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RESEARCH ON SYNTHESIS AND APPLICATION ORIENTATION OF NANOSTRUCTURED CARBON MATERIALS FROM CHITIN SOURCE

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INTRODUCTION

1. Reason for choosing research topic

Hierarchical biomaterials inspired by nature are often developed by molecular self-assembly of micro- and nanoscale elements [1]. Multilayer self-assembly from biopolymers, particularly liquid crystal (LC) layers, is a reliable biomimetic approach to fabricate sustainable materials with hierarchical structures, similar to micro/nanoscale biomaterials found in nature [2]. Biopolymers, especially polysaccharides with hierarchical structures and self-assembly capabilities, are used as biological templates and carbon sources for synthesizing solid-state materials with superior properties due to their ability to mimic, replicate, and transform [1, 2].

Chitin - the second most abundant natural resource on Earth after cellulose - is a biopolymer widely used in various fields due to its properties, such as biocompatibility, biodegradability, non-toxicity and adsorption capacity, among others [3]. Over the years, scientists developed new materials from the original source of chitin. When hydrolyzed in acidic media, the naturally amorphous chitin fibers are broken down and forming crystalline regions with a rod-shaped nanostructure. These rod-shaped chitin nanocrystals can be stable in water and can self-organize into anisotropic LC at a critical concentration [4]. In 1992, Kresge and his colleagues made a breakthrough in synthesizing templates for porous materials. These templates have the special ability to capture complex liquid crystal organizations when solidified to create a new material. This discovery led to the use of chitin liquid crystals as guiding templates for the assembly of other materials. Additionally, based on the process of evaporation-induced self-assembly (EISA), liquid crystals, after mixing, assembling and evaporating the solvent, can form a layered material with mechanical strength greater than the original monolayers. For example, the assembly of LCs of graphene oxide (GO) nanosheets and chitin nanofibers through the EISA method results in a layered support structure for assembling other substances, thereby creating new materials with numerous advantages. TiO_2 is a metal oxide that is being widely studied for its photocatalytic properties. However, TiO_2 only shows photocatalytic activity under ultraviolet light, and it is difficult to separate and recover from the solution after the reaction, leading to the possibility of secondary pollution. Assembling TiO_2 semiconductors with layered supports into a nacre-like structured material is a feasible approach to fabricate efficient photocatalytic films while addressing these drawbacks. These TiO_2/rGO/chitin composites can function as a photocatalytic inorganic-organic hybrid film for environmental applications [5]. In such chitin-based membranes, GO nanosheets can incorporate TiO_2 nanoparticles to form a semiconductor-graphene heterojunction with potential synergistic interactions, which can enhance the charge transfer efficiency and improve the reaction rates [6]. This combination can not only create a new class of photocatalytic membranes for photodegradation, water splitting, and air treatment, but also make them useful for energy storage, conversion and gas sensing.

Chitosan is a deacetylated form of chitin, prepared by treating chitin with strong bases. Similar to natural chitin, chitosan retains its complex hierarchical structure and possesses valuable properties, making it a renewable resource for developing applications in drug delivery, gelling, absorbents, and tissue engineering. In addition, chitosan is a cationic polymer, which is often protonated in acidic to dissolve into a homogeneous solution. Acidic chitosan solutions can self-assemble, either independently or with additives, upon drying to form functional films with hierarchical organization. The chitosan structure can be used as a template for solid-state materials to produce hierarchical porous structures with high surface areas. Furthermore, chitosan is also a carbon source for research and development of carbon materials used in energy storage and conversion applications [7]. After carbonization and conversion, the hierarchical porous structure of chitosan macromolecules and/or nanofibers can be preserved in bio-derived carbon materials. The chemical stability of chitosan, combined with its structure, composition, and self-assembly ability, is attractive for exploitation and utilization for the improvement and innovation of advanced functional materials to enhance the applications of the materials. Chitosan itself can be converted into a water-soluble form to create gels, fibers, and films or can even undergo carbonization to decompose into luminescent carbon nanorods [8]. Despite these capabilities, little attention has been paid to fully exploiting chitosan’s dual role as both a template and a carbon source.

Based on the properties of chitin and chitosan, the thesis with the topic: "*Research on synthesis and application orientation of nanostructured carbon materials from chitin source*" was conducted.

2. Research objectives

- Investigation of the synthesis of photocatalytic materials based on self-assembling liquid crystal templates of chitin, TiO_2 and GO; Evaluation of the applicability of the materials in photocatalysis.
- Based on the ability of chitosan as a template and carbon source, synthesize carbon materials and mesoporous silica, and study the application potential of the synthesized carbon materials.

3. Research content

Based on the objectives outlined above, this thesis focuses on the following main areas of research:

1. Synthesis and characterization of TiO_2/rGO/chitin composite materials using the liquid crystal self-assembly process involving graphene oxide (GO) nanosheets, peroxotitanate and chitin nanosheets. The applicability of these materials will be evaluated in the photochemical degradation of methyl blue (MB);

2. Synthesis of mesoporous carbon materials and mesoporous silica membranes from chitosan and silicon alkoxide precursors. The potential application of the synthesized materials as supercapacitor electrodes will be investigated.

