Contemporary Engineering Sciences, Vol. 11, 2018, no. 38, 1863 - 1871
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2018.84186

Synthesis and Characterization of Cassava, Yam and Lemon Peels Modified with TiO_2 Nanoparticles

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Abstract

In the last decades, nanotechnology-based approaches have attracted global attention due to the development of a wide variety of novel materials useful for several applications. In this work, biomaterials from agricultural wastes (cassava peels, yam peels and lemon peels biomasses) were chemically modified with TiO_2 nanoparticles. These nanoparticles were synthesized via green chemistry with leaf extract of lemon grass and loaded to biomass using DMSO as organic solvent. The resulting modified biomaterials were characterized by FT-IR analysis in order to identify main functional groups. The crystalline size of TiO_2 nanoparticles was calculated using XRD pattern results and Sherrer's equation. SEM analysis was also performed to study the morphology of CP- TiO_2, YP- TiO_2 and LP- TiO_2. It was found that TiO_2 nanoparticles exhibited a crystalline nature with average size of 19 ± 4 nm. SEM micrographs showed an amorphous and agglomerated morphology indicating the dispersion of nanoparticles on biomaterials. In addition, the presence of Ti-O-Ti, Ti-O-C and Ti-O-N bonds in modified biomaterials spectra suggested a successful loading of titanium dioxide into biomasses.

Keywords: nanotechnology, biomass, characterization techniques, nanoparticles

1. Introduction

Nanotechnology is a rapidly expanding field due to the improvement of chemical, physical and biological properties of materials when its particle size is reduced to nanometer range [1]. Nanotechnology has had several thriving applications as food packaging, drug delivery, wastewater treatment, device and tools for fabrication and transportation [2]. Different novel approaches have been proposed to prepare nanomaterials using polymers or magnetic nanoparticles as titanium dioxide, cerium oxide and zinc oxide. Among these, titanium dioxide (TiO_2) nanoparticles is widely used due to its interesting properties that include chemical stability, good optical transparency, high refractive index, low cost, and non-toxicity [3]. The TiO_2 nanoparticles have been synthesized by methods including sol-gel, mechanism of vapor phase reaction process and hydrothermal synthesis assisted by microwaves [4]. On the other hand, biomass has gained attention due to its applicability as source of a huge variety of materials [5], and agricultural wastes can provide large amounts of biomass for nanomaterials development, which increases the economic value of residues and reducing the environmental impacts of its disposal [6]. In processing food products (e.g. corn, cassava, bean, yam, fruits), the biomass that is left behind includes peels, leaves and roots, and in almost all cases, it is not used for any economical purposes [7]. In this work, biomasses from lemon, cassava and yam peels were used to prepare biomaterials chemically modified with TiO_2 nanoparticles. FT-IR, SEM and XRD analyses were implemented to identify chemical functionalization, morphology and crystalline size of the modified biomaterials.

2. Materials and Methods

2.1. Preparation of biomaterials

The lemon peels (*Citrus limonum*, LP), cassava peels (*Manhiot esculenta*, CP) and yam peels (*Dioscorea rotundata*, YP) were collected from a local market at Cartagena (Colombia) and used as biomaterials for modification with TiO_2 nanoparticles. The peels were cut into small pieces and washed with distilled water in order to remove tannins, reducing sugar resins and other surface-adhered particles that could affect adsorption process. The resulting biomaterials were dried in an oven at 80°C for 24 hours, grounded and sieve-meshed to 0.5 mm particle size [8, 9].

2.2. Synthesis of TiO_2 nanoparticles

A green synthesis of TiO2 nanoparticle was carried out according to the procedure described by Hussain et al.[10]. The titanium (IV) isopropoxide was reduced using a leaf extract of lemon grass in order to prepare these nanoparticles without toxic wastes. The extract was obtained by heating the leaf of lemon grass into an aqueous medium for 6 hours and mixed with $Ti[OCH(CH_3)_2]_4$ under continuous stirring for 12 hours. After that, nanoparticles were separated by centrifuging and dried at room temperature. A thermal treatment at 550°C for 3 hours was performed onto the TiO_2 nanoparticles to improve the presence of the crystal phases anatase (80%) and rutile (20%), as confirmed by X-ray diffraction [13].

