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International Conference

“Collaboration Seminar of Chemistry and Industry (CoSCI-2016)”

5-6 October, 2016

Surabaya, Indonesia

Invited Editor

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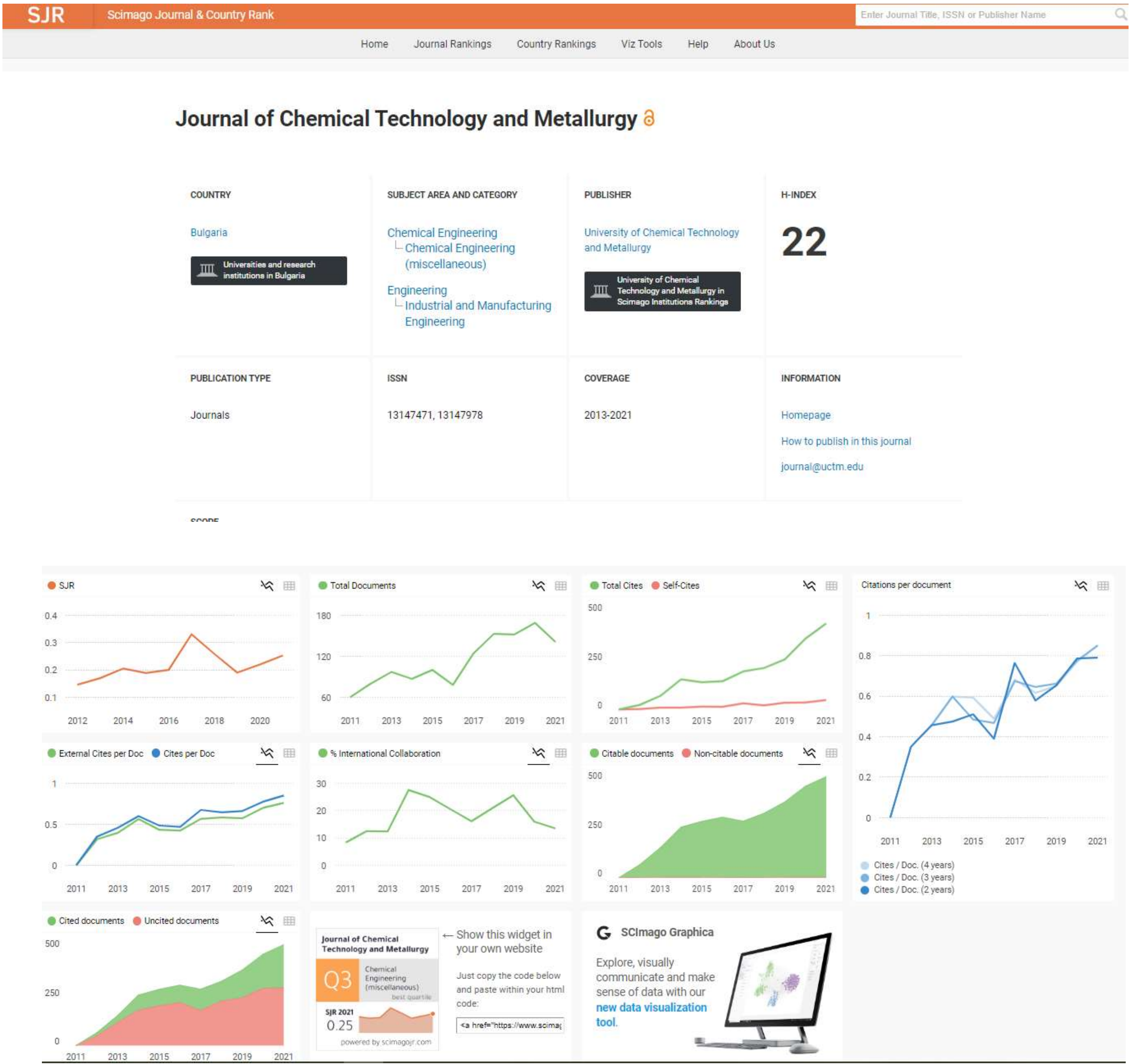

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PARTIAL OXIDATIVE SYNTHESIS OF FLUORESCENT CARBON DERIVED FROM LOCAL BAMBOO LEAVES

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ABSTRACT

The fluorescent carbon based materials have wide medical applications due to their less toxicity, and other attractive properties. Bamboo leaves are an interesting alternative precursor for fluorescent carbon synthesis. They have a good prospect as sustainable raw materials. The synthesis of fluorescent carbon from bamboo leaves by partial oxidation is performed at an optimum temperature of 300°C. Its photoluminescent property is measured by a spectrofluorometer. It shows a wavelength emission at 425 nm - 475 nm. The fluorescent carbon obtained has nanoparticles of the size about 4 nm based on the analysis using atomic force microscopy. It shows a peak at 22,7° by X-Ray diffractometer powder analysis.
Keywords: partial oxidation, bamboo leaves, fluorescent carbon.

