ABSTRACT

DEPARTMENT OF CHEMISTRY

AMSAAED, SALEM
B.S. OMAR AL-MUKHTAR
UNIVERSITY, 2009

COPPER GRAFTED TITANIUM DIOXIDE IN HYDROGELS FOR
PHOTOCATALYSTS

Committee Chair: Xiu R. Bu, Ph.D.

Thesis dated December 2018

This study is based on the premise that the incorporation of metal ions into nano
titania-PHEMA [poly (2-hydroxyethyl methacrylate)] hydrogels would enhance the
desirable properties in the photodecomposition of pollutants. The investigation is
centered in the use of Cu(II) as metal ion of interest. The development of TiO$_2$-PHEMA-
Cu hydrogels was conducted, and the characterization of the materials by FT-IR, XRD
and fluorescence was performed. The absorption of copper(II) from the solution was
monitored by UV-Vis. The FT-IR is found to be the most effective tool to analyze the
interaction of Cu(II) with PHEMA in the nanocomposite hydrogels. The free carbonyl
group has the IR band at 1715 cm$^{-1}$ in the TiO$_2$-PHEMA. Upon uptaking Cu(II), the
hydrogels showed a new band at 1595 cm$^{-1}$. Further examination establishes the
relationship between the two bands. The time-dependent study revealed that the intensity
of band at 1595 cm$^{-1}$ would increase while that at 1715 cm$^{-1}$ would decrease as the time
for uptaking Cu(II) increased. A concentration-dependent study also demonstrated the
same trend that showed the intensities of the two bands moved in the opposite directions.
COPPER GRAFTED TITANIUM DIOXIDE IN HYDROGELS FOR PHOTOCATALYSTS

A THESIS
SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

BY
SALEM AMSAAED

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA

DECEMBER 2018
ACKNOWLEDGMENTS

My experience during graduate studies at Clark Atlanta University has changed my life. I have met and have worked with many wonderful individuals. First, I would like to acknowledge my advisor, Professor Xiu-Ren Bu, for his valuable guidance of my research, for his ideas to improve the experiments, and for all his support. Without his generous advice, I would not be here. I would like to express special thanks to my committee members, Dr. Myron N.V. Williams, Dr. Cass D. Parker and Dr. Ishrat M. Khan for their valuable guidance. I would like to thank all my colleagues and coworkers at Clark Atlanta University who were a part of this study, for their patience, accessibility, unconditional training in the laboratory, and support which ensured the success of this research project.

I would like to thank my friend, Mr. Saad Alotaibi, for his guidance on my thesis. I would like also to thank Mr. Saki Golafale for his explanation of many technical concepts, as well as for his sample.

I would like to acknowledge the first sparkle of this effort, my sister, Dr. Alia, for giving me the courage to learn a different language and write a thesis in my domain of study. Without her, this work would not be possible. Thank you, sister.

I would like to express special thanks to my sponsor, the Canadian Bureau for International Education Scholarship (CBIE), for offering me the opportunity to continue my studies abroad.
# Table of Contents

**ACKNOWLEDGMENTS** .................................................................................................................. ii

**LIST OF FIGURES** ........................................................................................................................ v

**LIST OF TABLES** ........................................................................................................................... vii

**LIST OF ABBREVIATIONS** .............................................................................................................. viii

**CHAPTER**

I. **INTRODUCTION AND BACKGROUND** ......................................................................................... 1

1.1 Hydrogel........................................................................................................................................ 1

1.2 Chemical Structure and Application of Hydrogel ............................................................................ 2

1.3 Ultrasound Assisted Synthesis of TiO$_2$ and Doped TiO$_2$......................................................... 4

1.4 Titanium Dioxide .......................................................................................................................... 6

1.4.1 Toxicity of TiO$_2$ Nanoparticles............................................................................................... 8

1.5 TiO$_2$-PHEMA Composite ........................................................................................................... 9

1.6 Cu(II) Nanocluster-Grafted, Nb-Doped TiO$_2$ ............................................................................. 9

1.7 Characteristics of Metal Ions in Poly (2-hydroxyethyl methacrylate) Hydrogels............................. 15

1.8 Aim of Research ........................................................................................................................... 15

II. **MATERIAL AND METHODS** ...................................................................................................... 16

2.1 Materials ...................................................................................................................................... 16

2.2 Hydrogel PHEMA Synthesis ....................................................................................................... 16

2.3 Synthesis of TiO$_2$-PHEMA Hydrogel ....................................................................................... 17
CHAPTER

2.4 Absorption..............................................................................................................17

2.5 Characterization ...................................................................................................18

2.5.1 UV-visible Spectroscopy ..................................................................................18

2.5.2 X-ray Powder Diffraction (XRD) ......................................................................18

2.5.3 Fourier Transform Infrared Spectroscopy (FT-IR) ...........................................18

2.5.4 Fluorescence Plate Reader ................................................................................18

III. RESULTS AND DISCUSSION .................................................................................19

3.1 Density Study (ε) ...................................................................................................19

3.2 UV-visible Spectroscopy .......................................................................................22

3.3 Fourier Transform-Infrared Spectroscopy ..............................................................27

3.4 X-ray Powder Diffraction ......................................................................................32

3.5 Fluorescence Plate Reader .....................................................................................35

3.6 Efficient TiO2-PHEMA-Cu(II) .............................................................................36

IV. CONCLUSION ..........................................................................................................37

REFERENCES ...............................................................................................................38
LIST OF FIGURES

Figure

1. Crystal structures of rutile and anatase phases of TiO$_2$ .................................................. 8

2. Proposed photocatalytic processes for Nb$_x$Ti$_{1-x}$O$_2$, Cu(II)–TiO$_2$ and Cu(II)–
   Nb$_x$Ti$_{1-x}$O$_2$, respectively ................................................................................................. 12

3. Schematic diagram of the twin synergistic effects of Sm-C Co-doping and 
   the mixed phase TiO$_2$ .............................................................................................................. 14

4. Synthesis of TiO$_2$-PHEMA hydrogel ..................................................................................... 17

5. The proposed design of PHEMA nanocomposite hydrogel crosslinked with 
   EGDMA, and $\xi$ is the mesh size of a hydrogel ................................................................. 20

6. Characteristic mesh size $\xi$ of a hydrogel system drives both the permeability 
   k & $\xi$ and the timescale of single- chain polymer .................................................................. 21

7. The UV-Vis spectra of copper(II) in water ............................................................................. 22

8. The UV-Vis spectra of (1) copper solution (2) TiO$_2$ (A)-PHEMA-Cu(II) 
   (7 days) and (3) TiO$_2$ (A)-PHEMA-Cu(II) (9 days+ 10 hr) ............................................. 23

9. The UV-Vis spectra of (1) copper solution (2) TiO$_2$ (R)-PHEMA-Cu(II) 
   (3 days) and (3) TiO$_2$ (R)-PHEMA-Cu(II) (3 days + 6 hr) .................................................. 24

10. The UV-Vis spectra of (1) copper solution (2) TiO$_2$ (M)-PHEMA-Cu(II) (12 hr) 
    and (3) TiO$_2$ (M)-PHEMA-Cu(II) (20 hr) ......................................................................... 25