2.3. Modification of biomaterials with TiO_2 nanoparticles

The biomaterials were loaded with TiO_2 nanoparticles using dimethyl sulfoxide (DMSO) as organic solvent. A mixture of 0.5 g biomass and DMSO solution was placed on a stirring plate for 24 hours at 120 rpm. Then, 3 mL of tetra ethyl-o-silicate (TEOS) was added to this suspension and stirred for 48 hours in order to hydrolyze and condensate TEOS molecules. The TiO_2 nanoparticles (0.3 g) were mixed with the resulting biomass suspension, centrifuged at 3000 rpm for 15 min and washed thoroughly with ethanol [12, 13].

2.4. Characterization techniques

The synthesized TiO_2 nanoparticles were characterized by powder X-ray Diffraction (XRD) in order to determine the average crystallite size and analyze crystal phase and structure. The Fourier Transform Infrared Spectroscopy (FT-IR) technique was chosen to test diversifications of functional groups in both modified and unmodified biomaterials [14]. The morphology of the modified biomaterials was also studied by Scanning Electron Microscopy (SEM).

3. Results and Discussion

3.2. Characterization of TiO_2 nanoparticles

Figure 1 shows XRD pattern of TiO_2 nanoparticles, from which it was observed the characteristic peaks for the anatase crystal phase [13]. Sherrer's equation was used to determine the crystal size of the synthesized nanoparticles [15].

$$d = \frac{K\,\lambda}{\beta Cos\theta} \qquad (1)$$

Where d is the average particle size, λ the wavelength of the X-ray source applied (1.45 Å), β the reflection width (2θ), θ = the Bragg angle and K is the shape constant (0.89). The crystalline size was calculated in 19 ± 4 nm and both anatase (80%) and rutile (20%) phases were identified.

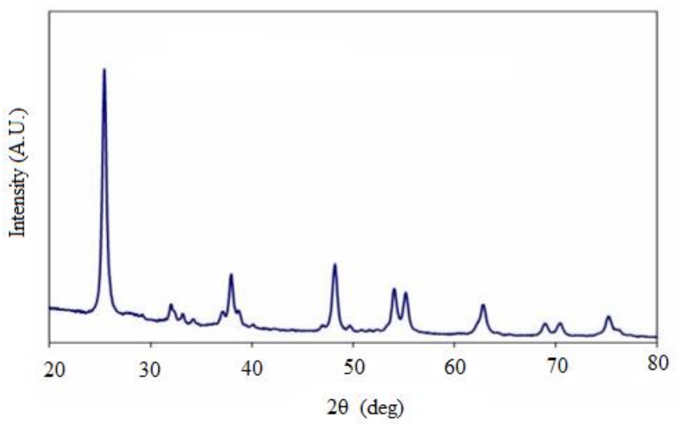

Figure 1. XRD pattern of TiO_2 nanoparticles

3.1. Characterization of modified biomaterials

Figure 2 shows the comparative results for FT-IR spectrum of yam peels biomass and its modification with TiO_2 nanoparticles in order to identify main functional groups before and after loading these nanoparticles onto biomaterials. It was observed sharp absorption bands at 1052, 1457 and 3582 cm^{-1} attributed to Ti-O-Ti bond or atomic nitrogen bonds with TiO_2 [16].

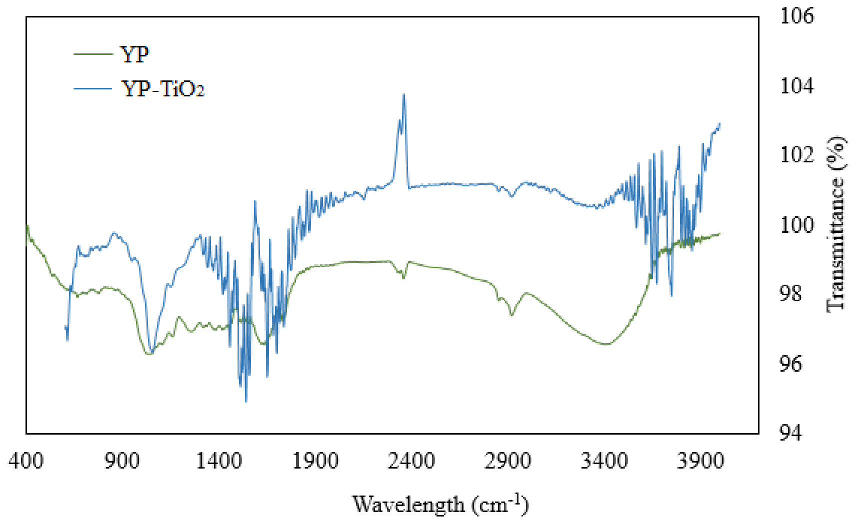

Figure 2. FT-IR spectrum of yam peels biomaterial and its modification with TiO_2 nanoparticles