4. The new contributions of the thesis

1. The layered TiO_2/rGO/chitin composite films were successfully fabricated through the liquid crystal (LC) self-assembly of chitin, graphene oxide (GO), and peroxotitanate. The simultaneous assembly of multiple layers promotes the formation of a lamellar structure that mimics the nacreous arrangement found in solidified rGO/chitin composites. This process results in the self-assembly of LC GO and LC chitin into a flexible, nacre-mimicking membrane, where chitin layers are wrapped around rGO nanosheets. The intrinsic electron mobility of the rGO nanosheets, combined with the mechanical strength of the chitin nanocrystals, imparts enhanced catalytic support functions to these reinforced membranes. The nacre-mimicking membrane material is homogeneously integrated with TiO_2 nanoparticles through the simultaneous LC co-assembly of GO, chitin, and peroxotitanate. The resulting multilayered TiO_2/rGO/chitin composites function as efficient photocatalytic membranes for the mineralization of organic compounds. These TiO_2/rGO/chitin

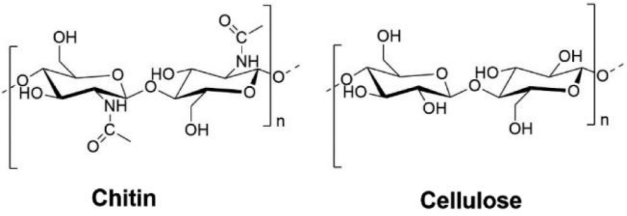
materials were demonstrated to be effective for the photochemical degradation of methyl blue (MB) solution, exhibiting high degradation efficiency and excellent recyclability.

2. A layered mesoporous carbon material was synthesized from chitosan - a derivative of chitin. The extracted chitosan macromolecules were able to self-assemble in an acidic medium to form a transparent, crack-free, flexible chitosan bioplastic-like membrane with a layered structure drying. Tetramethylorthosilicate (TMOS) was condensed onto chitosan in an acidic environment to cast a silica/chitosan composite membranes by self-assembly through evaporation. The silica/chitosan membrane was carbonized into a silica/carbon composite material, which was selectively etched to remove the silica components, resulting in a layered, mesoporous carbon material suitable for supercapacitor applications. Possessing the integrity of the semiconductor properties, the sustainable carbon material has significant potential for the development of energy storage materials. Additionlly, the process of calcining the silica/chitosan membrane in air produces free-standing porous silica films, which can be explored for use as hard templates, catalyst supports, adsorbents and in chromatography.

CHAPTER 1. OVERVIEW

1.1. Overview of TiO_2/rGO/chitin composite materials and application research

Chitin is the second most abundant natural carbohydrate on Earth after cellulose and is a biopolymer found in the exoskeletons of shellfish and insects, as well as in the cell walls of fungi. Chitin and cellulose have similar structures: cellulose is made of D-glucose units linked by β-(1→4) bonds while chitin is made of repeating units of 2-(acetylamino)-2-deoxy-D-glucose (Fig. 1.1) [9] .



Chitin **Cellulose**

Figure 1.1. Structure of chitin (left) and cellulose (right)

Partial N-deacetylation of chitin leads to the formation of its derivative compound: Chitosan (Fig. 1.2). This reaction includes the protonation of the chitin amino group at the C-2 position of glucosamine.

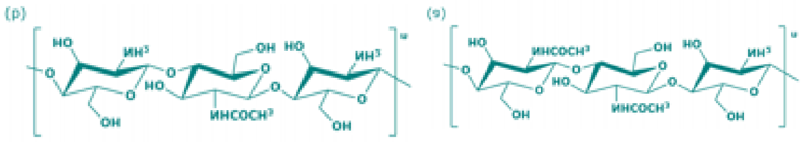


Figure 1.2. Structure of chitin (a) and chitosan (b) [16]

1.2. Overview of photocatalysis

Photocatalysis is a phenomenon in which photochemical reactions change their rate when a semiconductor catalyst is added to the reaction.

A semiconductor substrate that absorbs light and acts as a catalyst for chemical reactions is known as a photocatalyst. When a photocatalyst is exposed to light of the desired wavelength (provided with sufficient energy), the energy of photons is absorbed by an electron (e^-) of the valence band and it is excited to conduction band creating a hole (h^+) in the valence band. This process results to the formation of a photo-excitation state and an e^-/h^+ pair is generated. This excited electron is used for the reduction of the oxidant (electron acceptor) while the hole is used for the oxidation of the molecules of the reductant. This is also the advantage of a photocatalyst: it can provide both an oxidizing and a reducing environment. The ability to generate an excited electron/hole pair depends on the relative positions of the valence and the conduction bands with the redox potential of the reactants.

1.3. Overview of carbon materials from chitosan

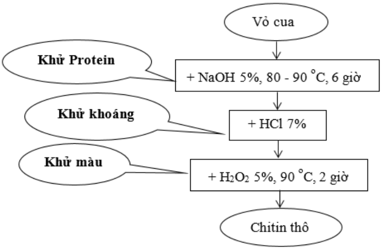
This study investigates the use of chitosan as a biotemplate and carbon source for fabricating hierarchical mesoporous silica and carbon from silica/chitosan assemblies. Chitosan, chemically extracted from crab shells, was dissolved in an acidic medium to condense with silica to form silica/chitosan composite membranes during self-assembly by evaporation. The synthesized materials were heated in air to remove the chitosan template to form transparent hierarchical mesoporous silica membranes. These materials were carbonized in a nitrogen atmosphere and treated with hot alkali to etch the silica, and finally a hierarchical mesoporous carbon membranes with supercapacitor performance were obtained.

