir,

**Sub: Request for permission to work at your esteemed research laboratory from 06-12-2023 to 20-12-2023**

Mr. Sivaraj R., S/O Mrs. Radhamma, Kochuveettil Vadakkathil, Melathil, Poonkodu, Chadayamangalam, Kollam, Kerala - 691534 is currently pursuing Ph. D under my supervision as a Full-Time research scholar (Registered in University of Kerala, Thiruvananthapuram) with St.John's College, Anchal as research centre. As a part of the collaboration work, he wish to perform in-depth characterizations and photocatalytic experiments of his samples in NCL. Towards this he wish to visit your lab from 06-12-2023 to 20-12-2023 and we sincerely acknowledge if you could provide laboratory and accommodation facilities for Mr. Sivaraj R. during the period of his visit.

This letter is for your kind consideration

Thanking you

Yours faithfully

Thomas Mathew

Dr. Thomas Mathew
Assistant Professor
Department of Chemistry
St. John's College
Anchal - 691306

I will accommodate Mr Sivaraj in my group for the period between Dec. 6 - 20, 2023 for the collaborative research work.

6/12/23

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