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One-step sol-gel preparation and enhanced photocatalytic activity of porous polyoxometalate-tantalum pentoxide nanocomposites

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Abstract

Porous polyoxometalate–tantalum pentoxide (POM/Ta₂O₅, POM = $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$) nanocomposites with different Keggin or Dawson unit loading levels (5.6–15.3%) were successfully prepared via hydrolysis of TaCl₅ in the presence of POM without the addition of any structure-directing reagent. Several characterization techniques, inductively coupled plasma atomic emission spectroscopy (ICP-AES), UV–vis diffuse reflectance spectroscopy (UV–vis/DRS), Fourier transform infrared (FT-IR), ³¹P magic-angle spinning (MAS) NMR, field emission scanning electron microscopy (FESEM), and nitrogen adsorption/desorption analysis were combined to confirm the structure integrity of the Keggen or Dawson unit in as-prepared composites and to investigate the optical absorption properties, morphology, and surface textural properties of the composites. The enhanced photocatalytic activity of the composites compared with that of solitary POM units or Ta₂O₅ was evaluated through decomposition of salicylic acid (SA) and rhodamine B (RB) under visible-light excitation. The large BET surface area (129.7–188.8 m² g⁻¹) and porous structure, small particle size (20–25 nm), homogeneous dispersion of the POM unit within Ta₂O₅ framework, decreased bandgap energy, and strong electron acceptance ability of POM can explain this high photocatalytic activity of the composites. © 2007 Elsevier Inc. All rights reserved.

Keywords: Visible-light photocatalysis; Sol-gel; Porous materials; Polyoxometalate; Tantalum pentoxide

1. Introduction

The development of visible-light-driven photocatalytic materials has become an imperative topic in current photocatalysis research for the practical utilization of solar energy. Recently, various types of visible-light-driven photocatalysts have been reported. Among them, some photocatalysts exhibits optical absorption ability in the visible-light region, e.g., Bi₂WO₆ [1,2], (CuIn)_xZn_{2(1-x)}S₂ [3,4], oxynitrides, and oxysulfides [5,6]. Others are coupled semiconductors that are prepared by doping a semiconductor such as WO₃, ZrO₂, or In₂O₃ with anatase TiO₂. The resulting coupled semiconductors permit an enhancement of the charge separation in the photocarrier generation process due to their synergistic effect; thus the photocatalytic activity is increased significantly [7,8]. Our group has reported a kind of composite photocatalysts recently, i.e., nanoporous H₃PW₁₂O₄₀/TiO₂ and H₆P₂W₁₈O₆₂/TiO₂ with anatase phase structure. They exhibited visible-light photocatalytic activity for decomposition of organophosphorus pesticide, parathion-methyl [9]. Previous studies indicated that the effective performance of a photocatalyst depends on a number of factors such as the crystal structure, surface textural properties and accessibility, particle size, and, most important, electronic structure of the catalyst. Underlying the optical response of any material is its electronic structure, related to its chemical composition [10]. By chemical doping of H₃PW₁₂O₄₀ or H₆P₂W₁₈O₆₂ into an anatase TiO₂ framework, the conduction band (CB) levels (Ti3d mixed with W5d) are decreased, resulting in relatively narrow bandgap energy compared with solitary H₃PW₁₂O₄₀, H₆P₂W₁₈O₆₂, or TiO₂. In order to further develop this kind of photocatalytic materials, the present work focused on tantalum pentoxide (Ta₂O₅) and POM. Both of these are photoactive with the excitation of UV-light energy [11–16]. Efforts were made to improve the photocatalytic activity of Ta₂O₅, e.g., fabrication of ordered porous Ta₂O₅ via sol-gel and ligand-assistant templating methods, and the

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