CHAPTER 2. RESEARCH CONTENT AND METHODS

2.1. Experiment

2.1.1. Raw materials and chemicals

2.1.2. Preparation of chitin



Scheme 2.1. Process of preparing raw chitin

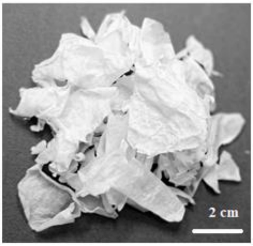
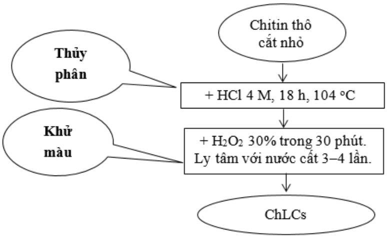


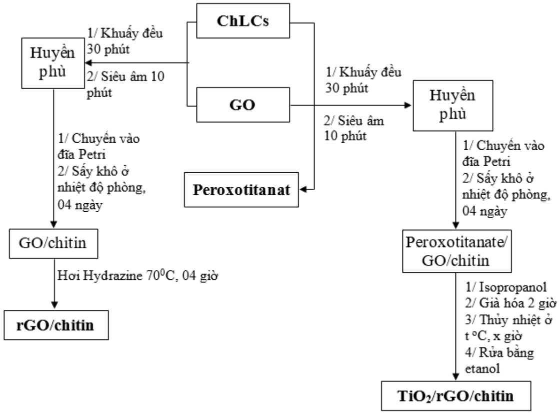
Figure 2.1. Photo of raw chitin

2.1.3. Preparation of chitin liquid crystals and chitosan



Scheme 2.2. Process of preparing chitin liquid crystals Figure 2.3. Photo of chitosan

2.1.4. Synthesis of TiO_2/rGO/chitin composite materials and application research



Scheme 2.3. Process of preparing rGO/chitin and TiO_2/rGO/chitin materials

* Evaluation of the photochemical ability of the material

* Investigation of factors affecting the material synthesis process:

- Ratio of ingredients in the material
- Hydrothermal temperature and time.

* Investigation of factors affecting photocatalysis:

- Amount of catalyst material
- Initial concentration of MB solution
- pH of the solution
- Evaluate of the reusability on the material.

2.1.5. Synthesis of modified carbon materials from chitosan solution and application research in electrochemical analysis

0.62 g of TMOS was mixed with 10 mL of chitosan solution (4.0%, pH ~2) at a silica/chitosan ratio of 40:60 and stirred at room temperature for 30 minutes to form a silica/chitosan mixture. Then, the mixture was poured into a plastic petri dish (60 mm) and dried at room temperature to form a silica/chitosan membrane composite after 3 days.

To produce carbon, the silica/chitosan membrane composite was carbonized under N_2 gas at 800 ^{o}C in a tube furnace with a heating rate of 5 ^{o}C.min^{-1} for 7 hours to form a black mesoporous carbon film.

Preparation with mesoporous silica membranes: the silica/chitosan membrane composite was calcined in air at 550 ^{o}C for 5 hours.

* Application study: The carbon material obtained from chitosan was directly used as a membrane electrode in capacitors without the need for a binder.

2.2. Characteristic analysis of materials

2.2.1. Powder X-ray diffraction (PXRD) method

2.2.2. Scanning electron microscopy (SEM) method

2.2.3. Transmission electron microscopy (TEM) method

2.2.4. Thermogravimetric analysis (TGA)

2.2.5. Fourier-transform infrared spectroscopy (FTIR)

2.2.6. Ultra violet-visible absorption spectrum

2.2.7. Polarized optical microscopy (POM) method

2.2.8. Nitrogen adsorption and desorption isotherms

2.2.9. Tensile strength test

2.2.10. Cyclic voltammetry method

2.2.11. Determination of zero charge point pH_{pzc} method

CHAPTER 3. RESULTS AND DISCUSSIONS

3.1. Synthesis of TiO_2/rGO/chitin and application research

In this section, chitin liquid crystals were studied as a layered support and structure-directing agent, combined with peroxotitanate and graphene oxide (rGO) by the Evaporation-Induced Self-Assembly (EISA) method and hydrothermal method to synthesize TiO_2 /rGO/chitin materials with photocatalytic property. The precursors, including chitin liquid crystals, liquid crystals of graphene oxide and peroxotitanate, were synthesized and characterized. Factors affecting the synthesis process of the materials, including hydrothermal time and temperature, as well as the ratio of components in the materials, were investigated. The photocatalytic ability of the materials was also tested using methyl blue degradation.

3.1.1. Preparation of precursors

3.1.1.1. Chitin and chitin liquid crystals

The synthesized chitin suspension is milky white and can form a nematic LC when its concentration reaches the critical level of ~ 6.6% at pH ~ 4. Liquid chitin crystals were characterized by the following methods: FTIR, XRD, TEM and SEM spectra.

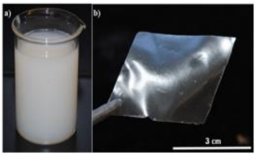


Figure 3.1. Aqueous chitin LC (a) and assembled membrane (b)

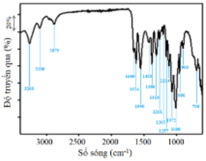


Figure 3.2. IR spectrum of chitin nanocrystals

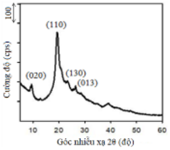


Figure 3.3. PXRD of chitin nanocrystals

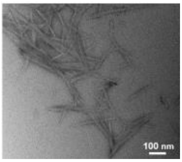


Figure 3.4. TEM image of chitin nanocrystals

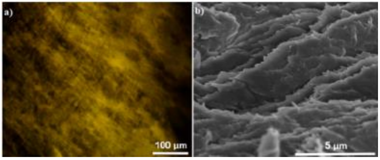


Figure 3.5. POM image (a) and SEM image (b) of chitin membrane obtained by EISA

3.1.1.2. Graphene oxide (GO)

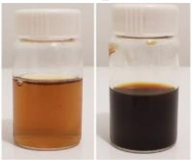


Figure 3.6. GO aqueous dispersions at ~ 0.1% (left) and 1.5% (right)