11. The UV-Vis spectra of comparison between three phases TiO$_2$- PHEMA ................. 25

12. The color change of three phases of hydrogel during a period of time .................... 26

13. The UV-Vis spectra of Cu(II) in the solution after being in contact three 
    phases of TiO$_2$ at different times ....................................................................................... 27

v
Figure

14. FT-IR spectra of TiO$_2$ (A)-PHEMA- Cu(II). ................................................................. 28
15. FT-IR spectra of TiO$_2$ (R)-PHEMA- Cu(II) ................................................................. 29
16. FT-IR spectra of TiO$_2$ (M)-PHEMA-Cu(II) ................................................................. 29
17. FT-IR spectra of TiO$_2$ (M)-PHEMA-Cu(II)- in different concentration of Cu(II) ........ 30
18. Percentage of copper ions of C=O free and C=O--Cu coordinated ............................. 31
19. FT-IR spectra of TiO$_2$ (M)-PHEMA- Cu(II) same concentration and a different time ................................................................. 32
20. XRD patterns for TiO$_2$ (A)-PHEMA and TiO$_2$ (A)-PHEMA-Cu(II) ......................... 33
21. XRD patterns for TiO$_2$ (R)-PHEMA and TiO$_2$ (R)-PHEMA-Cu(II). ......................... 34
22. XRD patterns for TiO$_2$ (M)-PHEMA and TiO$_2$ (M)-PHEMA-Cu(II) ......................... 34
23. Fluorescence plate reader for TiO$_2$ (M)-PHEMA-Cu(II) ............................................. 35
24. UV-Vis spectra for phases TiO$_2$- with Cu(II) in hydrogel. ......................................... 36
LIST OF TABLES

Table

1. The Swelling Ratio (Q) and Mesh Size (ξ) of Synthesized Hydrogel-TiO$_2$
   Anatase, Rutile and Mixed.................................................................21

2. The Absorption Cu(II) in New TiO$_2$-PHEMA Hydrogel at the Time ............26

3. TiO$_2$ (M)-PHEMA in the Cu(II) Solution for 5 Hours at Room Temperature. .....31
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>An</td>
<td>Anatase</td>
</tr>
<tr>
<td>B</td>
<td>Path length of light</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>EGDMA</td>
<td>Ethylene glycol methacrylate</td>
</tr>
<tr>
<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>L</td>
<td>Distance between two carbons in the polymer backbone</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>Mw</td>
<td>Average molecular weight</td>
</tr>
<tr>
<td>PHEMA</td>
<td>Poly (2-hydroxyethyl methacrylate) hydrogel</td>
</tr>
<tr>
<td>$m_{air}$</td>
<td>Mass in air</td>
</tr>
<tr>
<td>$M_c$</td>
<td>Average molecular weight between crosslinkers</td>
</tr>
<tr>
<td>$m_{hex}$</td>
<td>Mass in hexane</td>
</tr>
<tr>
<td>N</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>Q</td>
<td>Volume swelling ratio</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>R</td>
<td>Rutile</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Uv-vis</td>
<td>Ultraviolet/ visible</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>$V_d$</td>
<td>Dried volume</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Swollen volume</td>
</tr>
<tr>
<td>$\mathcal{E}$</td>
<td>Molar absorptivity or Beer’s law constant</td>
</tr>
<tr>
<td>$\rho_{2,r}$</td>
<td>Density of the hydrogel in the relaxed state</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>End to end distance between crosslinker</td>
</tr>
<tr>
<td>$\nu_{2,r}$</td>
<td>Polymer fraction in the relaxed state</td>
</tr>
<tr>
<td>$\nu_{2,s}$</td>
<td>Polymer fraction in the swollen state</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Mesh size</td>
</tr>
<tr>
<td>SMBS</td>
<td>Sodium metabisulfite</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium persulphate</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION AND BACKGROUND

1.1 Hydrogel

Hydrogels are three-dimensionally cross-connected network polymers composed of functional hydrophilic groups which have the ability to absorb a lot of water and solute molecules.\(^1,2,3\) Hydrogels are otherwise also called smart materials which show reaction and swelling when there is a little change in the external environment. The hydrogels react to physical stimuli such as temperature, electric field, magnetic field, light, pressure, sound, and chemical stimuli such as pH, ionic strength, solvent composition and molecular species.\(^4,5\) The formation of the hydrogel is subject to the presence of hydrophilic functional groups such as –OH, –COOH, CONH–, –CONH\(_2\) and –SO\(_3\)H.\(^6,7\) These groups impart hydrophilic nature of the hydrogel. The diffusion of water into the hydrogel due to capillary action and difference in the osmotic pressure. The pH- delicate hydrogels contain ionizable groups in the polymer, e.g. COO– ions in polyacrylic acid, which shows a response to pH change.\(^4,5\) The presence of functional groups, the nature of cross-linking agents, and the polymerization methods control the swelling capacity of the hydrogels.\(^8\) The swelling of a hydrogel is initiated by the electrostatic repugnance of the ionic charges of its network. Swelling includes larger-scale segmental movement resulting in an increased distance of separation between the hydrogel chains include
movement of water into pre-existing formed space between the hydrogel chains.\textsuperscript{9,10,11}

1.2 Chemical Structure and Application of Hydrogel

In 1960, Wichterle and Lim became the first scientists to portray hydrogels as synthetic materials that could be beneficial for applications in contact lenses.\textsuperscript{3} The hydrogels were made of poly-2-hydroxyethyl methacrylate (PHEMA).\textsuperscript{3} The contact lenses were utilized in 1962 despite the fact there was a limited. From that point forward, these gels have been put to different applications.\textsuperscript{3} Hydrogels have high swelling proportions, perfect hydrophilic properties, and a high biocompatibility.\textsuperscript{3} They are presently utilized in biosensors, in tissue engineering, in biomedicine, in agriculture, and in sorbents for purposes of removal of heavy metals.\textsuperscript{3} They have also likewise been used in the advancement of delivery systems for drugs.\textsuperscript{3,12} There has been the generation of hydrogels of natural and synthetic polymers.\textsuperscript{3} Their end application are principally in pharmaceutical, engineering, and biomedical disciplines.\textsuperscript{3} Because of the high biocompatibility and high-water absorption ability, the hydrogels are used in injectable polymeric frameworks, implants, dental materials, transdermal systems, healthy pads, agriculture, drug delivery, wound dressing and in ophthalmic applications.\textsuperscript{3,13}