The characteristic peaks in biomass spectrum were also identified for YP- TiO_2 as 2919 y 1238 cm^{-1}, which could be due to stretching and bending vibrations of C-H, respectively, suggesting the presence of CH_3 and CH_2 groups. In addition, the absorption peak around 786 and 922 cm^{-1} were ascribed to vibrations of N-H [17, 18]. As is shown in Figure 3, absorption peaks at 1072, 1510 and 3722 cm^{-1} assigned to Ti-O-C bond confirmed the presence of TiO_2 and a successful modification of cassava peels biomass. The infrared band around 1456 cm^{-1} was attributed to Ti-O-N bond as reported by Li et al. [14].

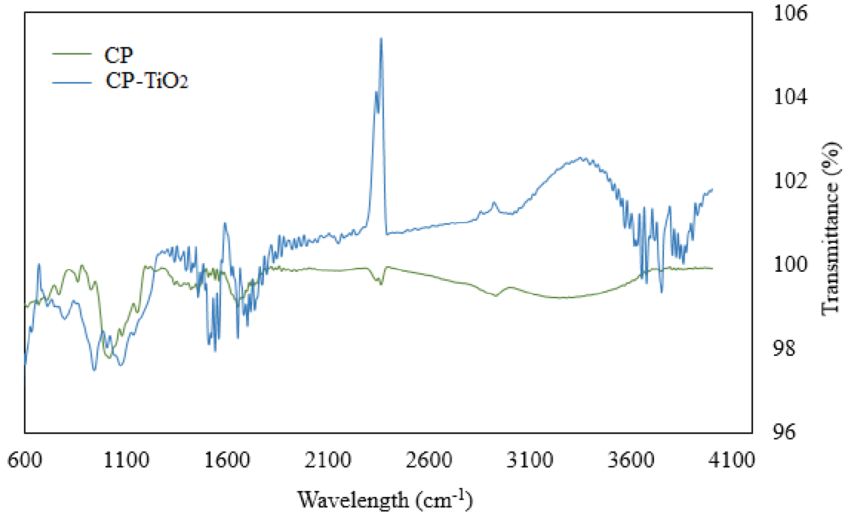

Figure 3. FT-IR spectrum of cassava peels biomaterial and its modification with TiO_2 nanoparticles

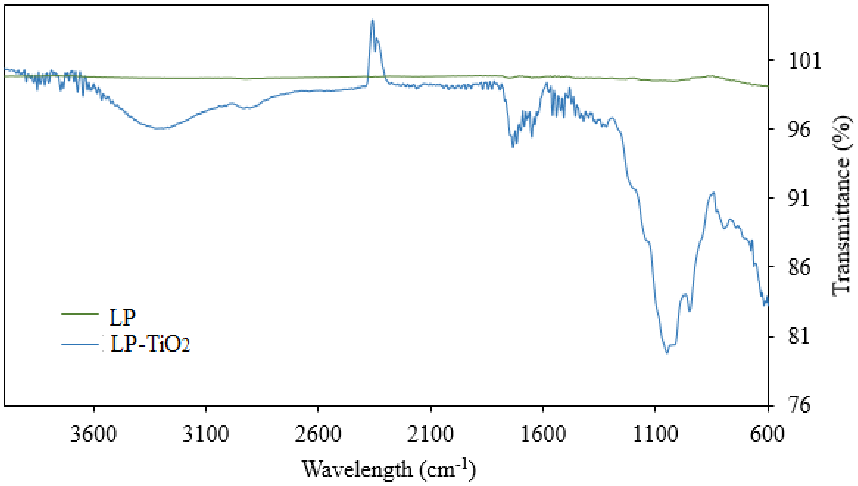

Figure 4. FT-IR spectrum of lemon peels biomaterial and its modification with TiO_2 nanoparticles

Figure 4 shows the FT-IR spectrum for both TiO_2 nanoparticles-modified and unmodified biomaterials from lemon peels residual biomass. It was found that LP spectrum exhibited several absorption bands below 1500 cm^{-1} attributed to simple bonding and carbonyl groups of biomass. As is observed from LP- TiO_2 spectrum, infrared peaks around 1047, 1507 and 1733 cm^{-1} were assigned to titanium bonding after loading TiO_2 nanoparticles onto biomass [19].