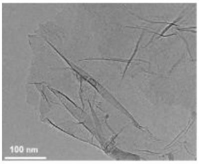


Figure 3.7. TEM image of GO nanosheet

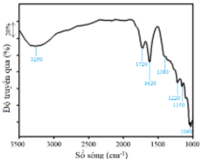


Figure 3.8. IR spectrum of GO nanosheet

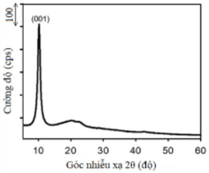


Figure 3.9. PXRD of GO nanosheet

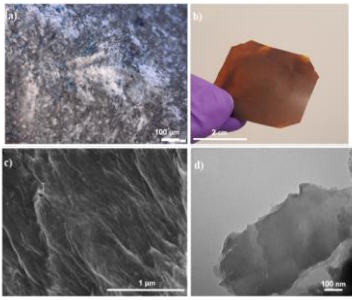


Figure 3.10. POM image (a), a flexible (b), SEM image (c) and TEM image (d) of assembled GO membrane

The synthesized GO was redispersed in water to form homogeneous, pale-orange GO suspensions without any precipitation or phase separation. The dilute GO aqueous solution tends to become more viscous at high concentrations (≥ 1.0%), but it retains its dispersibility rather than colloidal gelation (Fig. 3.2.a).

3.1.1.3. TiO_2

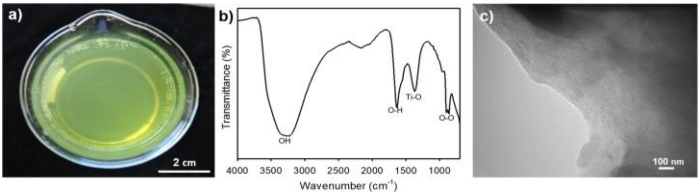


Figure 3.11. Images of peroxotinate

The peroxotitanate compound was prepared by hydrothermal alkaline treatment of bulk TiO_2, followed by oxidation with H_2O_2. The product was dissolved in water to form a homogeneous, water-solube yellow peroxotitanate solution (Fig. 3.11).

***3.1.2.* Characteristic properties of materials**

3.1.2.1. GO/Chitin composite

The obtained GO/chitin membranes were crack-free over the scale of several square centimeters with a relatively smooth surface on both sides (Fig. 3.12a). The infrared spectrum (Fig. 3.13) and PXRD spectrum (Fig. 3.14) confirmed the presence of the characteristic stretches of the GO and chitin in the GO/chitin material, indicating that the GO/chitin membrane was a composite assembled from liquid crystals of nano GO and chitin.

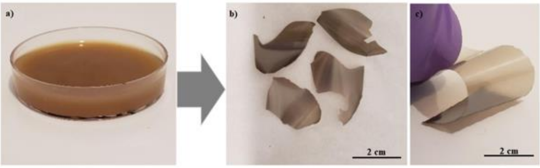


Figure 3.12. Mixed GO/chitin suspension upon EISA (a), crack-free, freestanding GO/chitin membrane (b), highly flexible graphene oxide/chitin membrane with bendable ability (c)

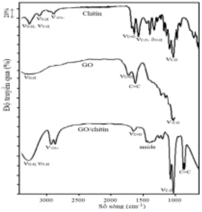


Figure 3.13. IR spectrum of chitin LCs, GO and GO/chitin

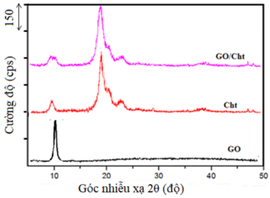


Figure 3.14. PXRD of GO (black), chitin (red) and GO/chitin (pink)

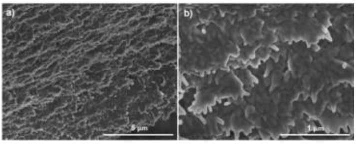


Figure 3.15. SEM image depicting the layered structure of nacre-mimicking GO/chitin composite membrane at two different magnifications

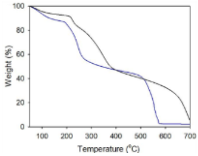


Figure 3.16. TGA curves of GO/chitin (black) and GO (blue)

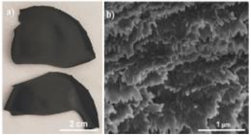


Figure 3.17. Image (a) and SEM image of GO/chitin after reducing by hydrazine vapor at 70°C

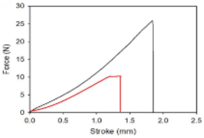


Figure 3.18. Micro-tensile stress-strain curve of rGO/chitin (black) and GO (red)

SEM images (Fig. 3.15) confirm the structural preservation of the two precursors during the assembly process via self-condensation. TGA curves (Fig. 3.16) show that the GO/chitin composite has higher thermal stability than the original GO.

The GO/chitin composite was reduced by exposure to hydrazine vapor at 70 ^oC for 4 hours to convert into rGO (reduced GO) (Fig. 3.17), and resulting in a more robust rGO/chitin film. The membrane change colour from brown to black during the reduction process and its mechanical flexibility and shape remained intact. Tensile mechanical testing (Fig. 3.18) shows that the rGO/chitin is stronger than GO.