Hydrogels can be classified into two kinds of cross-links.\textsuperscript{3} The classifications depend on the chemical and physical kinds of crosslinking junctions.\textsuperscript{3} Chemical crosslinking is caused as a result of the covalent bonding that has a multifunctional crosslinker.\textsuperscript{3} The physical crosslinking, otherwise, could be ascribed to the entanglement of the polymer chains. Also, it could be attributed to the intermolecular forces like Van der Waals forces, hydrogen bonding, and hydrophobic forces or crystalline forces.\textsuperscript{14} The hydrogels have an ability to absorb water a thousand times in relation to their dry
weight. This depends on the chemical and physical structures of the polymers. It is worth noting that hydrogels that are chemically cross-linked cannot dissolve in organic solvents. Conversely, hydrogels that are physically cross-linked can melt upon heating and then dissolve in organic solvents.\textsuperscript{14} Synthesis of hydrogels is brought out through free radical polymerization. The procedure could be started through photoinitiation. The polymeric spine of the hydrogels has hydrophilic groups like –COOH, -SO\textsubscript{3}H, -CONH, -OH and CONH\textsubscript{2}. These groups help the hydrogels in the assimilation of water.\textsuperscript{15} The polymer chain has oxygen and nitrogen atoms that are highly electronegative. They are in charge for the formation of the hydrogen bonds and the ingestion of the huge water quantities.\textsuperscript{14}

PHEMA hydrogels have been known to be utilized effectively for cornea implants and for vision rectification like the contact lens and the intraocular lenses.\textsuperscript{16} PHEMA is in a gel-like form and is synthesized using free radical polymerization of ethylene glycol dimethyl acrylate (EGDMA) and 2- hydroxyethyl methacrylate (HEMA) monomers. Here, the EGDMA assumes the part of a crosslinker. It is imperative to comprehend that PHEMA gels are crosslinked and are constantly produced through bulk polymerization. Consequently, results in homogeneous and straightforward networks of polymer, which include the pores.\textsuperscript{3} Permeable PHEMA that is set up in presence of huge amounts of water has a chemical identity to the homogenous hydrogel. Pores are framed as an outcome of stage detachment at the polymerization phase.\textsuperscript{3} The dispersion and the extent of pores can be changed through the modification of the states of polymerization. One of the factors to be changed contains the monomer to water ratio and the cross-linker concentration. The permeable PHEMA hydrogels have produced less interest when compared to homogenous PHEMA hydrogels. The intrigue has just been obvious when
the hydrogel started to be utilized as an essential segment of ophthalmic implants.\textsuperscript{17,18}

Hydrogels can best be characterized utilizing their water holding limits and their porousness. Upon contact with water, the polar hydrophilic groups become hydrated. They form essential bound water network and then swell, and as a result expose the groups. The hydrophilic groups are also able to interact with molecules of water, hydrophobically bound water is formed.\textsuperscript{3} The network absorbs additional water owing to the osmosis motive force of the chains. Unbounded weakening at that point happens. The physical crosslinks or the covalent crosslinks contradict the extra swelling. This prompts the effort of a withdrawal to compel on the network. The hydrogel achieves a balance swelling level. The retained water is alluded to as bulk water or free water. It fills the spaces amongst chains and the micropores.\textsuperscript{13}

1.3 Ultrasound Assisted Synthesis of TiO$_2$ and Doped TiO$_2$

Because of the dangerous environmental pollution problems caused by industries, different catalytic techniques have been studied to tackle this ever-increasing problem. A standout amongst the most generally utilized techniques to address this is heterogeneous photocatalysis which has an extraordinary potential to control watery sullies or air pollutants.\textsuperscript{19} Photocatalytic forms have been considered broadly, especially for entire annihilation or mineralization of the poisonous and non-biodegradable mixes to carbon dioxide and inorganic constituents in both water and gas phases.\textsuperscript{20} Photocatalytic degradation of several organic contaminants using wide bandgap semiconductor particles such as Titanium dioxide (TiO$_2$), ZnO and WO$_3$ has been considered extensively.\textsuperscript{21} Particularly attributable to astounding photocatalytic action, TiO$_2$ has been generally examined as a viable photocatalyst for condition purging with the insignificant danger of
the creation of unsafe byproducts.\textsuperscript{19,22} TiO\textsubscript{2} is the most prevalent photocatalyst in light of curious properties, for example, synthetic latency, appropriate band hole vitality, and non-lethality towards microorganisms. TiO\textsubscript{2} is photocatalytic stable, generally simple to create and to utilize, and can catalyze efficiently, it is not too expensive and does not represent any hazard to nature humans.\textsuperscript{23,24,25} TiO\textsubscript{2} exists in three mineral structures: anatase, rutile, and brookite. Anatase TiO\textsubscript{2} has a crystalline structure that compares to the tetragonal framework (with bipyramidal propensity) and is utilized chiefly as a photocatalyst under UV illumination. TiO\textsubscript{2} can be blended by different procedures, for example, solvothermal technique,\textsuperscript{26} hydrothermal method,\textsuperscript{27} sol-gel method,\textsuperscript{28} chemical vapor deposition (CVD),\textsuperscript{29} microwave method,\textsuperscript{30} and sonochemical method.\textsuperscript{31}

The combination of semiconductor oxide materials with traditional strategies also includes various advanced techniques. Sonochemistry has been proven to be an excellent method for the preparation of mesoporous materials. The physical and chemical effects generated by acoustic cavitation significantly influence the properties of materials.\textsuperscript{32} Under ultrasonic environment, various chemical reactions, and physical changes occur and many nano-structured materials such as alloys, oxides, metals, and biomaterials can be successfully synthesized with required particle size distribution. The extreme conditions created during ultrasonic irradiations can accelerate the hydrolysis or condensation reaction and it can induce many changes in the morphology of TiO\textsubscript{2} nanoparticles during preparation. The extreme conditions can crystallization of nanostructured materials.\textsuperscript{24,33-36} With sonochemical synthesis it is conceivable to prepare large amounts of pure anatase phase TiO\textsubscript{2} nanoparticles with the choice of a suitable precursor and appropriate experimental conditions as the yield is greater than 90\%.
Additionally, with ultrasound assisted synthesis, the time span involved is only 30-60 min. Hence, this technique can spare vitality and time and diminish the cost of definite items. The preparation is fast and reproducible compared to the regular strategies.\textsuperscript{37}

In most of the studies on TiO\textsubscript{2} synthesis by the sonochemical method, it is found that unadulterated TiO\textsubscript{2} or doped TiO\textsubscript{2} particles are readied, portrayed and their photocatalytic property has been evaluated.\textsuperscript{32, 38-40} In some investigation’s ultrasound is either utilized alone or joined with some other technique.\textsuperscript{24}

1.4 Titanium Dioxide

Titanium dioxide is a non-volatile and noncombustible powder. Its density at 25°C is 4.26 g/cm\textsuperscript{3}. The solubility of titanium oxide particles is poor in water. The material is used as a white color pigment. Among three crystalline structures, anatase is more chemically responsive than rutile.\textsuperscript{41, 42} The nanoparticles (NPs) of the mixed phases are a mixture of the two crystalline forms: rutile (R) and anatase (An). Physicochemical properties of the structures are influenced by intrinsic structure, size, shape, and surface characteristics.\textsuperscript{3} Titanium dioxide NPs are favored because they have high stability and they have photocatalytic and anticorrosive properties.\textsuperscript{43}

