BITLIS EREN UNIVERSITY
JOURNAL OF SCIENCE AND TECHNOLOGY

E-ISSN: 2146-7706

AN OVERVIEW OF THE CONVENTIONAL SYNTHESIS OF BIOMASS-DERIVED NANOCOMPOSITES AND APPLICATIONS TO SYSTEMS FOR ENERGY AND THE ENVIRONMENT

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KEYWORDS

Biomass-derived nanocomposites
Bio-nanocomposites synthesis methods
Nanocomposites energy applications
Environmental remediation and carbon capture

ARTICLE INFO

Review Article
DOI: 10.17678/beuscitech.1233168

Received	12 January 2023
Accepted	26 December 2023
Year	2023
Volume	13
Issue	1
Pages	61-75

ABSTRACT

Biomass-derived nanocomposites are very tiny carbonated solid materials synthesized by fusing metallic compounds with different types of plant-based materials, either in their raw forms or after processing into other substances such as biochar. This study aims to succinctly describe the principles often applied in the literature for the synthesis of biomass-derived nanocomposites. Furthermore, the most common applications of biomass-derived nanocomposites in the areas of sustainability of energy and the environment are summarized. The roles of bio-nanocomposites in the advancement of energy storage systems, supercapacitors, and hydrogen production through fuel cells are in focus for sustainable energy applications. For the environmental sustainability potential, emphasis is placed on the applications of the bio-based nanocomposites for environmental remediation and carbon-capture purposes by mitigating CO_2 emission through CO_2 sorption and sequestration.

1 INTRODUCTION

Global warming and other associated effects of greenhouse gas emissions have necessitated that drastic measures be taken to promote green processes in almost all sectors of human endeavors [1], [2]. In the energy sector, for instance, this connotes that usage of fossil fuels in energy infrastructures be reduced to the barest minimum [3] and replaced with renewable and clean fuels such as the solar [4], wind [5], biomass [6], hydrogen [7], geothermal [8], and hybrid renewable resources [9]. Adoption of green processes in materials science and engineering implies that the use of natural and renewable materials should be promoted, to reduce environmental wastes and energy use, among others [10], [11]. A very popular and feasible area where green chemistry applies in material science is in the combination of materials to form composites for complementary engineering properties required in some advanced applications [12], [13].

Composites are known technically as the unification of two or more materials with distinct properties to obtain a single material with superior characteristics [14], [15]. If one or more of the components in the unified materials is of nanoscale, the composite so formed is known as nanocomposite [16], [17]. And when a naturally occurring plant, animal waste, or any other form of biomass is included in the synthesis of a nanocomposite, it is generally referred to as biomass-derived nanocomposite or bio-nanocomposite [18], [19], [20].

So many methods have been adopted in the literature to synthesize bio-nanocomposites from different base materials and use diverse biomass types as carbon sources. This chapter aims to succinctly provide an overview of the different methods that have been so adopted to fuse biomass carbon with other materials to obtain bio-nanocomposites and to highlight the different biomass sources that have been explored in this regard.

2 SYNTHESIS OF BIOMASS-DERIVED NANOCOMPOSITES

2.1 Primary Synthesis Principles

Synthesis of biomass-derived nanocomposites involves about 4 general steps: the extraction of carbon materials from the biomass precursor, the preparation of the base metallic material and/or its solution, the formation of form-filling solutions by mixing the biomass carbon with the base material solution, and the production of the desired nanocomposite by an appropriate synthesis method vis-a-vis post-process procedure such as filtering, washing/cooling, and drying. A schematic is shown in Figure 1 to illustrate these basic steps.