3.1.2.2. TiO_2/rGO/chitin composite material

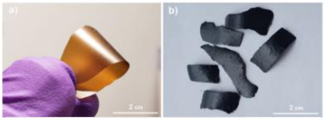


Figure 3.19. Image of peroxotitanate/GO/chitin (a) and TiO_2/rGO/chitin (b) membrane

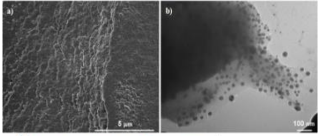


Figure 3.20. Image of SEM (a) and TEM (b) of TiO_2/ rGO/chitin material

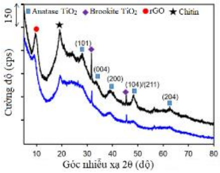


Figure 3.21. PXRD of peroxotitanate /GO/chitin (blue) and TiO_2/rGO/chitin (black)

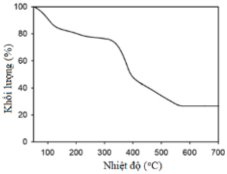


Figure 3.22. TGA curve of TiO_2/rGO/chitin

The TiO_2/rGO/chitin membranes remained intact after hydrothermal treatment and were more robust than the pristine samples, but still flexible due to the organic-inorganic hybrids structure (Fig. 3.19). The SEM image (Fig. 3.20a) shows that the as-prepared TiO_2/rGO/chitin composites had a nacre-mimicking layer structure, similar to that of GO/chitin, and small TiO_2 nanoparticles deposited on the graphene nanosheet-wrapped chitin nanofibers. The TEM image (Fig. 3.20b) of the TiO_2/rGO/chitin composite shows TiO_2 nano-articles deposited on the layers of the rGO/chitin esemblies. PXRD analysis (Fig. 3.21) revealed that the crystalline structures of GO and chitin in the composites were almost the same as those in the original samples. TGA pattern confirms that the material is stable at 340 ^oC and begins to decompose up to 550 ^oC.

3.1.2.3. Photocatalytic ability of materials

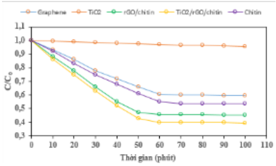


Figure 3.23. MB adsorption onto materials over time

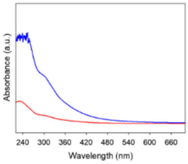


Figure 3.24. UV-Vis spectra of TiO_2/rGO/chitin (blue) and GO (red)

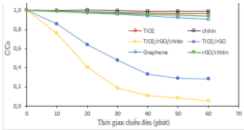


Figure 3.25. Photocatalytic decolorization of methylene blue with different irradiation times of different materials

$$TiO_2/rGO/chitin \rightarrow h^+ + e^- \quad (3.1)$$

$$h^+ + OH^- \rightarrow OH^\bullet \quad (3.2)$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \quad (3.3)$$

$$e^- + O_2 \rightarrow O^{\bullet 2-} \quad (3.4)$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (3.5)$$

$$e^- + H_2O_2 \rightarrow OH^\bullet + OH^- \quad (3.6)$$

$$OH^\bullet/O^{\bullet 2-} + MB \rightarrow CO_2 + H_2O + \text{các hợp chất đơn giản} \quad (3.7)$$

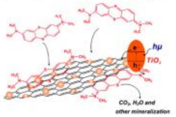


Figure 3.26. Photodegradation mechanism of MB

The TiO_2/rGO/chitin composite adsorbed MB (in the dark) and photodegradated (under the light) the MB molecules more strongly than single graphene and had negligible adsorption on P25 (Fig. 3.23, 3.25). The composite was able to absorb both UV and visible light to generate multiple electron-hole pairs (Equation 3.1 - 3.7) leading to the photochemical activity of the material (Fig. 3.24, 3.26).

3.1.3. Investigation of factors affecting the material synthesis process

3.1.3.1. Ratio of ingredients in the material

The ratio of components in the material was evaluated by determining the concentration of MB reagent consumed after each reaction times and under the light irradiation condition from a 100 W Hg lamp. The optimal result for the ratio of components was $V_{peroxo} : V_{GO} : V_{Ch} = 10:6:1.5$.

3.1.3.2. Hydrothermal temperature and time

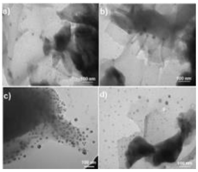


Figure 3.30. TEM image of TiO_2/rGO/chitin materials at different HTC temperatures

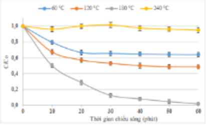


Figure 3.31. The change in MB concentration over time for each sample at different hydrothermal temperatures

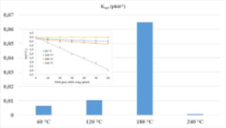


Figure 3.32. The kinetic constants of the material at different hydrothermal temperatures

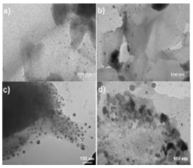


Figure 3.33. TEM image of TiO_2/rGO/chitin materials over different HTC times

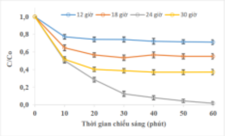


Figure 3.34. The change in MB concentration over time for each sample at different hydrothermal times

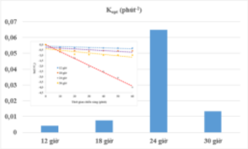


Figure 3.35. The kinetic constants of the material at different hydrothermal times

Based on the morphology of the material observed through TEM images, it can be concluded that the hydrothermal conditions for creating the material are 180 °C and 24 hours.

3.1.4. Factors affecting the photocatalytic properties of materials

3.1.4.1. Amount of catalyst material for photocatalytic reaction

The required amount of catalyst investigated was 0.5 g/L for MB solution with concentration of 20 mg/L.

