



Research paper

Hybrid visible-light responsive Al₂O₃ particles

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ABSTRACT

Detailed study of Al₂O₃, an insulator with the band gap of about 8.7 eV, and its different organic/inorganic charge transfer complexes with visible-light photo activity is presented. In particular, prepared Al₂O₃ particles of the size 0.1–0.3 μm are coated with several organic complexes – the specific details for catecholate- and salicylate-type of ligands are described below – and the light absorption properties and photocatalytic activity of such hybrids are scrutinized and compared with those of other organic/inorganic hybrid materials previously studied. In addition, the obtained experimental results are supported with quantum chemical calculations based on density functional theory.

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1. Introduction

Over the past decades, the metal oxides (TiO₂, ZnO, SnO₂ and CeO₂), which are abundant in nature, biocompatible, and stable, have been broadly investigated for photocatalytic purposes [1–8]. The promising photocatalyst must have proper combination of electronic structure and light absorption properties, as well as efficient separation of photo-formed charge carriers. The efficient solar light utilization of oxide materials is hindered by their large band gap. For instance, the most thoroughly studied photocatalyst TiO₂, with the band gap of $E_g = 3.2$ eV, at the high-frequency edge of the visible-light spectrum, absorbs less than 5% of the available solar light photons, allowing only UV photons ($\lambda < 380$ nm) to produce electron-hole pairs and stimulate redox processes on the catalyst surface. There has been tremendous interest over the recent years to improve visible-light absorption of TiO₂; the methods include dye sensitization for photo-excitation of TiO₂ in the visible spectral region via photo-induced interfacial electron transfer [9–11], doping with metal and nonmetal ions to promote less energetic excitation of electrons from mid-gap dopant levels to conduction band of TiO₂ [12–17], and the use of plasmonic noble metal nanoparticles [18–20]. Another emerging approach to extend photo-absorption of TiO₂ into a more practical range of solar spec-

trum involves charge transfer (CT) from surface modifier into the conduction band of nanocrystalline TiO₂ particles. The CT complex formation between surface Ti atoms and either catecholate- or salicylate-type of ligands, accompanied with red shift of absorption onset, has been primarily studied with colloidal TiO₂ nanoparticles [21–28]. Although, the main purpose of extending the absorption spectrum of TiO₂ towards the red spectral region is the usage of less energetic photons to drive photo-induced reactions, there is a lack of information regarding photocatalytic performance of surface-modified TiO₂ particles. Recently, hydrogen evolution under visible light illumination of surface-modified TiO₂ nanoparticles by catechol and its derivatives has been demonstrated [27,29], as well as degradation of organic dye crystal violet using commercial TiO₂ powder (Degussa P25) modified with catechol [30], and degradation of methylene blue and crystal violet using surface modified TiO₂ nanoparticles with ascorbic acid and dopamine, respectively [28,29].

In the present study we demonstrate that CT complex formation accompanied with the red shift of optical absorption peak is not exclusive of TiO₂. Coordination of small colorless organic molecules with the surface of Al₂O₃ particles also leads to the formation of composites whose optical absorption is extended into the visible spectral region. The degradation of organic dye was used to test photocatalytic ability of surface-modified Al₂O₃ particles. Having in mind that pristine Al₂O₃ has the band gap of about 8.7 eV [31], and does not absorb solar photons, photocatalytic reactions, driven

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using surface-modified Al_2O_3 particles, indicate that the CT complex formation is a promising way to enhance photocatalytic performance of metal oxides. The optical properties and photocatalytic abilities of surface-modified Al_2O_3 particles are discussed in terms of relative position of energy levels. To complement our experimental findings, corresponding quantum chemical calculations were performed using density functional theory (DFT), and the calculated values, obtained for a series of aluminum complex model systems analyzed here, compare well with experimentally determined band gap values. The details of the experimental results and theoretical model calculations are presented and summarized in figures and tables below.

2. Results and discussion

The thorough microstructural characterization of Al_2O_3 particles, prepared by a sol-gel process via hydrolysis of aluminum isopropoxide, followed with calcination [32], was performed and the results are presented in Fig. 1. The XRD pattern of samples calcinated at 700°C indicated the existence of crystalline $\gamma\text{-Al}_2\text{O}_3$ (JCPDS Card No. 00-010-0425). The presence of other coexisting alumina phases or impurities was not detected. The calcinations at higher temperature (1100°C) led to the formation of alumina with corundum crystal structure (JCPDS Card No. 00-056-0457); the XRD pattern is not shown since alumina particles with corundum phase are outside the scope of the present work. High-resolution TEM (Fig. 1B) revealed the presence of reasonably uniform spherical Al_2O_3 particles in the size range from 0.1 to $0.3\ \mu\text{m}$. Also, it can be seen that each submicron-size Al_2O_3 sphere is composed of many nanocrystal grains. This observation is consistent with the broadening of the XRD peaks and estimated size of constitutive building units of about 3.2 nm is determined by the use Scherrer's equation. Nitrogen adsorption-desorption

isotherm of synthesized $\gamma\text{-Al}_2\text{O}_3$ samples is shown in Fig. 1C, and specific surface area, calculated by BET method [33], was found to be $54.8\ \text{m}^2\ \text{g}^{-1}$. It should be noted that specific surface area of synthesized Al_2O_3 powder is similar to commonly used commercial Degussa P25 TiO_2 photocatalyst ($50\ \text{m}^2\ \text{g}^{-1}$) [34]. Pore size distribution of Al_2O_3 powder is shown in Fig. 1D. It is clear that the sample is mesoporous, and estimated pore radius was found to be in the size range 3–4 nm.

