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Experimental and theoretical study of optical properties and quantum size phenomena in the $BiVO_4/TiO_2$ nanostructures

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ABSTRACT

Novel $BiVO_4$/3DOM TiO_2 nanostructure has been synthesized by hydrothermal method. $BiVO_4$ nanoparticles and TiO_2 inverse opal structure have also been prepared as reference. The prepared samples were characterized by Diffuse reflectance UV–Visible and photoluminescence (PL) spectroscopy. The absorption spectra of $BiVO_4/TiO_2$ nanocomposite samples show an absorption edge in the visible region, suggesting the potential application of this composite as an active visible-light driven photocatalysts. Theoretically quantum confinement phenomena and size dependent optical properties of $BiVO_4$ quantum dots have been also studied. Using the effective mass approximation model, we computed the optical properties for spherical $BiVO_4$ nanoparticles incorporated in TiO_2 matrix. The size dependent of charge carrier's energies were calculated. The result shows that the confinement energy decreases with increase the size of $BiVO_4$ nanoparticles. Dielectric properties of the $BiVO_4$ nanoparticles were investigated and it was found that the dielectric constant decreases significantly as the size is reduced as a result the exciton energy decreases. It has been also found that the radiative recombination lifetime is concurrently enhanced with decreasing $BiVO_4$ QDs size.

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1. Introduction

During the last two decades, a great deal of attention has been focused on the optoelectronic properties of nanostructure semiconductors or quantum dots have many fundamental properties are size dependent in the nanometer range. $BiVO_4$ semiconductor is a versatile material that has many applications such as gas sensors, solid-state electrolytes, positive electrode materials for the rechargeable lithium-ion batteries, ferroelasticity [1–4], and especially in photocatalyse due the ability to photodegrade organic pollutants under visible-light irradiation [5]. There are three polymorphs of $BiVO_4$ existing in nature: monoclinic scheelite, tetragonal zircon and tetragonal scheelite. Among these three crystalline phases, the monoclinic $BiVO_4$ structure shows high photocatalytic performance for water splitting [6,7], O_2 evolution [8,9] and degradation of organic pollutant under visible light irradiation [10,11] compared to the other two phases [12–14]; due to its relatively narrow band gap energy of 2.4 eV [15].

Due to its unit properties and various applications the monoclinic $BiVO_4$ represents a promising metal oxide semiconductor. Many studies focus on a fundamental understanding of the electronic structure and optical properties of monoclinic $BiVO_4$. Walsh et al. [16], Yin et al. [17], and Zhao et al. [18,19], have made seminal progress towards this goal in applying density functional theory (DFT) calculations [20]. It is found that monoclinic clinobisvanite $BiVO_4$ has indirect band gap. The role of transition metals doping [18] optical properties and anisotropic behavior of monoclinic $BiVO_4$ were also studied by Zhao et al. [19], with the conclusion that monoclinic $BiVO_4$ shows promise as a photocatalytic material and that visible light absorption arises mainly from the contribution of polarization directed along the *a*- and *c*-axes. Sarkar et al. [21] reported the size-dependent optical and dielectric properties of $BiVO_4$. To this end $BiVO_4$ nanocrystals with different particle sizes were synthesized through solid-state reaction method followed by the mechanical ball milling for different time durations. It is found that the band gap energies are higher with respect to their values in the bulk $BiVO_4$ due to quantum confinement effects. Similarly, it is found that the dielectric constant decreased with the reduction of particle size.

Many attempts have been made to improve the optical property of $BiVO_4$ nanoparticles by coating with a wide band-gap semiconductor. Typically $BiVO_4$ is covered by TiO_2 matrix to enhance its quantum yield (QY) for radiative band gap recombination and to protect the core against photooxidation as well as environnement attacks [22–25]. The combination of $BiVO_4$ and TiO_2 nanoparticles lead to the formation of $BiVO_4/TiO_2$ nanostructures. In each structures, the charge carrier are three-dimensional confined, the confinement of electrons and holes rise to novel optical and electronic properties. The size dependence of the band gap is the most identified aspect of quantum confinement in semiconductors, the band gap increases as the size of particles decreases. When the dimension of nanocrystalline particles approaches the exciton Bohr radius a red shift in energy is observed due the quantum confinement phenomenon [26–28]. The tenability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new composite materials with optimized properties for various applications such as UV light emitting diode, biological imaging and solar cells.

The information of electronic structures and optical properties is the key step to understand the physical properties and to design functional nanodevices. The first theoretical study related to an exciton in a microsphere was reported by Efros and Efros [29]. Subsequently, numerous studies have been reported using different methods and approximations [30,31]. In most of these studies the description of the quantum confinement is based on the framework of the effective mass approximation (EMA). In strong confinement regimes, EMA has been shown to be sufficient for understanding electronic structure of these low-dimensional systems [32]. In these contexts, we compute the electronic structure and the resulting optical properties of an exciton in a spherical $BiVO_4$ QD incorporated in TiO_2 matrix using the EMA model which allowed calculating the confinement energies of electrons and holes in these nanostructures.

In this present study, we report the quantum size dependent optical properties of $BiVO_4/TiO_2$ nanostructure using EMA model. To this end, the Schrödinger equations are solved to determine the energy eigenvalue and the corresponding eigenfunction of the excitons in such structures. The QDs-size dependence on dielectric constant and the coulomb interaction between electron and hole