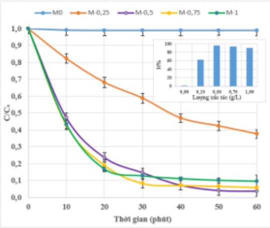


Figure 3.36. Effect of TiO2/rGO/chitin amount on MB degradation efficiency

3.1.4.2. Effect of pH

The isoelectric value of the material is 5.1, the pH of the MB solution is in the range of 6 – 7.

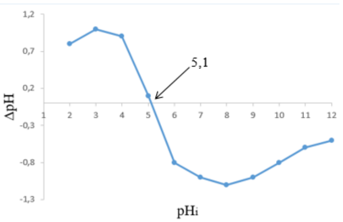


Figure 3.37. Graph of TiO2/rGO/chitin’s pH_{PZC} determination

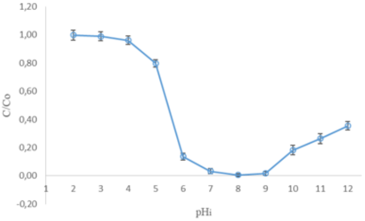


Figure 3.37. Effect of pH on MB degradation

3.1.4.3. Effect of initial MB solution

Table 3.4. Results of initial MB concentration survey

Lượng MB (mg/L)	10	15	**20**	25	30
C/Co	0,043	0,038	**0,043**	0,116	0,130
H%	95,71	96,33	**96,36**	88,33	86,67

The initial concentration of MB solution investigated was 20 mg/L.

3.1.4.4 . Material reusability

After 4 cycles, the MB degradation efficiency decreased insignificantly, indicating that high reusability of the material in MB treatment applications.

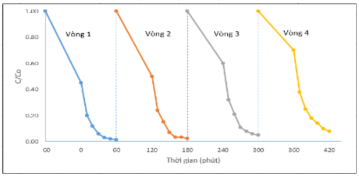


Figure 3.40. Repeated photocatalytic cycles of the material sample

3.2. Synthesis of modified carbon materials from chitosan solution and research on application in electrochemical analysis

3.2.1. Synthesis of chitosan membrane

The obtained chitosan film is transparent, flexible, and crack-free (Fig. 3.41). The IR spectrum (Fig. 3.42) of the film shows the characteristic peaks of chitosan at the wave numbers 3650-3140 cm^{-1}, 2930-2850 cm^{-1}, 1640-1548 cm^{-1} corresponding to the bonds of O-H/hydroxyl and N-H/amine groups, C-H bonds, and amide groups. The XRD pattern (Fig. 3.43) of chitosan still retains the main diffraction peaks of the chitin film, but the intensity is significantly reduced. The SEM and TEM images (Figs. 3.44-45) show the layered structure of chitosan.

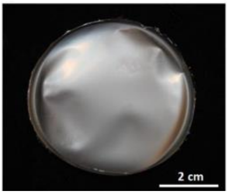


Figure 3.41. Photo of chitosan membrane prepared from crab shells

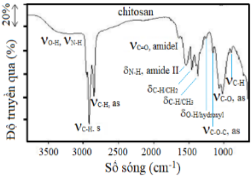


Figure 3.42. IR spectra of chitosan

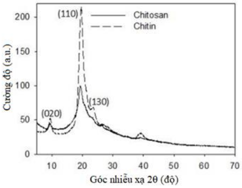


Figure 3.43. PXRD patterns of chitin and chitosan

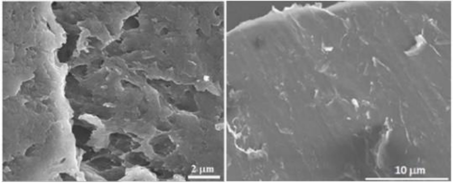


Figure 3.44. SEM image of chitosan membrane

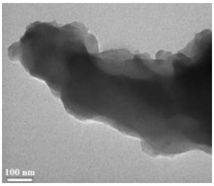


Figure 3.45. TEM image of chitosan membrane

3.2.2. Fabrication of silica/chitosan membrane

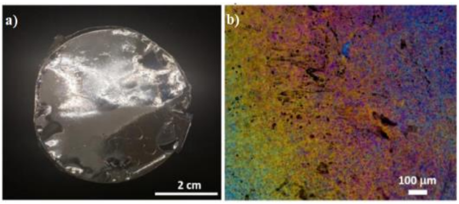


Figure 3.46. Image (a) and POM image (b) of self-assembly silica/chitosan

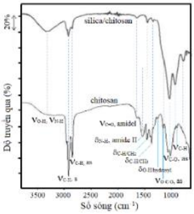


Figure 3.47. IR spectro of silica/chitosan

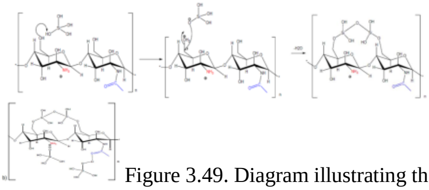


Figure 3.49. Diagram illustrating the formation (a) and the bonds (b) in the chitosan-silica membrane

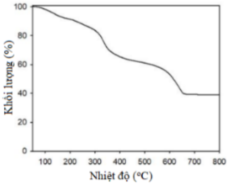


Figure 3.49. TGA curve of silica/chitosan

The evaporation process causes the self-assembly of TMOS with acidic chitosan to form silica/chitosan membranes. The obtained silica/chitosan samples were analyzed for morphological and structural properties. The results are shown in Figs. 3.46 – 3.49.