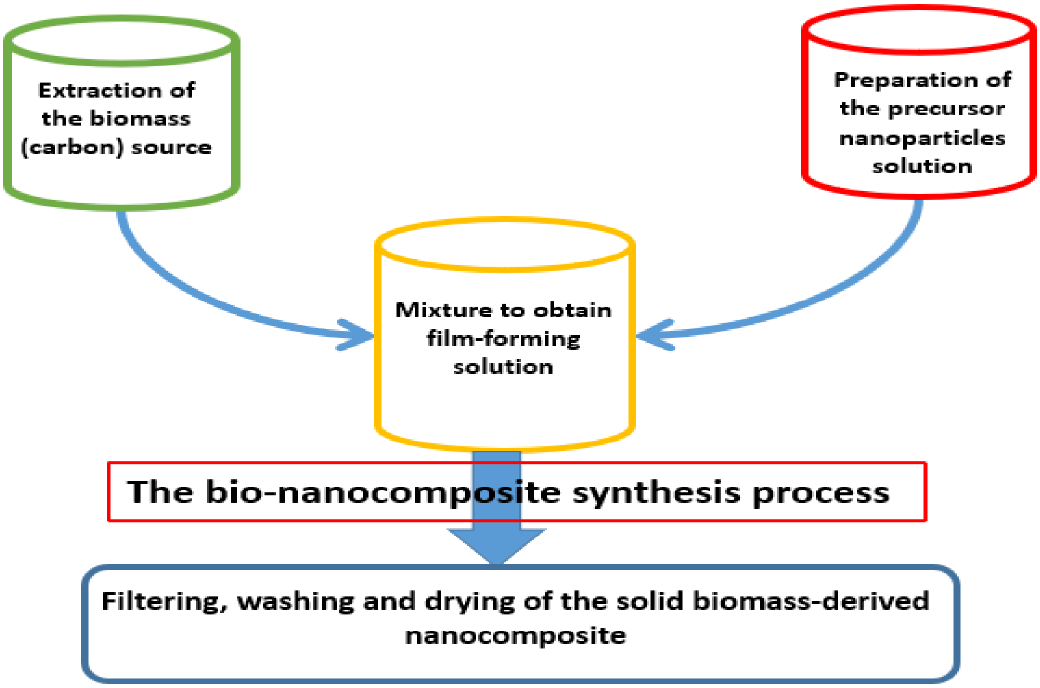

***Figure 1**. Basic steps for synthesizing bio-nanocomposites from prepared metallic nanomaterials and extracted biomass carbon*

Emphasis is placed in this chapter on the specific synthesis methods employed for fabricating the bio-nanocomposites from the biomass carbon and the precursor nanomaterial. The following paragraphs report the different conventional synthesis principles that have been used by several authors for the production of nanocomposites from different biomass sources. Additionally, Table 1 highlights the specific biomass sources, the precursor nanomaterial, and the basic synthesis methods adopted in the following paragraphs for the production of biomass-derived nanocomposites.

Wen et al. [21] presented one of such methods to fabricate core-shell carbon-coated CuO nanocomposites using humic acid (HA) as the main source of biomass carbon. Specifically, a synproportionation reaction was employed initially for the production of Cu_2O nanoparticles (NPs) by dissolving $CuCl_2.2H_2O$ in milli-Q water, adding Cu powder, and stirring intensely over a while without any exposure to air, and centrifuging and rinsing with Milli-Q water. Next, the Cu_2O NPs were dispersed in solutions of the humic acid extracted from soil, containing carbon predominantly and oxygen, nitrogen, hydrogen, and sulphur as the other constituent elements. The resulting HA-Cu_2O NPs, after collection through a centrifugation process, purification by rinsing in Milli-Q water, and drying in an oven, were **annealed with argon** at different temperature values to obtain carbon-coated CuO nanocomposites.

Sekar et al. [22] synthesized biomass-activated carbonated tungsten oxide (WO_3/B-AC) using a **sonochemical method**. Bulk WO_3 purchased commercially was first processed into nanoflakes by dissolving in deionized (DI) water, and sonicating the solution, after which the sonicated solution was washed, filtered, and oven-dried. The biomass-activated carbon (B-AC) employed in the study was synthesized from neem leaves. Raw neem leaves separated and washed were sun-dried, and the dried neem leaves, mounted into an alumina crucible, were carbonized in the air to process into ashes. The neem leave ashes were then mixed with potassium hydroxide (KOH) in a mortar and activated in the air at elevated temperature for some time. The potassium compounds that might have been captured in the process were eliminated by stirring the neem leaf ashes/KOH reaction residues in DI water to give proper B-AC nanosheet powder which was then filtered and washed in DI water, and oven-dried. Finally, to synthesize the desired WO_3/B-AC, a quantity of the WO_3 nanoflakes processed above was vigorously stirred in DI water to form a solution, and a portion of the synthesized B-AC nanosheet powder was added to the solution and stirred continuously over a time, and the solution was sonicated over some time, rinsed with DI water, filtered, and dried.

Leite et al. [23] produced biomass-derived nanocomposites by synthesizing gelatin with cellulose nanocrystals (CNCs) obtained from eucalyptus kraft pulp. Specifically, CNCs were prepared from the commercially-obtained eucalyptus kraft pulp by acid hydrolysis. Then, gelatin-CNCs film-forming solutions (FFS) were synthesized by mixing hydrated gelatin powder with CNCs at different concentrations. The desired bio-nanocomposites were produced by the **continuous casting approach** using a KTF-S labcoater casting machine.

Mahardika et al. [24] synthesized bio-nanocomposites using starch extracted from bengkoang tubers based on the method reported in [25] and cellulose nanofibres (CNB) isolated by sonication from pineapple leaf as described in [26]. The desired bio-nanocomposites were synthesized by the **ultrasonication** and drying of the film solutions obtained by mechanical mixing of hydrated bengkoang starch and CNB.

