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STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF Cu-Ag AND Ti-Ag CODOPED ZnO AS DYE-SENSITIZED SOLAR CELL PHOTOANODE MATERIAL USING DENSITY FUNCTIONAL THEORY

NORJULIYATI BINTI HAMZAH

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ABSTRACT

Zinc oxide (ZnO) is a promising dye-sensitized solar cell (DSSC) material due to its unique and multifunctional properties. However, its wide bandgap (3.37 eV) hinders effective light absorption in visible light regions, resulting in lower DSSC efficiency. The improvement of the conversion efficiency of ZnO-based DSSC by doping with transition metal (Tm) using copper (Cu), silver (Ag) and titanium (Ti) atoms has mainly been investigated. However, mono-doping has low solubility, limiting further increases light absorption. Thus, the modification of ZnO by codoping with two Tm atoms has been used for photoanodes in DSSC. However, the structural, electronic and optical properties of Tm-Tm codoped ZnO in DSSC are not fully understood. Therefore, the first-principles study based on density functional theory (DFT) is a barely suitable approach to calculating the properties of ZnO. The calculations were based on the local density approximation (LDA) and the generalized gradient approximation (GGA) by applying Hubbard U_d and U_p. The lattice parameters were closer to experimental data and underestimated when Hubbard U_d and U_p were applied. Combining the Hubbard U_d and U_p improved the underestimated bandgap of wurtzite ZnO, which might solve the standard DFT problems. The density of states (DOS) displays the O-2*p* state primarily dominates at the valence band (VB) maximum, while the Zn-4*s* state contributes to the conduction band (CB) minimum. The Hubbard U_d and U_p calculations led to a downward shift in hybridized Zn-3*d* and O-2*p* states and a slight upper shift in the bottom CB toward the broadening bandgap. The bandgap of ZnO at 3.360 eV makes it sensitive only to UV light, lacking sensitivity to the longer wavelength spectrum. Doping ZnO with Cu, Ag and Ti induces significant property alterations, enhancing dye absorption and reducing recombination rates. Ag-doped ZnO stands out, leading to further exploration via codoping with Cu and Ti. Cu-Ag codoped ZnO exhibits superior absorption and reduced bandgap, emerging as the optimal photoanode choice. The properties of novel materials from $Zn_{1-2x}Cu_xAg_xO$ at x = 0.0833, 0.167 and 0.25 were investigated. As the Cu-Ag concentration increases, the light absorption edge shifts towards a longer wavelength spectrum, indicating efficient light harvesting to boost the performance of DSSC. The best composition identified in this study was x = 0.25 for enhancing solar absorption and extending light absorption into the visible region. This study provides a theoretical reference for experimental investigations and offers essential insights for the development of photoanode materials in DSSC, highlighting the potential of Cu-Ag codoped ZnO for enhanced solar absorption and DSSC efficiency.

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CHAPTER 1
INTRODUCTION

1.1 Research Background

The rapid development of technology and population drives up the energy demand. The energy consumption rate in 1998 was about 12.7 TW and is expected to be 26.4 – 32.9 TW in 2050 and 46.3 – 58.7 TW in 2100 [1]. In 2021, global energy consumption reached 595 EJ, up 5.8% from the previous year, 1.3% higher than in 2019 [2]. Annual increases in global energy consumption will drive up demand for fossil fuels, i.e., natural gas, coal and oil. According to the primary global energy consumption in 2021, as depicted in Figure 1.1, fossil fuels accounted for 82.28% of primary energy use in 2021, against 83% in 2019 and 85% five years ago. Unfortunately, fossil fuel reserves for oil and natural gas are predicted to run out by 2042, while coal reserves last until 2112 [3]. The current global energy supply will eventually be depleted, prompting exploration and research into the usage of alternative renewable energy. Thus, renewable energy sources will play an increasingly important role in the future energy structure. Renewable energy is expected to be the most viable and cost-effective alternative to fossil-fuel energy by 2030 [4].

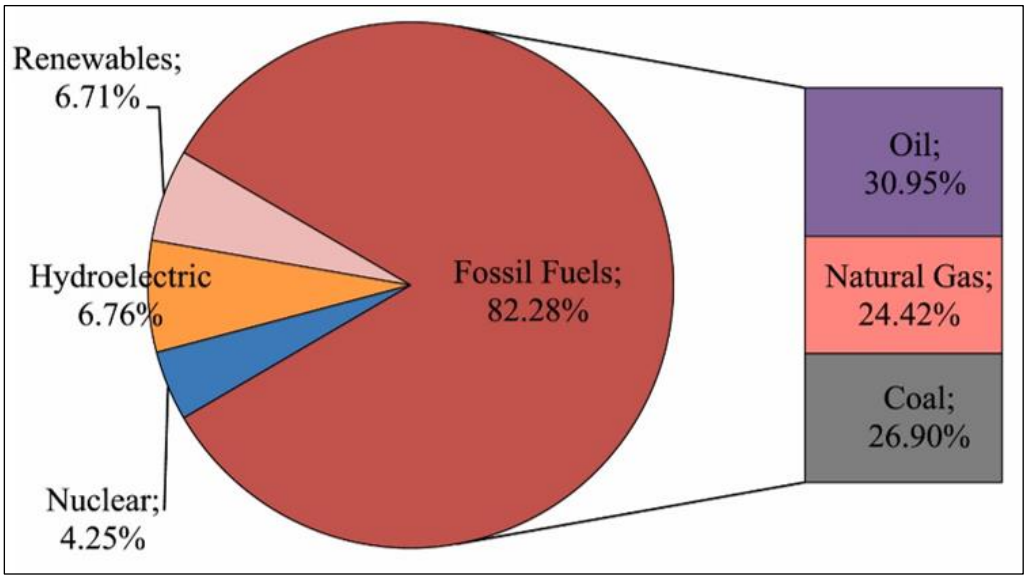

Figure 1.1 Primary Global Energy Consumption 2021
Notes/Sources: BP statistical review of world energy 2022. [2, 5]