Isfahan University of Technology

Ph.D. Defense

RuO_2/TiO_2 Photoelectrocatalyst in Hydrogen Evolution Reaction; Structure, Frontier Orbitals, and Electronic Spectra of Homonuclear and Heteronuclear Complexes of Ru(II) and Os(II) with Tetra(2-pyridyl)pyrazine Ligand

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Abstract

The first part of this thesis is a joint experimental and theoretical study of RuO_2/TiO_2 heterostructures. In the experimental section, RuO_2/TiO_2 heterostructures were prepared by impregnation of mesoporous TiO_2 nanoparticles which were synthesized from a new precursor. The photoelectocatalytic application of as-prepared heterostructures was then investigated toward hydrogen evolution reaction (HER). The loading of RuO_2 on TiO_2 decreases the band gap energy and extends the absorption edge to the visible light region. To obtain a deeper understanding of the increase of the photoelectrocatalytic activity of RuO_2/TiO_2 heterostructures compared to the pure TiO_2, the theoretical calculations at the density functional theory (DFT) were performed on some model clusters of the pure TiO_2 and RuO_2/TiO_2 heterostructure. The theoretical results elucidated that the recombination ratio of electron-hole pair decreases effectively for RuO_2/TiO_2 compared to the pure TiO_2.

In the second part, to investigate the impact of metal center type and its arrangement on the electronic transitions of one-dimensional multimetallic complexes, this study employed a combined experimental and computational study of homo- and hetero-metallic complexes of Ru(II) and Os(II) with TPPZ. In the experimental section, four mono- and bimetallic complexes were synthesized and characterized according to the literature. On the computational side, the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to investigate geometry, electronic structure, and optical absorption spectra of mono-, bi-, and trimetallic complexes. Finally, this study presents a comprehensive description of the effect of the type and arrangement of the metal centers in one-dimensional conjugated complexes which have potentially interesting molecular wire properties.

Keywords: Heterostructures, Titanium dioxide, Ruthenium dioxide, Photoelectrocatalyst, Hydrogen evolution reaction, Density functional theory.