Titanium semiconductors have established, its place in a group of photocatalysts which are utilized for the most part for the obliteration of natural contaminations in terms of their physical properties and their long-term stability.\textsuperscript{3} In addition, they are favored in term of the suitable conducting levels. This position enables oxygen to go about as an acceptor of the photogenerated electrons.\textsuperscript{3} When titanium dioxide is irradiated up by ultraviolet light, the near UV light at a wavelength of more than 385 nanometers, is absorbed.\textsuperscript{3} There is additionally a generation of the hole and electron pairs. They then
initiate radical chain reactions and this in effect degrades the organic pollutants.\textsuperscript{44} It forms a hydrocolloid that has a high stability.\textsuperscript{3,45} In the chain reaction, the photogenerated hole helps in the chemical oxidation. It can do this either straight or tortuously through the 'OH radicals that are produced by hole oxidation of the surface adsorbed OH /H\textsubscript{2}O. The photo-generated electron, in contrast, is removed by the adsorbed oxygen. It then produces O\textsuperscript{-}\textsubscript{2} and or HO\textsuperscript{-}\textsubscript{2}.\textsuperscript{46}

The TiO\textsubscript{2} powder is difficult to be isolated and recouped from watery media.\textsuperscript{47} The suspended TiO\textsubscript{2} powder additionally tends at high fixations and decrease light assimilation efficiency.\textsuperscript{47} With this, many configurations of photoreactors have been advanced counting thin film slurry device, fluidized-bed reactor, fixed-bed reactor, and visual fiber reactor.\textsuperscript{47} Among them, the thin film slurry reactor requires the immobilization of TiO\textsubscript{2} on the surface of solid Support.\textsuperscript{47,48,49} The sol-gel technique is one of the most public methods to the immobilization which usually primes to a comparatively homogeneous TiO\textsubscript{2} layer.\textsuperscript{47}

Naturally, there are four polymorphs of titanium oxide: rutile (tetragonal), anatase (tetragonal), TiO\textsubscript{2} (B) (monoclinic), and brookite (orthorhombic).\textsuperscript{50} The rutile titanium dioxide is made up of a tetragonal structure. It has six atoms in each unit cell (Figure 1). Octahedron (TiO\textsubscript{6}) is one-sided to a slight extent. The brookite and anatase structures change to rutile phase upon attaining a certain particle size.\textsuperscript{3} The rutile phase becomes more stable than the anatase phase for particles with sizes that are greater than 14 nm. The rutile phase forms much faster than the anatase phase.\textsuperscript{3} The former is generally poor when used as a photocatalyst. The anatase titanium oxide has a tetragonal structure.
However, the distortion of TiO$_6$ octahedron is, larger in the anatase phase.$^3$

**Figure 1.** Crystal structures of rutile and anatase phases of TiO$_2$.$^{3,51}$

### 1.4.1 Toxicity of TiO$_2$ Nanoparticles

Some studies suggest recommends that titanium dioxide nanoparticles could have contributed to tumor advancement and immunomodulation impacts through the impedance of the immune cells.$^3$ This proof was found after an in-vivo investigation consider. Studies uncover that titanium dioxide nanoparticles (NPs) are more harmful than fine particles (FPs).$^3$ Titanium dioxide nanoparticles that are managed by means of the lungs cause more aggravation than the FPs of a similar chemistry at equal mass concentrations. Notwithstanding, on a similar particle surface area basis, the pulmonary inflammation is similar to the titanium oxide FPs.$^{3,4}$
1.5 TiO$_2$-PHEMA Composite

The hydrogel made up of PHEMA can be utilized to coat TiO$_2$. The PHEMA-TiO$_2$ composite can be formed. PHEMA is a thermoset polymer that cannot be corrupted by enzymes, neither would it be able to be hydrolyzed by alkaline and acid solutions. TiO$_2$ nanoparticles can be used as a filler in PHEMA. PHEMA materials have amazing biocompatible properties while the TiO$_2$ positively affects the bioactivity of cells. The calcification properties of PHEMA were incredibly upgraded when the polymer was strengthened by novel TiO$_2$. It was demonstrated that the joining of TiO$_2$ NPs could advance an enhanced arrangement of calcium phosphate and still keep up interconnectivity and porosity of the hydrogel polymers. The transformation efficiency of sun-powered photocells has been turned out to be 3.5 % when a TiO$_2$-PHEMA electrode is used. The composites can be enhanced to upgrade light reaping, decrease recombination of charge, and enhance the infiltration of electrolytes of the polymer in the pores.

1.6 Cu(II) Nanocluster-Grafted, Nb-Doped TiO$_2$

Titanium dioxide (TiO$_2$) has pulled in significant ongoing consideration as an efficient photocatalyst for applications, for example, in water splitting, organic decomposition, and photovoltaic cells. However, on the grounds that TiO$_2$ is a wide band-hole semiconductor, with band hole estimations of 3.2 and 3.0 eV for the anatase and rutile forms, individually, it can only be started under ultraviolet (UV) light irradiation, thus limiting its practical applications. To raise the usage of sunlight based and indoor light sources, TiO$_2$ has been doped with several transition metal
cations, such as Cr, Mn, Fe, Pb, and Cu, and anions, with N, C, and S, trying to expand the light absorption limit into the noticeable visible light region.\textsuperscript{66-75} Despite broad research effort being made to alter the properties of TiO\textsubscript{2}, most doped TiO\textsubscript{2} frameworks remain unacceptable for practical utilization on the grounds that their quantum efficiencies (QEs) under the visible light are too low to support the efficient photocatalytic reactions.\textsuperscript{55,66-77}

In the case of cationic doping, the expansion in visible light affectability is for the most part caused by polluting influence levels in the forbidden band, which go about as recombination places for photogenerated charge.\textsuperscript{61-63} Conversely, anionic doping of TiO\textsubscript{2} mostly introduces isolated levels above the valence band (VB) that involve holes generated with lesser oxidation power and movement than those in the VB, subsequent in low photocatalytic performance.\textsuperscript{76,77} Lately, the surface change of TiO\textsubscript{2} with Cu(II) or Fe(III) nanoclusters appeared to expand its visible-light sensitivity without exciting debasement levels in the band gap.\textsuperscript{55,78-83} Under visible-light irradiation, electrons in the VB of TiO\textsubscript{2} are eager for these surface nanoclusters through an interfacial charge exchange (IFCT) process.\textsuperscript{84,85} Concurrently, the excited electrons are expended in the multi-electron decrease of oxygen-interceded by the nanoclusters.\textsuperscript{86-91} Thus, Cu(II) or Fe(III) nanocluster-grafted TiO\textsubscript{2} shows a high QE under visible light. Nonetheless, the limit of this photocatalytic system for visible-light assimilation is restricted because IFCT only happens at TiO\textsubscript{2} particle/nanocluster interfaces.\textsuperscript{55} Surface nanoclusters have additionally exhibited the growth of the noticeable light activities of semiconductors.\textsuperscript{81,83,92-95} For instance, Ti\textsuperscript{3+} self-doped TiO\textsubscript{2}, which is indolent even under
UV light irradiation, is changed into an efficient visible-light-sensitive photocatalyst by the surface grafting of Cu(II) or Fe(III) nanoclusters.⁸¹ Though this result shows that photogenerated electrons are transferred from the doping levels to the surface Cu(II) or Fe(III) nanoclusters, the QEs of metal-doped TiO₂ photocatalysts cannot surpass that of Cu(II)- or Fe(III)-grafted TiO₂, as the charge transfer is inadequate from doped levels to surface nanoclusters.⁵⁵ Consequently, efficient charge transfer between the doping levels and surface nanoclusters is basic for the photocatalytic execution of these systems.⁵⁵

