UNIVERSITI TEKNOLOGI MARA

FIRST-PRINCIPLES STUDY ON PROPERTIES OF LANTHANIDE (Ln)-DOPED TiO_2 (Ln = Ce, Nd AND Er) FOR DYE-SENSITIZED SOLAR CELLS USING DENSITY FUNCTIONAL THEORY

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ABSTRACT

In dye-sensitized solar cell (DSSC), titanium dioxide (TiO_2) acts as a support for dye. However, TiO_2 alone in DSSC has low light absorption in ultraviolet (UV) spectrum which causes low efficiency of DSSC. Thus, modification of TiO_2 by doping with lanthanide (Ln) elements have been used as photoanodes in DSSC. However, an understanding on the structural, electronic and optical properties of Ln-doped TiO_2 in DSSC is not fully understood. Therefore, the first-principles study on the properties of TiO_2 and Ln-doped TiO_2 using density functional theory (DFT) were investigated with special reference to their role as photoanodes in DSSC. The structural parameters of TiO_2 in rutile, anatase and brookite phases are different because of the difference in atomic position of titanium (Ti) and oxygen (O) atoms. The large cell volume of anatase offers more space for dye loading capability which is desirable for inducing higher light harvesting. The DFT plus Hubbard U (DFT+U) yields a good electronic properties and phase stability of TiO_2 compared to DFT. The high band gap of anatase describes its high photovoltage and the density of states (DOS) displays the hybridization between Ti 3*d* and O 2*p* states. The electron distribution and chemical bonding nature of TiO_2 were explained from the electron density map while the Mulliken population analysis presents the net charge (*e*) of Ti and O atoms. The band gap of anatase TiO_2 at 3.2 eV makes it sensitive only in UV light which neglects the light absorption in longer wavelength spectrum. Hence, the effect of TiO_2 doping with Ln using cerium (Ce), neodymium (Nd) and erbium (Er) were determined. The Ln-doped TiO_2 has lower band gaps compared to pure TiO_2 due to the presence of impurity energy levels (IELs) from Ln 4*f* states. The presence of Ln 4*f* states in Ln-doped TiO_2 can be seen from the DOS. Among the Ln-doped TiO_2, the shifting of light towards longer wavelength spectrum is from Nd-doped TiO_2. For further study on Nd-doped TiO_2, the properties of novel materials from different Nd concentrations in TiO_2 with stoichiometry $Ti_{1-x}Nd_xO_2$ at x = 0, 0.0625, 0.125 and 0.18750 were investigated. As the Nd concentration increases, the light absorption edge shifts towards longer wavelength spectrum, indicating efficient light harvesting to boost performance of DSSC. Overall, the first-principles study from the deepest atomic level in this work can clarify the doping effects in TiO_2 and may improve the understanding on DSSC.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Research

Nowadays, global total energy usage is about 14 terawatts (TW) where the main source of this energy came from fossil fuels (coal, oil and natural gas). Out of this amount of energy usage, 28% is required by the developing countries such as China and India. By the year 2035, the estimated energy consumption by these two countries is up to 31%. Unfortunately, the scientist predicted the source of fossil fuels will be depleted drastically and last up until year 2112 [1]. In order to replace the source of energy from the fossil fuels, renewable energy from regenerative and inexhaustible resources such as solar, wind, biomass and geothermal can be the promising sources and have potential to meet the rising energy demand [2]. According to the global energy investment as shown in Figure 1.1, the total investment in the energy sector reached USD 1.8 trillion in 2015, down from USD 2.0 trillion in 2014, with a drop in oil and gas upstream. On the other hand, robust investment is continuous for renewables, electricity networks and energy efficiency.

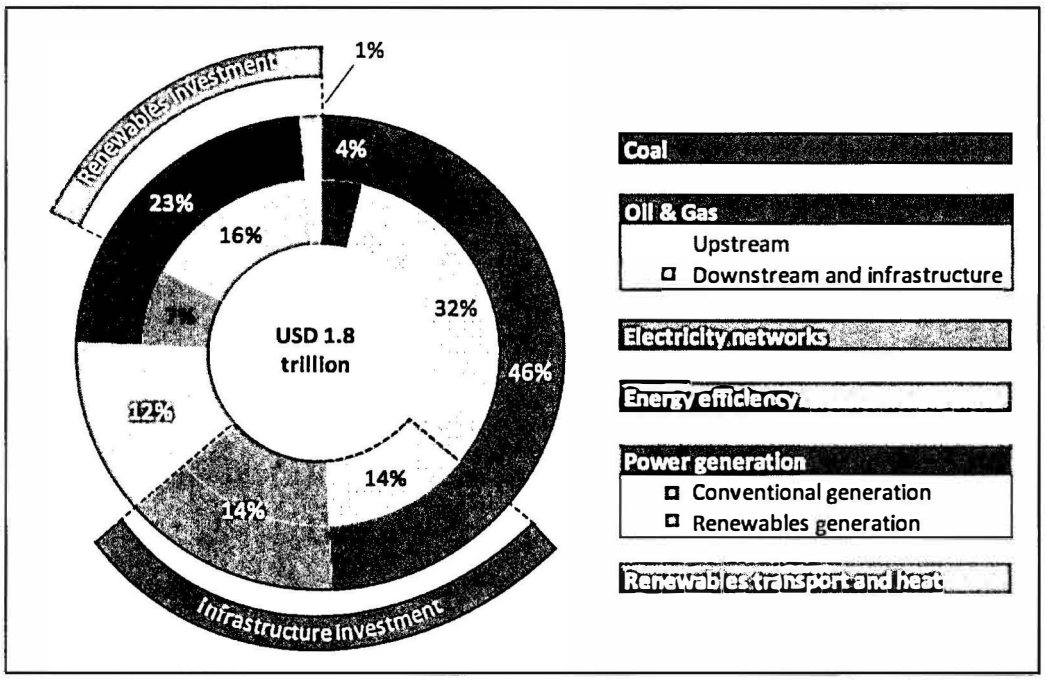

Figure 1.1 Global Energy Investment in 2015 by Sector. Source: World Energy Investment (WEI) 2016