Adsorption and Photocatalytic Studies Using Porous WO₃, SiO₂-WO₃, and Their Au-Doped Analogs

Daniel P. DePuccioᵃ, Pablo Botellaᵇ, Bruce O'Rourkeᵃ, Christopher C. Landryᵃ

ᵃUniversity of Vermont, Department of Chemistry, Burlington, VT 05405, U.S.A.
bInstituto de Tecnología Química (UPV-CSIC), 46022 Valencia, Spain

Abstract

Tungsten oxide (WO₃) is a semiconductor that has been studied for applications in solar energy conversion and photocatalysis using visible light. Doping WO₃ with Au is expected to improve exciton separation on the WO₃ surface, enhancing photocatalytic activity toward adsorbed molecules. Here, we show a new sonochemical method to deposit Au nanoparticles on porous WO₃ and SiO₂-WO₃ composites, and we test the photocatalytic properties of the resulting materials using methylene blue (MB) as a probe molecule. Mesoporous SiO₂-WO₃ composites were prepared by nanocasting from mesoporous silica spheres; sonication of composites in solutions of the Au precursor and NH₃ was followed by calcination at 500 °C to produce Au-doped composites. Monodisperse Au nanoparticles (3-5 nm) were deposited on porous WO₃-SiO₂ composites. Selective etching of the SiO₂ matrix in HF yielded pure Au-WO₃ with well-dispersed 10 nm Au nanoparticles and moderate porosity. This combined sonochemical-nanocasting technique has not been previously used to synthesize Au-WO₃ photocatalysts. X-ray diffraction, high-resolution transmission electron microscopy, energy dispersive X-ray spectroscopy, and N₂ physisorption were used to confirm the physical properties of the materials. Adsorption of MB from solution and photocatalysis using undoped and Au-doped materials was followed by electrospray ionization-mass spectrometry. Extensive MB demethylation and polymerization of demethylated MB products in the presence of undoped and Au-doped SiO₂-WO₃ and WO₃ occurred even in dark conditions. Photoirradiation of suspensions containing porous solids and MB led to further degradation primarily through demethylation and polymerization; ring-opening sulfur oxidation was a secondary photocatalytic pathway. Pure WO₃ was a far better adsorbent for MB than SiO₂-WO₃, leading to more total degradation of MB. Additionally, the rates of MB photodegradation over Au-WO₃ and Au-SiO₂-WO₃ during 300 min of irradiation were significantly greater than those over their undoped counterparts.