Xu et al. [27] produced bio-nanocomposites by synthesizing chitosan (CS) obtained commercially with nanocrystalline cellulose (NCC) extracted from rice straws. The NCC was extracted from rice straws using acid hydrolysis and ultrasonication procedures [28], [29]. The CS/NCC biocomposites were synthesized by **casting** the film-forming solutions prepared by mixing hydrated CS particles (CS solution) with homogenized NCC suspensions in a polystyrene mold and drying in an oven.

Liou et al. [30] produced a biomass-derived nanocomposite by synthesizing graphene oxide (GO) with silica, which was extracted from rice husk as described in [31]. The desired bio-nanocomposites were obtained by **hydrothermal treatment** of the film-forming solution of GO and the RH-derived silica using a surfactant mixture [32].

Goncalves et al. [33] prepared a carbon/iron nanocomposite by **precipitating** carbonated babassu coconut endocarp in iron nitrate with ammonium hydroxide as the precipitating agent, and by **heat-treating** the ensuing film-forming solutions to obtain the desired bio-nanocomposite.

Zhang et al. [34] synthesized a biomass-derived nanocomposite based on a **facile hydrothermal reaction** that fused MnO_2 with activated carbon derived from silkworm excrement biomass. Specifically, film-forming solutions were derived by the reaction between the calcinated biomass porous material and $KMnO_2$, which were then heated over time, washed, filtered, and dried to obtain the desired MnO_2/carbon nanocomposite.

Gai et al. [35] employed synthesized a nickel-based bio-nanocomposite, a catalyst, using a hydrochar produced from lignocellulosic biomass, pinewood sawdust, as the carbon material infused with the nickel metal precursor. The biomass-derived nanocomposite was fabricated using a newly-developed **one-step hydrothermal reaction**. Specifically, the film-forming solutions, obtained from the dispersed mixture of the biomass hydrochar with nickel nitrate solution, were thermally treated, the slurry formed therefrom filtered and oven-dried, and then calcined under nitrogen gas at high temperature.

Table 1*. Highlights of biomass sources and synthesis methods for the production of biomass-derived nanocomposites*

Bio-nanocomposite	Metallic nanomaterial precursor	Biomass source(s)	Bio-nanocomposite synthesis method	Reference(s)
Core-shell carbon-coated CuO	CuO	Humic acid	Annealing in an argon gas environment	[21]
Biomass activated carbonated tungsten oxide (WO_3/B-AC)	WO_3	Neem leaves	Sonochemical reaction	[22]
Gelatin-cellulose nanocrystals	Gelatin powder	Eucalyptus	Continuous casting	[23]
Bengkoang-cellulose nanofibres	Cellulose nanofibres	Bengkoang tubers and pineapple leaf	Ultrasonication	[24]
Chitosan-nanocrystalline cellulose	chitosan	Rice straws	Casting	[27]
Silica-graphene oxide	graphene oxide	Rice husk	Hydrothermal treatment	[30]
Carbon-iron	Iron nitrate	Babassu coconut endocarp	Thermal reaction	[33]
Activated carbon-MnO_2	MnO_2	Silkworm excrement	Facile hydrothermal reaction	[34]
Carbon-nickel	Nickel	Pinewood sawdust	One-step hydrothermal reaction	[35]
Carbon-iron	Iron/Chitosan	Rice husk	Solvothermal carbonization coprecipitation	[36]
Protein templated-TiO_2	TiO_2	Expired eggs	Mechano-chemical treatment involving milling	[37]

Siddiqui et al. [36] employed the **solvothermal carbonization coprecipitation** (STCC) approach to synthesize a bio-nanocomposite derived principally from rice husk as the biomass carbon source, chitosan, and iron oxides. The STCC is a single-step approach where the biomass source carbonization process is embedded in the overall synthesis of the nanocomposite. The film-forming solutions were derived by the mixture of ground rice husk with chitosan, $FeCl_3.6H_2O$, and $FeCl_2$ in water and/or ethanol employed as solvents. After the PH modification process using NaOH, the solution was covered with a blanket under a pressurized nitrogen gas condition over time, cooled, filtered, and centrifugated to recover the bio-nanocomposite solid, which was then washed and oven-dried. The authors emphasized the potential of the STCC approach employed in the study to facilitate improved commercial production of biomass-derived nanocomposites relative to the usual facile synthesis methods.

Rodriguez-Padron et al. [37] fabricated a protein-templated TiO_2 (PT-TiO_2) nanocomposite based on a water-free mechanochemical synthesis method. White egg obtained from expired eggs was employed as the carbon source which was mixed with titanium isopropoxide for the film-forming solution, which was then **mechanochemically treated** in a Retsch PM 100 ball mill. Thereafter, the nanocomposite slurry was over-dried and then calcined to obtain the desired PT- TiO_2.

