A joint theoretical and experimental approach of electronic structure and photocatalytic properties of MgWO_4 powders

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1. Introduction

Recently, the industrial organic dyes are large fluvial water contaminants that cause serious environmental problems [1]. A well-known industrial dye is the Rhodamine B (RhB), which is employed for the dyeing of cotton, weed, for example [2].

From a practical viewpoint, the photocatalytic (PC) properties with the action of a semiconductor catalyst is an alternative way for the removal of soluble toxic compounds, especially because of its significant advantages, such as: low cost, easy to handle, the reaction is promoted by means of visible or ultraviolet electromagnetic energy [3].

Therefore, the magnesium tungstate (MgWO_4) can be used for photocatalytic activity. We present first-principles calculations based on the density functional theory (DFT) to find a correlation between experimental results and electronic levels.

2. Methodology

MgWO_4 powders were synthesized by the complex polymerization method modified [4] and was characterized by X-ray diffraction (XRD) patterns and Rietveld refinement. Their optical properties were investigated by UV-Vis spectroscopy. The PC properties for degradation of RhB were conducted under illumination UV-light up to 120 min. The theoretical calculation based on the DFT was performed with the *CRYSTAL14* package [5].

2. Results and Discussion

This powder heat-treated at 900 °C for 2 h, exhibits all XRD patterns ascribed to pure MgWO_4 phase with monoclinic structure and also the structural refinement by means of Rietveld method. According to our theoretical calculations of the EBS, it was noticed that the MgWO_4 is characterized by direct electronic transitions ($E_{\text{gap}} = 4.49$ eV). This value is in concordance with the experimental UV-Vis spectrum value ($E_{\text{gap}} = 4.33$ eV), but it is a little higher because in the theoretical calculations the system is in the ideal structure without deep local defects. The projected DOS on the O atoms is principally determined in the VB with the $2p$ orbitals while the CB is mainly determined by the $5d$ orbitals from W atoms. In systems that present local defects, different $M\text{--O}$ bonds in the $[\text{MO}_6]$ clusters, where $M = \text{Mg}$ and/or W, it is to expected orbitals not degenerated. In this way, in the top of the VB there are contributions of $2p_x$ and $2p_z$ orbitals from O atoms whereas in the bottom of the CB a little contribution of $4s$ orbitals from Mg atoms and $5d_{z^2}$, $5d_{xz}$ and $5d_{x^2-y^2}$ orbitals from W atoms.

4. Conclusions

In summary, we explained by means of distortions effects and proposed a PC mechanism based in a wide model related the presence of intermediate electronic levels between the VB and CB.

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