To accomplish this rule, the idea of vitality level coordinating between the doped particles and surface-joined nanoclusters has been as of late analyzed utilizing Fe(III) particle doped and -grafted TiO₂ as a mod system.⁵⁵,⁸² The Fe(III)-doped and -grafted TiO₂ system displays a QE of 47.3% and a response rate of 0.69 mmol h⁻¹, suggesting the plausibility of this method.⁵⁵ Compared with Fe(III)-based compounds, cupreous compounds have the additional benefit of essential anti-pathogenic properties under both murky and light conditions,⁹⁶-⁹⁸ as was confirmed for a Cu-deposited thin film of TiO₂.⁵⁵,⁹⁶ Notwithstanding, this useful characteristic, the visible-light absorption and quantum efficiencies of Cu(II)-grafted TiO₂ is a lesser amount of than those of Fe(III)-grafted TiO₂.⁷⁸,⁷⁹ Accordingly, for the improvement of Cu(II)-based photocatalysts that are appropriate for indoor applications(for diminishing concoction bothering or spread of irresistible sickness), it is compulsory to markedly grow the visible-light sensitivity and photocatalytic efficiency of these materials.⁹⁶-⁹⁸ Constructed on the concept of energy level matching, we assumed that this could be accomplished by modifying TiO₂ to have matching interband energy levels to the redox potential of Cu(II) nanoclusters.⁵⁵
Niobium (Nb)-doped TiO$_2$ has attracted current attention because of its electronic properties and potential applications in the straightforward conductive oxide.\textsuperscript{55} Photovoltaic cells and devices.\textsuperscript{55} Hypothetical and exploratory studies have revealed that the doping of TiO$_2$ with Nb ions produces an energy level of 0.1 to 0.2 eV below the conduction band (CB),\textsuperscript{99-102} a value that closely matches the redox potential of Cu$^{2+}$/Cu$^+$ (0.16 V vs. SHE, pH = 0).\textsuperscript{78,79} Though, Nb-doped TiO$_2$ exhibitions little efficiency for photocatalytic reactions because pentavalent Nb ions are substituted for tetravalent Ti leading to the bulk formation of Ti$^{3+}$ species that attend as recombination centers.\textsuperscript{81,99} As a replacement for, Cu(II) nanocluster-grafted (Cu(II)–TiO$_2$) can raise its visible-light activity without the impurity levels in the band gap. But, the visible-light assimilation of Cu(II)–TiO$_2$ is restricted because IFCT proceeds only at the bulk/nanocluster interface.\textsuperscript{55} Figure 2 delineated coupling of the bulk doping of Nb ions and surface grafting of Cu(II) clusters on TiO$_2$ under visible light irradiation. The excited electrons in the doped Nb levels would transmit to the Cu(II) nanoclusters in arrears to their comparable energy levels.\textsuperscript{55}

![Figure 2](image_url)

**Figure 2.** Proposed photocatalytic processes for Nb$^x$Ti$_{1-x}$O$_2$, Cu(II)–TiO$_2$ and Cu(II)–Nb$_x$Ti$_{1-x}$O$_2$, respectively.\textsuperscript{55}

Metal ion dopants, such as Fe,\textsuperscript{103,104} V,\textsuperscript{104,105} Bi,\textsuperscript{104,106} and Sm,\textsuperscript{104,107} can go about as electron or hole traps and, therefore, decrease the electron-hole pair
recombination rate.\textsuperscript{108} Surely, extraordinary endeavors have been committed to examining TiO_2 doped with metal particles. Among metal particles, uncommon rare earth metals regularly fill in as an impetus or elevate reactant properties due to their not entirely possessed 4f and 5d blank orbitals. Sm\textsuperscript{104-107,109} has gotten much consideration because of its high effectiveness in enhancing photocatalytic movement and additionally its low cost. Torres et al. have demonstrated that Sm\textsuperscript{3+} doped TiO_2 shows enhanced photocatalytic activity under light deprivation of diuron herbicide related to that of TiO_2.\textsuperscript{104,108}

Deng et al. have set mesoporous Sm-TiO_2 and presented that the Sm\textsuperscript{3+} doping improved the photocatalytic activity of TiO_2 in the removal of gassy acetone and methanol.\textsuperscript{10} In the meantime, the doping of some non-metal ions, such as N,\textsuperscript{104,110} C,\textsuperscript{104,111} S,\textsuperscript{104,112} or B\textsuperscript{104,113} likewise appears to be active for enhancing the photocatalytic activity of TiO_2. Additionally, co-doped TiO_2 with two or more ions has been studied. The theoretic and empirical finding suggest that the photocatalytic activity of TiO_2 co-doped with more than one ion is better than that of the TiO_2 doped with a single ion, due to the synergistic effect of co-doped ions.\textsuperscript{104,114,115} Huang et al. have made Sm and N co-doped TiO_2 and confirmed that the co-doped photocatalysts have improved activity than that of N doped TiO_2 in the dissolution of 4-chlorophenol.\textsuperscript{104,113} Though, there is no statement on the co-doping of C and Sm ions into the TiO_2 lattice.\textsuperscript{104}

The heterostructure between the anatase and rutile phases of TiO_2 was established to be useful in controlling the photo-produced charge migration cross the heterojunction interface, and attractive in the charge separation.\textsuperscript{104,113-117} So the mixed phase TiO_2
displays higher photocatalytic activity than that of the separate components. Among the tested TiO$_2$ materials, it has been revealed in many studies that there is a positive interaction between anatase and rutile TiO$_2$ particles in Degussa P25, which is commonly believed as the benchmark. The synergistic effect of the two phases is an approach to promoting the electron-hole separation, hence enhancing the photocatalytic activity.$^{118-120}$ Really, the experimental discovery suggests that the effect was related to the relative Fermi levels and shapes of anatase and rutile particles, indicating that the charge migration between the mixed phases is reliant on the experimental conditions.$^{104,121-123}$

Moreover, the synergetic impact amongst anatase and rutile is another purpose for the high photocatalytic activity. It has been described that the active arrangement occurs in the band limits between both TiO$_2$ phases with anatase keeping the higher electron affinity and work function.$^{104,120,124}$ Upon consolidating these two phases, an astounded band gap is designed, and the synergistic effect causes an efficient charge separation across the phase intersections. Consequently, the probable photodegradation machinery of the as-prepared Sm and C co-doped TiO$_2$ is shown in (Figure 3).$^{104}$

![Figure 3](image_url)

**Figure 3.** Schematic diagram of the twin synergistic effects of Sm-C Co-doping and the mixed phase TiO$_2$.$^{104}$
1.7 Characteristics of Metal Ions in Poly (2-hydroxyethyl methacrylate) Hydrogels