2.2 Microwave-Assisted Bio-Nanocomposites Synthesis

The microwave-assisted method is described as a green synthesis method due to the reduction of the need for solvents and other ancillary substances during the process, and significant reduction of energy usage. It was affirmed in Ming Guo-Ma [38] that the microwave-assisted method has found wide applications in the synthesis of biomass-derived nanocomposites. For instance, cellulose, a biomass material, which can be any of microfibrillated cellulose, microcrystalline cellulose, nanofibrillated cellulose, bacteria cellulose, cellulose nanocrystals, plant fiber, wood fiber, etc [39], has been fused in different forms with other materials to form biomass nanocomposites based on the microwave-assisted method. Some examples of cellulose-based nanocomposites synthesized using the microwave method include cellulose-carbonated hydroxyapatite (CHA) nanocomposite [40], [41], cellulose-F-substituted hydroxyapatite (FHA) nanocomposite [42], cellulose-$CaCO_3$ [43], $CaCO_3$ particles-filled wood powder nanocomposites [44], cellulose-calcium silicate nanocomposite [45], cellulose-Ag nanocomposites [46], cellulose-AgCl and cellulose-AgBr nanocomposites [47], cellulose-CuO nanocomposites [48], etc.

3 APPLICATIONS TO SYSTEMS FOR ENERGY AND THE ENVIRONMENT

Biomass-derived nanocomposites are being explored widely to promote the production of clean and renewable fuels which can both enhance energy security in the future and minimize carbon emissions to the environment. Specifically, biomass-derived nanocomposites, when used as catalysts in the hydrogen production process from biomass wastes, have been reported to enhance both the quality and quantity of hydrogen produced. Rambabu et al. [49] studied the effects of adding iron oxide and date seed activated carbon (Fe_3O_4/DSAC) nanocomposites to the fermentation media for hydrogen production from the dark fermentation of date-palm fruit wastes. The authors reported that the application of the appropriate dosage of the Fe_3O_4/DSAC nanocomposites would increase the yield of hydrogen by about 205% compared to when no nanoparticle is added to the fermentation media. Also, it was obtained that the Fe_3O_4/DSAC nanocomposites would improve the quality of the hydrogen produced by acting as an adsorbent buffer due to the carbon support in the nanocomposites.

The study by Sekar et al. [22] reported that electrodes of the WO_3/B-AC nanocomposites synthesized in the study exhibited superior electrocatalytic features for water splitting in the case of hydrogen production.

Gai et al. [35] reported that the bio-nanocomposite synthesized from nickel metal and pinewood sawdust exhibited highly active catalytic properties that enhanced yields of hydrogen-rich syngas and very low tar yields.

Biomass-derived nanocomposites have also been gaining traction in the literature recently for use in electrochemical energy storage applications, comprising supercapacitors, batteries, and fuel cells [50]. Several biomass-derived nanocomposites have been proven specifically to exhibit very good electrochemical features that afford them competitive advantages over other materials for use as electrode materials in supercapacitors and batteries, few of which are reported in this section.

The carbon-coated CuO nanocomposites fabricated in Wen et al. [21] were reported to possess excellent capacitance and current density values required of electrode materials in supercapacitors and lithium-ion batteries.

The bio-derived carbon synthesized with iron by Goncalves et al. [33] was characterized to possess electrochemical features for energy storage applications in supercapacitors and batteries.

Zhang et al. [34] characterized the MnO_2/carbon nanocomposite obtained with the carbon having silkworm excrement biomass as its precursor. They reported high specific capacitance and outstanding cycling stability for the synthesized MnO_2/carbon nanocomposite, which positioned the nanocomposite as a high-performance energy storage material in supercapacitors.

The PT-TiO_2 biomass-derived nanocomposite synthesized by Rodriguez-Padron [37] was characterized to possess excellent electrochemical properties for energy storage applications in lithium-ion batteries, and outstanding features for use as catalysts.

4 CONCLUSIONS

An overview has been provided in this chapter of different methods for synthesizing very tiny carbonated solid materials, known technically as bio-nanocomposites, by fusing metallic compounds with different types of plant-based materials (biomass). The basic general steps for fabricating bio-nanocomposites have been highlighted, and the applications of such basic steps in the literature for producing different bio-nanocomposites have been summarised. Additionally, microwave-assisted approaches to synthesizing bio-nanocomposites have been succinctly discussed. Moreover, the most common applications of biomass-derived nanocomposites in the areas of sustainability of energy and the environment have been concretized. The roles of bio-nanocomposites in the advancement of energy storage systems, supercapacitors, and hydrogen production through fuel cells are in focus for sustainable energy applications. For the environmental sustainability potential, emphasis is placed on the applications of bio-based nanocomposites for environmental remediation and carbon-capture purposes.

Research and publication ethics

The study is complied with research and publication ethics.

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