Figure 5 shows SEM micrographs of TiO_2 nanoparticles and the resulting materials after biomasses modification. As can be clearly seen from the micrographs, the TiO_2 nanoparticles are in aggregated form exhibiting an approximately spherical appearance [20]. For YP- TiO_2, CP- TiO_2 and LP- TiO_2 modified biomaterials, it was observed a highly amorphous and agglomerated morphology, which suggested the dispersion of nanoparticles into these biomasses.

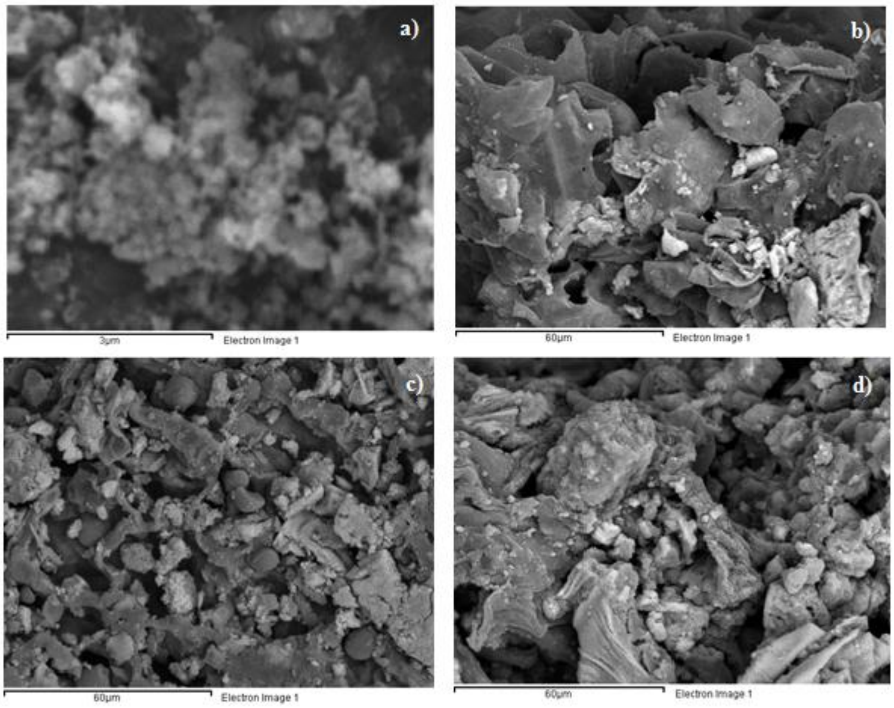

Figure 5. SEM micrographs of: a) TiO_2 nanoparticles, b) YP- TiO_2, c) CP- TiO_2 and d) LP- TiO_2 modified biomaterials

4. Conclusions

This work was focused on green synthesizing TiO_2 nanoparticles used to modify biomaterials from agricultural wastes (cassava peels, yam peels and lemon peels). FT-IR, SEM and XRD analyses were carried out in order to identify functional groups, morphology and crystalline phase, respectively. The crystalline size of TiO_2 nanoparticles was calculated in 19 ± 4 nm by XRD results and Sherrer's equation. Anatase and rutile crystal phases were also identified in this pattern. Regarding FT-IR analysis, similar absorption bands of biomasses were identified in the modified biomaterials spectra and the presence of Ti-O-Ti, Ti-O-C and Ti-O-N bonds suggested that TiO_2 nanoparticles were successfully loaded into biomasses. The SEM micrographs exhibited an amorphous and agglomerated morphology attributed to the dispersion of these nanoparticles onto biomasses.

Hence, it was concluded that the methodology described in this study is recommended for synthetizing novel biomaterials through biomass modification with TiO_2 nanoparticles.

Acknowledgements. The authors are thankful to COLCIENCIAS and to the University of Cartagena for providing materials and equipment for carrying out this study. Moreover, we would like to thank the financial support of Ana Reyes through the Young Researcher Program (Grant No.110752128546).

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Received: April 30, 2018; Published: May 28, 2018