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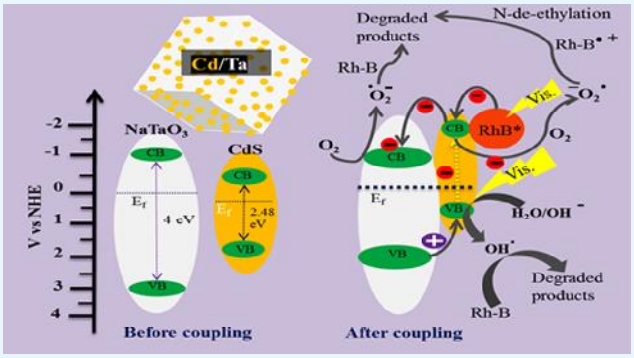
Efficient Charge Transfer in Heterostructures of CdS/NaTaO$_3$ with Improved Visible-Light-Driven Photocatalytic Activity

Ajay Pratap Singh,[†] Sandeep Kumar,[‡] and Meganathan Thirumal*,[†]

[†]Department of Chemistry, University of Delhi, Delhi 110007, India
[‡]Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Supporting Information



ABSTRACT: Photocatalyst NaTaO$_3$ with a cube-shaped morphology and an average particle size of 100 nm was synthesized using an effortless hydrothermal method. The composite heterostructures of CdS/NaTaO$_3$ with variable concentrations of CdS were fabricated after the surface functionalization of bare NaTaO$_3$ using 3-mercaptopropionic acid. As-synthesized photocatalysts were characterized using powder X-ray diffraction analysis, Raman spectroscopy, field-emission scanning and transmission electron microscopes with energy-dispersive X-ray spectroscopy furnished with elemental mapping, multipoint Brunauer−Emmett−Teller (BET), and UV−vis diffuse reflectance spectroscopy. Average lifetime (τ_{avg}) of photoexcitons in heterostructures was studied using photoluminescence (PL) empowered with the time-correlated single-photon counting technique. The diminishing PL peak intensity and reduced average lifetime (τ_{avg}) of photoexcitons in heterostructures indicate the inhibition of photoexciton recombination along with efficient photoexciton exchange between heterostructures. As-synthesized heterostructures demonstrate enhanced visible-light harvesting and appreciably increased the photocatalytic performance toward the degradation of dye rhodamine B. This work highlights the importance of heterostructures with new archetypes which may provide a lead to develop highly capable and reusable photocatalysts to organic dye degradation.

INTRODUCTION

The dye pollutants continue to be the major source of environmental pollution; in particular, the effluents from the textile industries contain approximately 15% nonfixed dyes.[1] The conventional technologies are insufficient to reduce them down to a nonhazardous level to protect the environment.[2] Recently, the metal-oxide semiconductors (e.g., TiO$_2$, NaNbO$_3$, ZnO, and WO$_3$) have attracted wide attention because of their reasonable photo-oxidation of organic pollutants under UV−vis irradiation.[3−7] Among others, the perovskite-type metal oxides with a simple perovskite unit ABO$_3$ (A = Sr^{2+}, Na$^+$, Ba^{2+}, Ca^{2+} and B = Ti^{4+}, Nb^{5+}, Ta^{5+}) have garnered noticeable attention to the degradation of organic dye pollutants;[8,9] in particular, tantalates exhibit a remarkable photocatalytic activity.[10] Several tantalate nanomaterials have been employed for the degradation of organic dye pollutants, for example, alkali and alkaline earth tantalates KTaO$_3$, NaTaO$_3$, LiTaO$_3$ SrTa$_2$O$_6$, Ca$_2$Ta$_2$O$_7$, and BaTa$_2$O$_6$.[11−15] The promising photocatalytic performance of tantalates can be attributed to two factors: (a) conduction band of Ta$_{5d}$ orbital situated at a more negative potential as compared to others like Ti$_{3d}$, Nb$_{4d}$ (pot. vs NHE) and (b) efficient photoexciton delocalization produced by the proper orientation of TaO$_6$ octahedra. These factors are allied with the crystalline structure that is synthesis route-dependent. With regard to the aforementioned, NaTaO$_3$ is a prominent candidate with a distinctive perovskite-type structure and some other useful properties including abundance, low environmental impact, photochemical stability, and high crystallinity that directly reduce the defects and recombination rate. Generally, NaTaO$_3$ shows three very close synthetic route-dependent crystal structures—orthorhombic, monoclinic, and cubic.[16−20]

As reported earlier, the monoclinic phase has the better response to photocatalysis because of the following reasons: (a) Because of indirect band gap, phonons are involved in the gap transition that decreases the recombination rate of photoinduced excitons than that in orthorhombic NaTaO$_3$ which have a direct band gap. (b) This phase has a larger number of effective high-density states close to the band edges for the photoinduced excitons. (c) Monoclinic phase of NaTaO$_3$ is much closer to an ideal perovskite because its Ta−O−Ta bond angle is near to 180° (i.e., cubic phase) rather than a traditionally orthorhombic phase.[21,22] However, owing to the large band gap of NaTaO$_3$, most of its photocatalytic applications are restricted to the UV-spectrum range alone that

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