The analytical results showed that there was a combination between chitosan and silica through hydrogen bonds or Van der Wall interactions of the OH, NH_2 groups of chitosan with the silanol groups of silica.

3.2.3. Mesoporous silica membrane

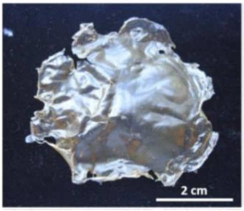


Figure 3.50. Image of silica membrane

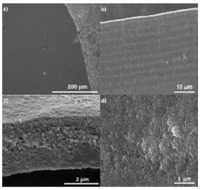


Figure 3.51. SEM images of hierarchical mesoporous structure of silica film

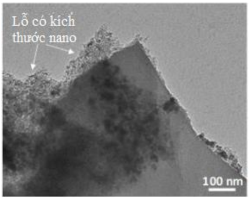


Figure 3.52. TEM image of silica mesoporous

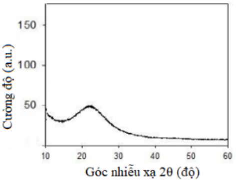


Figure 3.53. PXRD patterm of silica

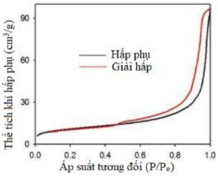


Figure 3.54. Nitrogen adsorption-desorption isotherms of silica mesoporous films

The silica film obtained after calcination for 5 hours at 550 ^oC has a similar shape to the original sample but is shrunk in volume due to the complete decomposition of chitosan (Fig. 3.50). Observation of SEM images (Fig. 3.51) and TEM images (Fig. 3.52) shows that the silica film has copied the layered structure of chitosan. On the XRD diagram (Fig. 3.53), a peak at $2\theta = 23^o$ characteristic of silica appears. Based on the adsorption-desorption curve (Fig. 3.54), it shows that the obtained silica film has a surface area of 280 $m^2.g^{-1}$.

3.2.4. Carbon membrane fabrication

The carbon composite material was black in color, shrunk in volume and had a shape similar to the original silica/chitosan membrane (Fig. 3.55) after calcination in an inert atmosphere and immersion in dilute NaOH to remove the silica.

Figure 3.55. Carbon film produced after silica removal

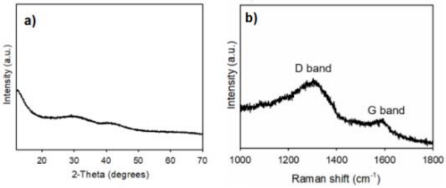


Figure 3.57. PXRD pattern (a) và Raman spectrum (b) of carbon

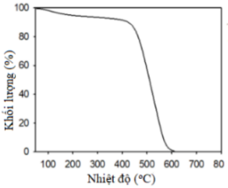


Figure 3.56. TGA curve of carbon

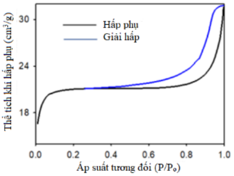


Figure 3.58. Nitrogen ad-desorption isotherms

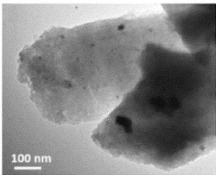


Figure 3.60. TEM image of carbon film

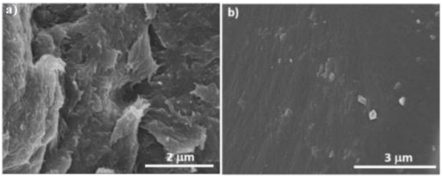


Figure 3.59. SEM image of carbon film

The TGA of the carbon membrane (Figure 3.56) shows that the combustion of carbon occurs between 400°C and 600°C in an air environment, with complete combustion at 600°C, indicating that the carbon membrane produced is pure.

The PXRD pattern of the carbon sample shows two broad peaks at about $2\theta = 26.3^o$ and 42.3^o, attributed to amorphous carbon (Fig. 3.57a). The Raman spectrum of pure carbon shows the D band at 1350 cm^{-1} and the G band at 1580 cm^{-1}, corresponding to the amorphous carbon structure (Fig. 3.57b).

The porosity of the carbon materials was studied using nitrogen adsorption/desorption isotherms. Fig. 3.8 shows that the carbon films have a type IV isotherm with a typical H2 hysteresis loop of a porous structure with a BET surface area of 520 $m^2.g^{-1}$. The nanoscale porous networks and hierarchical structure of the materials can also be observed by TEM (Fig. 3.60) and SEM (Fig. 3.59). These morphological features are consistent with the original shape of the parent chitosan in the composites assembled before carbonization and silica removal.

3.2.4. ***Research on carbon membrane applications***

Chitosan, like chitin, with its high nitrogen content from the N-acetyl group, was fabricated into mesoporous N-doped carbon films via sol-gel condensation and self-assembly with silica. These films were carbonized under an inert atmosphere, and the silica was removed by hot alkali treatment [119]. The N-doped carbon material enhanced the pseudocapacitive effect of the supercapacitor. The pseudocapacitance was introduced through positively charged nitrogen atoms (N), which promote electron transfer through the carbon (C) atoms.

This chitosan-derived mesoporous carbon membrane was herein initially tested for use as a binder-free, stand-alone supercapacitor. To evaluate its electrochemical properties, cyclic voltammetry (CV) was used. Two sections of porous carbon membrane electrodes were fabricated in symmetrical cells with 1 M H_2SO_4 electrolyte. The electrochemical performance of the mesoporous carbon electrode at various scan rates is shown in Fig. 3.61. The mesoporous carbon electrode exhibits quite leaf-like CV curves from 2 to 200 $mV.s^{-1}$. The specific capacitance (C_s) of the carbon calculated from the CV charge curve at 2 $mV.s^{-1}$ is 210 $F.g^{-1}$, which is comparable to previously reported mesoporous carbon supercapacitors .

