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Synthesis and photocatalytic application of ternary Cu–Zn–S nanoparticle-sensitized TiO_2 nanotube arrays

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HIGHLIGHTS

- ▶ An enhanced photocatalytic activity of Cu–Zn–S/TiO_2 NTAs catalyst was fabricated by pulse electrodeposition method.
- ▶ The new catalyst was successfully applied in the photodegradation of 2,4-D and 9-AnCOOH under AM1.5G illumination.
- ▶ Photoelectrocatalytic process with excellent stability was established.

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ABSTRACT

A novel photocatalyst is prepared by pulse-electrodeposition of ternary Cu–Zn–S nanoparticles of 2.3 eV bandgap onto the surface of TiO_2 nanotube array films. Under AM1.5G illumination the Cu–Zn–S sensitized TiO_2 nanotube arrays (Cu–Zn–S/TiO_2 NTAs) exhibit a significantly increased capability for photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and anthracene-9-carboxylic acid (9-AnCOOH). After 150 min illumination 100% of 2,4-D is removed, compared to 51.8% using the non-sensitized TiO_2 NTAs; while after 60 min illumination 100% of 9-AnCOOH is removed, compared to 68.5% using the non-sensitized TiO_2 NTAs. Herein we consider synthesis details and application of the material system.

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1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most widely used systemic pesticide/herbicides while anthracene-9-carboxylic acid (9-AnCOOH) is toxic to the epithelium, inhibiting transport, that in turn increases the permeability of the paracellular pathway. Unfortunately, due to their excellent chemical stability it is difficult to remove 2,4-D and 9-AnCOOH from contaminated wastewater [1–4]. Our interest is in the photocatalytic degradation of these agents. Among photocatalytic materials, nano-architectured TiO_2 is one of the most useful due to its low cost, widespread availability, non-toxicity, high photocatalytic activity, and excellent chemical stability [5–8]. However as is commonly known, photocatalytic application of TiO_2 is limited by its relatively large bandgap of ≈3.0 eV for rutile and 3.2 eV for the anatase phases, which limits photoactivity to the ultraviolet region [9,10]. Many studies have focused on shifting the optical response of titania by doping with transition and/or noble metals [11,12], nonmetals [13–15], or semiconductors [16–18]. Sensitization of TiO_2 with binary [19,20] and ternary [16,21] low bandgap semiconductors has attracted considerable, particularly since the photocorrosion stability can be improved by doping or shelling one material with another. Further, the bandgap can be tuned by elemental doping. For example, ternary metal sulfides have excellent photocorrosion stability and greater photocatalytic activity than binary metal sulfides [22,23]. As a ternary metal sulfide, Cu–Zn–S has a direct band gap of 2.3 eV making it well suited for solar applications [24–27].

In this work, semiconducting low bandgap ternary Cu–Zn–S nanoparticles are used to sensitize highly-oriented TiO_2 nanotube arrays (NTAs). Pulse electrodeposition [28] is used for deposition

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