The previous study reported that Ca\(^{2+}\) ions not only diffuse through PHEMA hydrogel networks.\(^{125}\) Ca\(^{2+}\) ions have an irresistible affinity to interact with oxygen atoms.\(^{125}\) Even though such interactions may also take place with the hydrophobic groups or areas of the polymer.\(^{125}\) Most studies on polymer complexation with Ca\(^{2+}\) ions have been achieved in systems where there is a strong interaction between the Ca\(^{2+}\) ions and hydroxyl or carboxylic groups.\(^{125}\) Under these conditions, the polymer interaction with the Ca\(^{2+}\) ions can be suitably determined by analyzing infrared spectral or zeta potential data. For instance, from analysis of infrared spectra, Elvira and Roman,\(^{125}\) revealed that the formation of stable Ca–polymer complexes in polyacrylates covering aminosalicylic acid was because of ionic interactions between Ca\(^{2+}\) ions and hydroxylic or carboxylic groups. Amongst the three kinds of oxygen atoms in PHEMA, hydroxyl oxygen atoms appear to be the most sensitive to the presence of Ca\(^{2+}\) ions. Complexation at the ester oxygen atoms was also shown by a new band in the infrared spectra at 1,550 cm\(^{-1}\). Conversely, there were no signals that the hydrophobic domains in the backbone and the methyl groups at the side chain of PHEMA interact significantly with Ca\(^{2+}\) ions.\(^{125}\)

1.8 Aim of Research

The research here is focused on the investigation titanium dioxide in PHEMA hydrogels incorporated by metal ions. This research objective is to find out if Cu(II) can be a metal ion to be incorporated into TiO\(_2\) in PHEMA.
CHAPTER II
MATERIAL AND METHODS

All chemicals were of analytical grade, and all the copper solutions were prepared using deionized (DI) water.

2.1 Materials

HEMA (2-hydroxyethyl methacrylate) supplied by Electron Microscopy Sciences and ethylene glycol dimethyl acrylate (EDGMA) from Acros Organic, were passed through a packed column to remove the inhibitors. Sodium metabisulfite (SMBS, Fisher Scientific, USA) and ammonium persulfate (APS, Acros, lot # B0132486) were used as initiators. Nano titanium (IV) oxide of pure anatase, pure rutile, and mixed phase was received from Aldrich-Sigma (lot # MKBJ0873V). The titania of the mixed phase comprised of 84% anatase and 16% rutile. Copper(II) chloride dihydrate was also obtained from Alfa Aesar (lot # W18A029).

2.2 Hydrogel PHEMA Synthesis

The procedure was carried out in a 10 mL beaker to which 4 mL of HEMA were mixed in 2 mL of DI water; 15 µL of EDGMA 0.25 wt% was added to the solution then purged using argon gas for 30 minutes. The reaction was started by the initiators 0.0429 mg of SMBS and 0.0429 mg of APS. After 2 minutes, the solution was pipetted into a chamber consisting of two plates by syringe and at that point held at room temperature
for 12 hours.

2.3 Synthesis of TiO$_2$-PHEMA Hydrogel

HEMA (4 mL) and 2 mL of DI water were added to a 10 mL beaker, followed by 15 µL of EDGMA and 0.42 mg of TiO$_2$ was added to the solution. The mixture was bubbled with argon gas for an hour. Subsequently, at room temperature, the initiators were added into the stirred solution at the mixture was stirred for 2 more minutes. The obtained mixture then was transformed with a syringe into a chamber consisting of two glass plates. Figure 4 illustrates the synthesis of TiO$_2$-PHEMA hydrogel.

![Synthesis of TiO$_2$-PHEMA hydrogel](image)

Figure 4. Synthesis of TiO$_2$-PHEMA hydrogel.$^3$

2.4 Absorption

Copper chloride has a chemical formula of CuCl$_2$.2H$_2$O. It has a strong absorption peak at $\lambda_{\text{max}} = 800$ nm. A stock solution was prepared by dissolving 6.72 mg of CuCl$_2$.2H$_2$O into 50 ml of DI water.
2.5 Characterization

2.5.1 UV-visible Spectroscopy

The absorption spectra of Cu(II) solution were recorded on a CARY 500 Scan. The absorption maximum was found at 800 nm for the aqueous solution.

2.5.2 X-ray Powder Diffraction (XRD)

X-ray powder diffraction Panalytical Empyrean 2 with an RT spinner stage in transmission mode with a copper-focusing mirror is the analytical technique used for the identification of unit cell dimensions and crystalline materials. The crystalline titanium dioxide nanoparticles have intense XRD patterns with sharp lines corresponding to the TiO$_2$ phases.

2.5.3 Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transmission Infrared Spectroscopy (FTIR) Perkin Elmer model 1600 is a useful technique to determine organic samples. Infrared (IR) spectrums were recorded with KBr as a medium.

2.5.4 Fluorescence Plate Reader

Fluorescence plate reader (Synergy Hybrid Reader H1-BioTek) is designed for the measurement of fluorescence excitation and emission spectra. The fluorescence includes two grating monochromators, one for irradiating a sample with monochromatic light in the 200 to 800 nm range (excitation monochromator), and the other for permitting selective measurement of the intensity of the light emitted by the sample in the 220 to 900 nm range (emission monochromator).
CHAPTER III
RESULTS AND DISCUSSION

3.1 Density Study ($\varepsilon$)

After polymerization, the mass of 5 samples of PHEMA hydrogel was measured in the air than in the hexane by using the special technique in order to analyze the density in three conditions: relax, swelling (wet), and dry. By using Archimedes' principle, we could calculate the volume of the samples. Determining the volume is calculated as

$$V = \frac{m_{\text{air}} - m_{\text{hex}}}{\rho_{\text{hex}}}$$  \hspace{1cm} (1)

where $V_r$ is the volume of the relaxed gel, $m_{\text{air}}$ is the mass of the gel in the air, $m_{\text{hex}}$ is the mass of the gel in hexane, $\rho_{\text{hex}}$ is the density of hexane (0.659 g/mL). The samples were soaked in DI-water for 3 days at room temperature to achieve equilibrium swelling, then samples were weighted in air and hexane for wet condition. The volume-swelling ratio of gel induced by water was calculated as the following:

$$Q = \frac{1}{V_{2,s}} \cdot \frac{V_s}{V_d}$$  \hspace{1cm} (2)

where $Q$ is the swelling ratio which is used to determine the volume fraction of the gel in the swollen and dry conditions. $V_d$ is the volume of the dry gel. $V_s$ is the volume in the swollen state and $V_{2,s}$ is the volume fraction in swollen the state.
The mesh size ($\xi$) and the molecular weight between crosslinks ($M_c$) were evaluated according to the equilibrium swelling result.

The mesh size of the gel can be expressed as the following: $^{3,10}$

$$\xi = (V_{2\,s})^{1/3} \left( r_0^2 \right)^{1/2}$$

where $r_0$ is the end-to-end distance of the polymer between two consecutive crosslinks and can be expressed by the following equation:

$$\left( r_0^2 \right)^{1/2} = \left( \frac{2M_c}{M_r} \cdot Cn \right)^{1/2}l$$

where $M_c$ is the average molecular weight between crosslinks, $M_r$ is the molecular weight of a repeating unit which is 130.4 for PHEMA. $^3$ $Cn$ is the characteristic ratio of the PHEMA hydrogel, and $l$ is the bond length (Figure 5 and Figure 6).

