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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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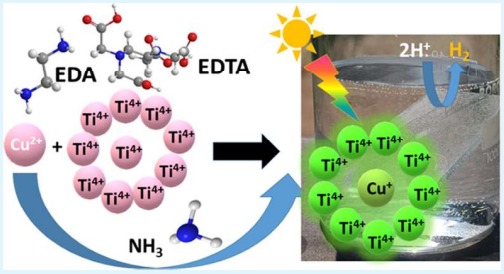
ABSTRACT: Development of highly efficient Cu_xO/TiO_2 photocatalysts by regulating the oxidation state of Cu exclusively in either single or mixed oxidation state(s) is desirable but difficult to achieve without employing any external reagents. The present work describes a one-pot synthesis strategy 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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