Experimental and computational studies on doped-Ag_2O photocatalysts

Thesis submitted in partial fulfillment

for the Award of Degree

Doctor of Philosophy

by

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Symbols Used

$\mathbf{E_g}$	Bandgap
VB	Valence band
CB	Conduction band
$\mathbf{h^+}$	Holes
$\mathbf{e^-}$	Electrons
$\mathbf{^{\bullet}\mathit{O}H}$	Hydroxyl Radical
NaOH	Sodium Hydroxide
$\mathbf{O_2^{\bullet-}}$	Superoxide Radical
OVs	Oxygen vacancies
UV-DRS	Ultraviolet Visible Diffuse Reflectance Spectroscopy
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
XPS	X-ray photoelectron spectroscopy
SEM	Scanning Electron Microscopy
W	Watt
λ	Lambda
Å	Angstrom
θ	Theta
MO	Methyl orange
RhB	Rhodamine B
CIP	Ciprofloxacin
$\mathbf{k_{app}}$	Apparent rate constant

TOF	Turnover frequency
IPA	Isopropyl alcohol
KI	Potassium iodide
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
UV-Vis	Ultraviolet-visible
t	Time
α	Absorption coefficient
DDDW	Deionized double distilled water
LED	Light emitting diode

Preface

Photocatalysis is a green and economical technique for wastewater treatment (organic pollutants degradation). A semiconductor photocatalyst absorbs photon energy when it is exposed to light. The absorbed energy excites the material's electrons from valence band (VB) to the conduction band (CB). Therefore, generating a substantial amount of holes (h^+) and electrons (e^-) makes the material capable of performing various oxidation and reduction reactions, respectively. An extensive literature survey reveals little research on developing doped small bandgap photocatalysts and their heterostructures with other semiconductors.

In this context, Ag_2O is a widely used photocatalyst with a bandgap range of 1.2-1.5 eV. Although it has a narrow bandgap giving an advantage of absorbing the maximum portion (UV and Visible) of the solar spectrum, it faces several issues. For instance, the narrow bandgap restricts its redox ability. Other significant issues are the photo-stability of the material and the recombination of photo-generated charge carriers (h^+ and e^-). Essentially, proper charge separation in the materials can reduce these problems. Doping of Ag_2O or its composite with other visible range bandgap semiconductors can give efficient photocatalysts. There are many reports on the construction of heterostructures with Ag_2O as one of the components. For instance, Ag/Ag_2O/reduced TiO_2, Ag_2O/WO_3, Curcumin/Ag/Ag_2O, Ag_2O/Ag_3PO_4, Ag_2O/Bi_2O_3, etc., have been synthesized and found to possess efficient photocatalytic activities towards certain organic pollutants.

Before this thesis, only one report, on preparing Sr-doped Ag_2O nanostructures for photocatalytic degradation of organic pollutants, was available in the literature on

doped Ag_2O. Few computational investigations (plane-wave DFT calculations) also reported on Ag_2O and oxygen vacancies in Ag_2O. Structural and band structures can be collected from the DFT studies. Before this thesis, no plane-wave DFT investigations have been reported on doped Ag_2O nanomaterials in the literature. The limited knowledge of doped-Ag_2O photocatalysts inspired the present investigations.

This thesis investigates the effects of cation and anion doping on the photocatalytic properties of Ag_2O. Furthermore, an efficient heterostructure with a doped Ag_2O system has also been prepared. A simple hydrothermal protocol was followed for preparing photocatalysts investigated in this thesis. The hydrothermal protocol introduced oxygen vacancies in the prepared Ag_2O nanoparticles. Different characterization techniques, like XRD, UV-DRS, TEM, SEM, XPS, etc., were applied to characterize the synthesized photocatalysts. XRD, EDS (SEM or TEM), and DFT calculations were used to analyze the doping phenomena. The DFT calculations, along with XRD data, on formation energies revealed the position of the dopant atom in the Ag_2O crystal structure. The XPS characterization found the elements, their oxidation states, oxygen vacancies, and the VB edge of the photocatalyst. Then, the photocatalytic performances of these photocatalysts were evaluated towards particular organic pollutant degradation. Hence, the thesis seeks to investigate the doping of Ag_2O both experimentally and through computational investigations.