**Figure 5.** The proposed design of PHEMA nanocomposite hydrogel crosslinked with EGDMA, and $\xi$ is the mesh size of a hydrogel. $^3$
The swelling ratio of PHEMA hydrogel, TiO$_2$-PHEMA mixed hydrogel had a swelling ratio higher than the swelling ratio of either TiO$_2$-PHEMA anatase and TiO$_2$ PHEMA rutile because it had the free volume to be expanded for solution or water. The mesh size of the different hydrogels suggests that the adding of the nanoparticle in the hydrogel causes reducing of the mesh size. After the density test, the samples were examined in different experiments. The swelling ratio and the mesh size of different hydrogels are in Table 1.

**Table 1**: The Swelling Ratio (Q) and Mesh Size ($\xi$) of Synthesized Hydrogel- TiO$_2$-Anatase, Rutile and Mixed

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q</th>
<th>$\xi$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-PHEMA Anatase</td>
<td>1.76</td>
<td>27.33</td>
</tr>
<tr>
<td>TiO$_2$-PHEMA Rutile</td>
<td>1.87</td>
<td>27.86</td>
</tr>
<tr>
<td>TiO$_2$-PHEMA Mixed</td>
<td>5.21</td>
<td>39.03</td>
</tr>
</tbody>
</table>
3.2 UV-visible Spectroscopy

The absorption spectra of Cu(II) were recorded on a CARY 500 Scan. The absorption maximum was found at 800 nm in the aqueous solution (Figure 7).

![Absorbance spectrum](image)

**Figure 7.** The UV-Vis spectra of copper(II) in water.

According to Beer’s law, the concentration of Cu(II) in the solution should be proportional to the absorbance at 800 nm. As a result, $A/A_0$ would be equal to $C/C_0$, where $A$ is the absorbance of the solution at time $t$ after turning on the lamp, and $A_0$ is the absorbance of the solution at time zero. It is noteworthy that when TiO$_2$ was soaked in the solution. The absorption of the visible band at 800 nm decreases with the increasing duration of time.

The band at 800 nm was monitored by UV-Vis. For the anatase phase TiO$_2$-PHMEA gel in copper solution, the band intensity decreased after 7 days, then the band intensity decreased gradually up to (9 days + 10 hr). Subsequently, the band intensity was reduced in that it illustrates the anatase phase TiO$_2$–PHEMA gel was saturated Cu(II)
Figure 8. The UV-Vis spectra of (1) copper solution (2) TiO$_2$ (A)-PHEMA-Cu(II) (7 days) and (3) TiO$_2$-(A)-PHEAM-Cu(II) (9 days+ 10 hr).

For the rutile phase TiO$_2$-PHMEA gel in copper solution, the band intensity decreased after 3 days then the band intensity decreased more to come (3 days + 6 hr). Afterward, the band intensity was reduced that suggesting the rutile phase TiO$_2$–PHEMA gel was saturated with Cu(II) (Figure 9).
Figure 9. The UV-Vis spectra of (1) copper solution (2) TiO$_2$ (R)- PHEMA-Cu(II) (3 days) and (3) TiO$_2$ (R)-PHEAM-Cu(II) (3 days + 6 hr).

For the mixed phase TiO$_2$-PHMEA gel in copper solution, the band intensity reduced after 12 hr. Afterwords, the band intensity continued to decrease all the way 20 hr. The then, the band intensity was not reduced any more that illustrating that the mixed phase TiO$_2$ – PHEMA gel was saturated with Cu(II) is listed displayed (Figure 10). The comparison of the spectra of three phases of TiO$_2$- PHEMA Hydrogel with Cu(II) is listed displayed (Figure 11). The color change of three phases of hydrogel was observed during a period when the Gel was saturated ions of copper. The color was change for the TiO$_2$ (A)-PHEMA – Cu(II) after 226 hr. However, the color was change for the TiO$_2$ (R)-PHEMA – Cu(II) after 78 hr. While the color was change for the TiO$_2$ (M)-PHEMA – Cu(II) after 20 hr (Figure 12).
Figure 10. The UV-Vis spectra of (1) copper solution (2) TiO₂ (M)-PHEMA-Cu(II) (12 hr) and (3) TiO₂ (M)-PHEMA-Cu(II) (20 hr).

Figure 11. The UV-Vis spectra of comparison between three phases TiO₂-PHEMA.
Figure 12. The color change of three phases of hydrogel during a period of time.

According to Beer’s law, the concentration of copper in the solution should be proportional to the absorbance at 800 nm. The absorption of free copper without hydrogel was (Abs 0.13). The absorption of Cu(II) in TiO₂- PHEMA Hydrogel at the time in Table 2. The UV-Vis spectra of Cu(II)-TiO₂ for three phases PHEMA at the time (Figure 13).

Table 2: The Absorption Cu(II) in New TiO₂- PHEMA Hydrogel at the Time

<table>
<thead>
<tr>
<th></th>
<th>Anatase Phase- Cu (II)</th>
<th>Rutile Phase- Cu (II)</th>
<th>Mixed-Phase- Cu (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs</td>
<td>Time (hr)</td>
<td>Abs</td>
<td>Time (hr)</td>
</tr>
<tr>
<td>0.133</td>
<td>0</td>
<td>0.133</td>
<td>0</td>
</tr>
<tr>
<td>0.132</td>
<td>168</td>
<td>0.135</td>
<td>72</td>
</tr>
<tr>
<td>0.126</td>
<td>226</td>
<td>0.129</td>
<td>78</td>
</tr>
<tr>
<td>0.113</td>
<td>226</td>
<td>0.048</td>
<td>174</td>
</tr>
<tr>
<td>0.031</td>
<td>328</td>
<td>0.010</td>
<td>250</td>
</tr>
</tbody>
</table>
Figure 13. The UV-Vis spectra of Cu(II) in the solution after being in contact three phases of TiO$_2$ at different times.

3.3 Fourier Transform-Infrared Spectroscopy

The chemical structures of PHEMA - TiO$_2$ were investigated by FT-IR spectra in KBr. Figures 14, 15 and 16 show FT-IR spectra of TiO$_2$- PHEMA hydrogels along with nanotitania. The absorption band at 1727 cm$^{-1}$ indicates the presence of C=O stretching and the band at 3427 cm$^{-1}$ corresponds to O-H stretching. The C=O bands are solely from PHEMA while O-H bands could come from both PHEMA and titania. The OH groups exist on the surface of the NPs of titania. In TiO$_2$-PHEMA there is no other significant band in the range of 1550 cm$^{-1}$ to 1750 cm$^{-1}$ except the C=O from PHEMA. Upon up taking Cu(II), the TiO$_2$-PHEMA showed a nears absorption band at 1595 cm$^{-1}$. The band was observed no matter what type of titania in TiO$_2$-PHEMA. It is tentatively ascribed to another of carbonyl absorption band, i.e. Cu(II)- coordinated carbonyl. The absorption band at 1595 cm$^{-1}$ indicates the presence of C=O--Cu. The peak of C=O--Cu at 1595 cm$^{-1}$
for PHEMA- TiO₂ anatase was weak. However, the peak of C=O--Cu at 1595 cm⁻¹ for PHEMA- TiO₂ rutile and mixed phase were strong, that delineates the hydrogel with rutile or mixed phased titania contain more Cu(II) than hydrogel- anatase. The peak O-H at 3366 cm⁻¹ for PHEMA without TiO₂ was very broad and shifted in TiO₂-PHEMA, and even more in Cu(II)- contain of TiO₂-PHEMA.