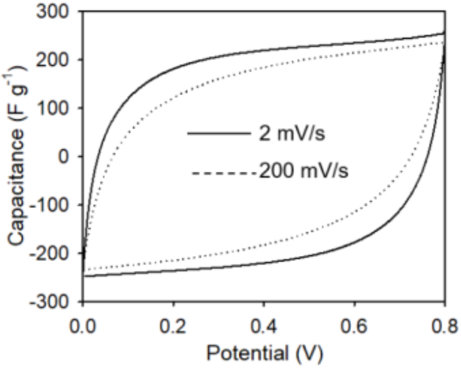


Figure 3.61. CV curve of mesoporous carbon membrane

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

From the research results achieved, the thesis has the following contributions:

1. Thanks to the self-assembly ability of liquid crystals of anisotropic nanocomponents, chitin and GO liquid crystals were prepared and used as a nematic phase to synthesize TiO_2/rGO/chitin composite materials with an ordered, nacre-like layered structure, which exhibited photocatalic properties.

- The combination of chitin liquid crystals and graphene oxide with peroxotitanate enabled the creation of TiO_2/rGO/chitin films via the Evaporation-Induced Self-Assembly (EISA) method, in combination with hydrothermal treatment. This approach facilitated the formation of films with a well-defined structure suitable for photocatalytic applications.

- The synthesized rGO/chitin and TiO_2/rGO/chitin films were thoroughly analyzed using several techniques, including IR, TGA, SEM, and TEM. The results confirmed that TiO_2 nanocrystals were uniformly distributed around the rGO/chitin film while preserving its original layered structure. XRD analysis revealed that the TiO_2 component in the composite was predominantly in the anatase phase, contributing to the material's photocatalytic properties.

- The TiO_2/rGO/chitin composite films were successfully synthesized under hydrothermal conditions at 180°C for 24 hours. The optimal ratio of peroxotitanate, graphene oxide, and chitin in the material was found to be 10:6:1.5 by volume.

- UV-Vis spectra of the TiO_2/rGO/chitin composite demonstrated an extended absorption peak up to 450 nm, indicating enhanced photocatalytic properties compared to pure TiO_2 and graphene oxide.

- The photocatalytic degradation of Methylene Blue (MB) was used as a test, showing that the TiO_2/rGO/chitin catalyst could degrade up to 99% of MB after 60 minutes of illumination with a catalyst dose of 0,5 g/L, an initial MB concentration of 20 mg/L and pH was in the range of 6-7. The degradation efficiency remained above 90% after 4 cycles, demonstrating the material's excellent reusability.

2. Chitosan derived from crab shells has been used as both a biological precursor and a carbon source to fabricate layered mesoporous materials: Silica and carbon films with free-standing, mesoporous thin-film properties via evaporation-induced self-assembly (EISA).

- When silica/chitosan films were calcined in air at 550 ^{o}C, mesoporous silica films were obtained. After complete decomposition of chitosan, a layered structure was left for the silica films. The surface area of the obtained silica films was 280 m^2/g.

- When silica/chitosan films were carbonized at 800 ^{o}C withou oxygen and treated with alkali to remove silica components, carbon supercapacitors were produced. The obtained carbon materials preserved the ordered pore structure of silica, while replicating the layered structure of the original chitosan film. The surface area of the obtained carbon materials was 520 m^2/g. These factors indicate that the material has semiconducting properties, is a stable carbon material with great potential for development as an energy storage material. The carbon electrode exhibits quite leaf-shaped CV curves from 2 to 200 $mV.s^{-1}$. The specific capacitance (Cs) of the mesoporous carbon calculated from the CV charge curve at 2 $mV.s^{-1}$ is 210 $F.g^{-1}$, which is also a favorable factor.

RECOMMENDATIONS

- Hierarchical structures at the nanoscale can enhance the permeability of TiO2/rGO/chitin composite membranes, offering great potential for combining photocatalysis and filtration processes in water and air treatment. These new composite materials can serve as promising precursors for further research into their electronic, electrocatalytic, and photochemical properties to develop applications in energy storage and conversion, as well as gas sensors.
- Research on the application of mesoporous silica films derived from chitosan/silica composites with hard-template functionality, supporting catalysis, adsorption, and catalysis based on hierarchical structures and free-standing without the need for a support.
- Based on the semiconducting properties and the ordered porous structure of mesoporous carbon materials, further in-depth research is needed in the fabrication of binder-free electrode materials and in other energy storage materials.

LIST OF PUBLICATIONS RELATED TO THE DISSERTATION

1. Le Thi Anh Phuong, Tuyen Vu Phi, Hoa Thi Le, Do Van Phan, Ca Xuan Nguyen, Thanh Duy Luong, Nhan Thi Thanh Dang Nguyen Dinh Thanh, “Nacre-Mimicking Titania/graphene/chitin Assemblies in Macroscopic Layered Membranes and Their Performance”, Journal of Electronic Materials, vol. 49, pp. 3791-3803, 2020.
2. Le Thi Anh Phuong, Vu Phi Tuyen, Nguyen Xuan Ca, Le Thi Hoa, Phan Van Do, Luong Duy Thanh, Dang Thi Thanh Nhan, Nguyen Dinh Thanh, “Sustainable chemsistry of chitosan assemblies prepared through templating and carbonization”, Vietnam Journal of Science and Technology, vol. 60, pp. 350-361, 2022.