The Kubelka-Munk transformations of diffuse reflection data for surface-modified Al_2O_3 particles with catechol (CAT) and 5-amino salicylic acid (5-ASA) are shown in Fig. 2. As can be seen in this Figure, the absorption spectra of surface-modified Al_2O_3 are red-shifted due to formation of CT complexes between ligand molecules and surface Al atoms. The effective band gap energies of CAT/ Al_2O_3 and 5-ASA/ Al_2O_3 , determined from the absorption onset, are found to be 1.26 and 1.66 eV, respectively. Our preliminary results (not detailed here) with a series of catecholate-type of ligands (catechol, 2,3-dihydroxy naphthalene, caffeic acid, dopamine, gallic acid) showed, as a general trend, that they induce larger red-shift than salicylate-type of ligands (salicylic acid, 5-amino salicylic acid) and ascorbic acid. Finally, the largest red-shift of optical absorption was observed upon coordination of CAT to the surface of Al_2O_3 particles (compare band gap value for bulk $\gamma\text{-Al}_2\text{O}_3$ (8.7 eV) [31] with absorption onset of CAT/ Al_2O_3 at 1.26 eV). It transpires that the surface-modification, as described here, is a simple way to transform the insulator into a hybrid semiconductor-like material capable of harvesting the large portion of the solar spectrum. The small differences in the optical properties of surface-modified Al_2O_3 particles, i.e. fine tuning of the absorption properties, can be achieved by changing different electron donating/withdrawing functional side groups attached to the basic backbone structure of catechol or salicylic acid [27].

The ways the ligands bind to the Al_2O_3 surface was investigated using FTIR spectroscopy, and the FTIR spectra of free and adsorbed

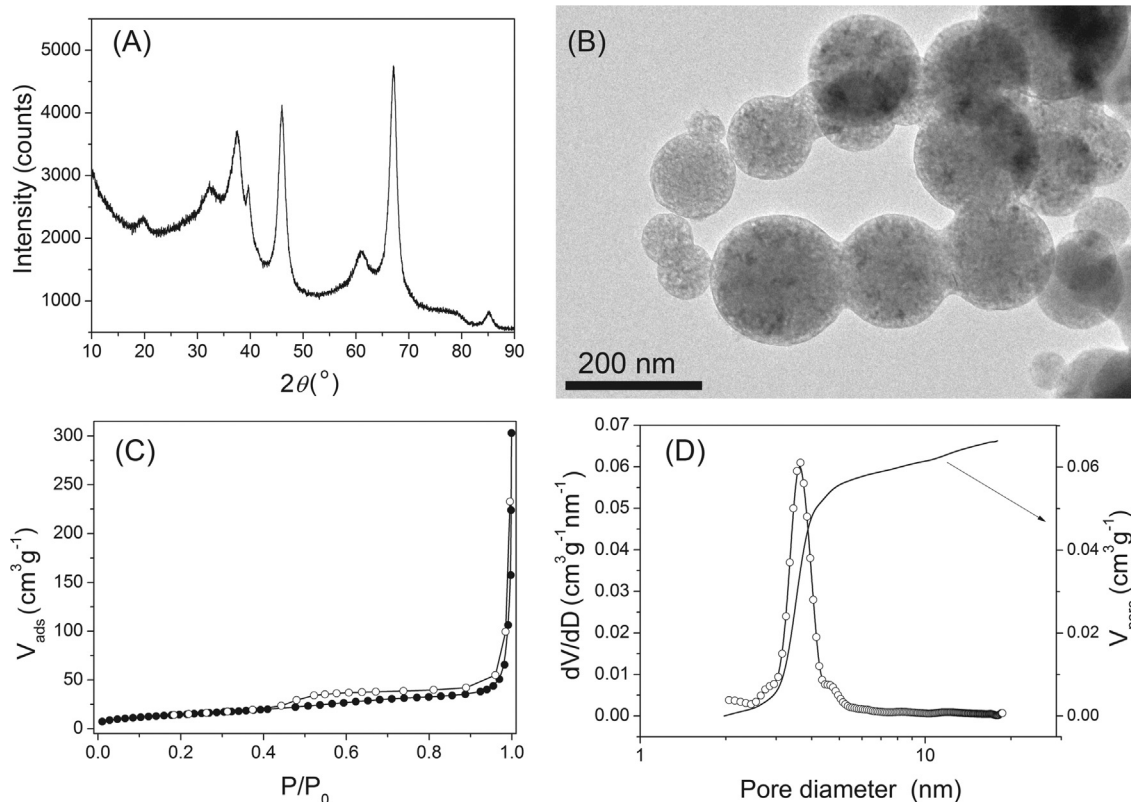


Fig. 1. Microstructural characterization of synthesized Al_2O_3 samples: (A) XRD, (B) high-resolution TEM, (C) nitrogen adsorption-desorption isotherms, and (D) pore size distribution.

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