![Diagram](image)

**Figure 14.** FT-IR spectra of TiO₂ (A)-PHEMA- Cu(II).
**Figure 15.** FT-IR spectra of TiO$_2$ (R)-PHEMA- Cu(II).

**Figure 16.** FT-IR spectra of TiO$_2$ (M)-PHEMA- Cu(II).
TiO$_2$ (M)-PHEMA hydrogel was submerged in different concentration of copper solutions. Subsequently, the solutions were slightly shaken for 5 hr. The gels were taken out of the solution and were examined by FT-IR spectra. Figure 17 illustrates two bands in the FT-IR spectra of TiO$_2$-PHEMA-Cu(II) one band at 1719 cm$^{-1}$, indicating the presence of stretching vibration of free C=O and the other band at 1595 cm$^{-1}$, indicating the presence of coordinated C=O (C=O--Cu). The peak at 1595 cm$^{-1}$ for TiO$_2$ (M)-PHEMA-Cu(II) from C$_4$ concentration was stronger than peaks from C$_3$, C$_2$ or C$_1$ because C$_4$ contained the highest concentration of copper ions. The different concentrations of the copper solution are shown in Table 3. As more free groups C=O decreased more C=O groups from C=O--Cu coordinated increased (Figure 18).

![Figure 17](image_url)  
*Figure 17. FT-IR spectra of TiO$_2$ (M)-PHEMA-Cu(II) in different concentration of Cu(II).*
Table 3: TiO₂ (M)-PHEMA in the Cu(II) Solution for 5 Hours at Room Temperature

<table>
<thead>
<tr>
<th>Concentrations of solution Cu (II) (mol/L)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁ 2.0x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>C₂ 4.0x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>C₃ 6.0x10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>C₄ 1.0x10⁻³</td>
<td></td>
</tr>
</tbody>
</table>

Figure 18. Percentage of copper ions of C=O free and C=O–Cu coordinated.

TiO₂ (M)-PHEMA hydrogels were placed in the Cu(II) solution 10⁻³ M under the condition. The solutions were slowly shaken. The gels stayed in the solution for period time (1,2,3,4,5,6,7 and 24 hr). The hydrogels then were investigated by FT-IR spectra one absorption band at 1715 cm⁻¹ as of them showed anther absorption band at 1595 cm⁻¹. The band at 1595 cm⁻¹ for gels exposed to the Cu(II) solution for longer time. was shaken
a long time. At the same time, the band at 1715 cm$^{-1}$ decreased accordingly. This decrease correlates with the increase of band at 1595 cm$^{-1}$ clearly demonstrates the origin of change, i.e. the carbonyl group (Figure 19).

![FT-IR spectra of TiO$_2$ (M)-PHEMA-Cu(II) same concentration and a different time.](image)

**Figure 19.** FT-IR spectra of TiO$_2$ (M)-PHEMA-Cu(II) same concentration and a different time.

### 3.4 X-ray Powder Diffraction

The scanning was carried out from 10° to 80° with a step size of 0.02° and a count time of 1.5 s/step. Figure 20 represents X-ray diffraction patterns of phases TiO$_2$ (A)-PHEMA, the high-intensity diffraction peaks corresponding to the anatase TiO$_2$ phase at
$2\theta = 25, 37, 55, 48, 63$ and $70^\circ$ were observed. The high-intensity diffraction peaks corresponding to TiO$_2$ (A)-PHEMA-Cu(II) were observed at $2\theta = 17, 21, 30, 35, 55$ and $58^\circ$. The diffraction at $2\theta = 25, 27$ indicates the presence of rutile (Figure 21). The high-intensity diffraction peaks corresponding to the TiO$_2$ (R)-PHEMA-Cu(II) were corresponded with anatase phase. For TiO$_2$ (M)-PHEMA were observed at $2\theta = 25, 27, 55, 63$ and $70^\circ$. The high-intensity diffraction peaks TiO$_2$ (M)-PHEMA-Cu(II) were correlated with anatase and rutile phase -PHEMA (Figure 22).

**Figure 20.** XRD patterns for TiO$_2$ (A)-PHEMA and TiO$_2$ (A)-PHEMA-Cu(II).
Figure 21. XRD patterns for TiO$_2$ (R)-PHEMA and TiO$_2$ (R)-PHEMA-Cu(II).

Figure 22. XRD patterns for TiO$_2$ (M)-PHEMA and TiO$_2$ (M)-PHEMA-Cu(II).
3.5 The Fluorescence Plate Reader

The measurement of the intensity of the light emitted by the sample was conducted in the 300 to 500 nm range (emission) and 270 nm (excitation). Figure 23 illustrates TiO$_2$ (M)-PHEMA and TiO$_2$ (M)-PHEMA-Cu(II) were investigated by the Fluorescence Plate Reader. The scanning was carried out from 300 nm to 500 nm with a step size of 1 nm. The absorption band at 420 nm indicates the presence of Cu in the PHEMA-TiO$_2$ mixed phase. The quenching takes place when Cu(II) is absorbed into the hydrogels (TiO$_2$ (M)-PHEMA-Cu(II)) (Figure 23).

![Fluorescence Plate Reader](image)

**Figure 23.** Fluorescence plate reader for TiO$_2$ (M)-PHEMA-Cu(II).
3.6 Efficient TiO$_2$-PHEMA-Cu(II)

The samples of TiO$_2$-PHEMA-Cu(II) hydrogels were exposing by sunlight. Subsequently, the samples were measured by UV-vis for different time periods. The results show that the mixed phase TiO$_2$ (M)-PHEMA is found to be the most efficient for the absorption of Cu(II)(Figure 24).

![Figure 24. UV-Vis spectra for phases TiO$_2$- with Cu(II) in hydrogel.](image-url)
CHAPTER IV

CONCLUSION

All three TiO$_2$ NPs have been used to obtain TiO$_2$-PHEMA hydrogels. The mixed phase TiO$_2$(M)-PHEMA is found to be the most efficient for the absorption of Cu(II). FT-IR has been found to an effective tool to recognize the interaction of Cu(II) with PHEMA in TiO$_2$-PHEMA hydrogels. We have demonstrated that Cu(II) ions are coordinated to PHEMA in TiO$_2$-PHEMA hydrogels. Time-dependent and concentration-dependent studies revealed that Cu(II) is coordinated to carbonyl (C=O) groups. The IR band at 1595 cm$^{-1}$ emerged when the interaction took place. The intensity of the band is directly proportional to time during which the hydrogel is exposed to the solution or to concentration of Cu(II) solution. Fluorescence study also shows the quenching takes place when Cu(II) is absorbed into the hydrogels. XRD also demonstrates the presence of Cu(II) in the hydrogels.
REFERENCES