Chapter 1 of this thesis highlights the basics of the subject area (photocatalysis). An extensive literature survey is performed to find out the lacuna of the research. There are several issues involved in the photocatalytic material. Therefore, designing an efficient photocatalyst has become very important. It has been found that doping can be an efficient strategy to encounter those issues. Introducing cationic and

anionic dopants in pure Ag_2O is hardly reported. The main objectives of the thesis have been clearly discussed at the end of the chapter.

Chapter 2 details all the chemicals used for the sample preparation. The sample preparation protocol is also mentioned. The instrumentations involved in the present investigations are discussed in a proper manner. The design of the photocatalytic experiment and computational investigation are given at the end.

Chapter 3 focuses on the 1st objective of the thesis. The Zn doped Ag_2O is prepared to understand how the dopant affects the nanoparticle's lattice structure. When dopant is introduced into the lattice structure, there is a vital question of whether it will occupy a substitutional or interstitial position. A proper XRD analysis confirmed interstitial doping formation. A parallel DFT investigation supported this evidence. Further, experimental and qualitative DFT calculations demonstrated the bandgap widening phenomenon in the material. The Zn doping widened the bandgap up to 1.65 eV. The density of states (DOS) calculation gave the reason for the bandgap widening. The dopant mainly extends and shifts the valence band (VB) region, introducing the dopant's energy states. The Zn doping also improved the photocatalytic performance of the Ag_2O nanoparticles towards organic pollutant (methyl orange and rhodamine-B) degradation.

Chapter 4 deals with the second objective on incorporating Ni dopant in Ag_2O nanoparticles. This doping also affects the nanoparticle's lattice structure and bandgap. The material's bandgap decreased slightly due to the doping. The XRD and DFT results showed that Ni substitutes Ag in the Ag_2O lattice structure. Ni doping shifts the VB edge to a lower energy region. The XPS investigation highlights a synergistic effect of doping and oxygen vacancy defects in photocatalytic performance. Hence, the Ni-doped

Ag_2O nanoparticles showed an improved photocatalytic activity towards ciprofloxacin degradation.

Chapter 5 involves the preparation and characterization of sulfur (S) doped Ag_2O nanoparticles. Initial DFT calculations demonstrated oxygen substituted by sulfur in Ag_2O lattice could result in bandgap widening. This result inspired the preparation of S-doped Ag_2O nanoparticles. Experimentally, the bandgap widens up to 1.89 eV. XPS analysis revealed S doping increases the oxygen vacancy defects proportion. The VB edge shifted to a higher energy region due to doping. Extensive DFT calculations were undertaken to investigate the most stable sulfur dopant position in the Ag_2O crystal structure. Furthermore, DFT calculations also showed the qualitative effect of such crystal structure on the doped Ag_2O band structure. Eventually, the S-doped Ag_2O nanoparticles showed an enhanced visible light photocatalytic activity towards rhodamine-B degradation.

Chapter 6 of the thesis investigated the efficacy of a composite prepared with Cd doped Ag_2O nanoparticles. First, different Cd doped Ag_2O systems were synthesized by a hydrothermal protocol. A particular Cd-doped Ag_2O system was selected by XRD and DFT analysis. Next, the selected Cd doped Ag_2O system and $BiVO_4$ (another visible light photocatalyst previously prepared by a well-established protocol) were joined together by a similar hydrothermal technique. The generated heterostructure gave better efficiency and appropriate recyclability for photocatalytic ciprofloxacin degradation. The increased efficiency was due to its Z scheme electron transfer mechanism, which was proved by XPS analysis. DFT calculations showed that H_2O adsorbed and activated on the Cd-doped Ag_2O part, while O_2 interacted better with the $BiVO_4$ surface. This investigation and the scavenger experiment results helped elucidate the appropriate photocatalytic mechanism.

Chapter 7 is the last chapter of the thesis, which ends with a summary of all investigations and the future scope of these studies. These prepared photocatalysts' turnover frequency (TOF) values have been compared with those in the existing literature.