INTRODUCTION

The bamboo leaves are abundant, underutilized and low economic value materials in East Java. They contain mostly hydrocarbon compounds such as cellulose that can be a potential source of synthesizing carbon. The latter can be used as a biomedical material because of its less toxicity, good solubility in water, good chemical inertness, high biocompatibility and easy functionalization processes [1].

Carbon nanoparticles have good fluorescence and magnetic properties [2]. Fluorescent carbon is widely used as a biomaterial, pattern coding, sensors fabrication and optoelectronics. Its biomedical applications refer to bioimaging, drug transport and viral inhibitor formulations [3]. Fluorescent carbon generally consists of graphene quantum dots, carbon nanodots, and polymer dots [4].

Top-down and bottom-up synthesis methods of fluorescent carbon nanoparticles are used. The partial oxidation is a favorable bottom-up method of synthesizing fluorescent carbon because it provides a good temperature control and optimum photoluminescence [5]. Fluorescent carbon is synthesized using finely structured organics precursors like graphene and carbon nanotubes or citric acid monohydrate, carboxylate [6], and carbohydrates [7]. However, an improvement of the synthesis method and the choice of the raw material source is needed to provide eco-friendly carbon materials.

Application of bamboo leaves to synthesis carbon dots has been previously proposed by Liu et al. [4]. They show that these leave can be used as a raw material to make precisely carbon dots via a hydrothermal process. A different method of synthesizing carbon dots from bamboo leaves, especially from scrap leaves, is required in view of the effort to develop eco-friendly process of nanomaterials synthesis. The present communication reports a synthesis of fluorescent carbon on the ground of bamboo leaves via partial oxidation. Partial oxidative synthesis of fluorescent carbon is an alternative to pyrolysis. It enhances the product solubility and fluorescent properties preserving carbon functional groups. This refers especially to carbon carboxylic group increases the solubility and the fluorescence of the material obtained.

It can also affect the modification to carbon dots, which in turn leads to wider application [7].

EXPERIMENTAL

Bamboo leaves of the rope type (Asparagus cochinchinensis) were collected from Surabaya, Indonesia. Prior to processing they were washed with water. Then they were heated for 2 h at 150°C. The extraction of cellulose was conducted in 2 % (w/v) aqueous solution of NaOH and refluxed for 4 h at 60°C. The extract was rinsed and centrifuged at 2000 rpm for 15 min. The precipitate of the bamboo leaf extract was burned to synthesize fluorescent carbons by partial oxidation for 2 h at 200°C, 250°C, 300°C, 350°C, and 400°C. The product obtained was dissolved in 2 % (w/v) aqueous NaOH solution. This step was followed by filtration with using 0.22 μm syringe to separate particles by size. The filtrates were dialyzed for 24 h with a membrane MWCO 1000 Da for 24 hours.

Sodium hydroxide (NaOH, 98 %) was purchased from Showa Kako Corp., Japan. It was used without further purification.

The solubility percentage of the resulting carbon dots was determined by measuring the weight of the insoluble bamboo leaves after the partial oxidation process and referring to the weight of the initial bamboo leaves. The fluorescence of carbon solutions was observed by using a portable UV-lamp (365 nm) and analyzed on a JASCO FP-6500 luminescence spectrometer. The fluorescent carbon particles size was measured using an atomic force microscope (AFM) BRUKER. Their powder crystallinity was analyzed by a X-ray diffractometer (XRD) X'PERT-PRO PA using CuKα radiation (λ = 1,5418 Å). The functional groups present were identified by a Fourier transform infrared spectroscopy (FTIR) SHIMADZU-8400S.

RESULTS AND DISCUSSION

The fluorescent carbon obtained at different temperature values shows different solubility in NaOH solution. This is illustrated in Fig. 1. It is evident that the solubility increases going from FC 200 to FC 300 and then decreases – the solubility of FC 400 is less than that of FC 300. Obviously the latter is the optimum one. The product obtained at lower temperatures is not as good as that produced at higher temperature values in terms of the area and the fluorescent ability [8].

The absorbance spectrum of FC 300 is presented in Fig. 2a. It shows a clear shoulder peak at 350 nm.

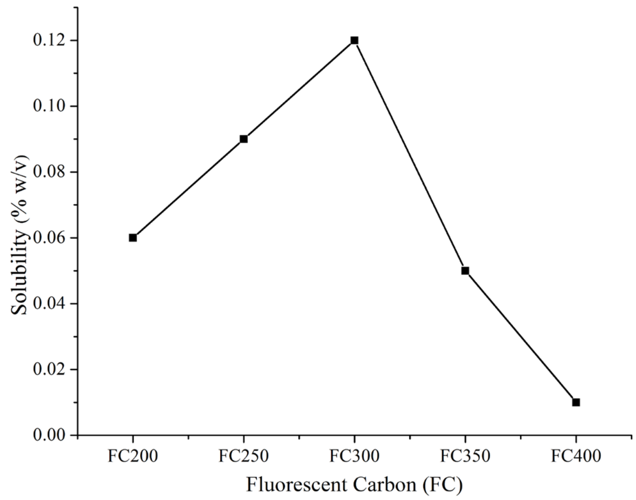

Fig. 1. Solubility of fluorescent carbons (FC).

a)

b)

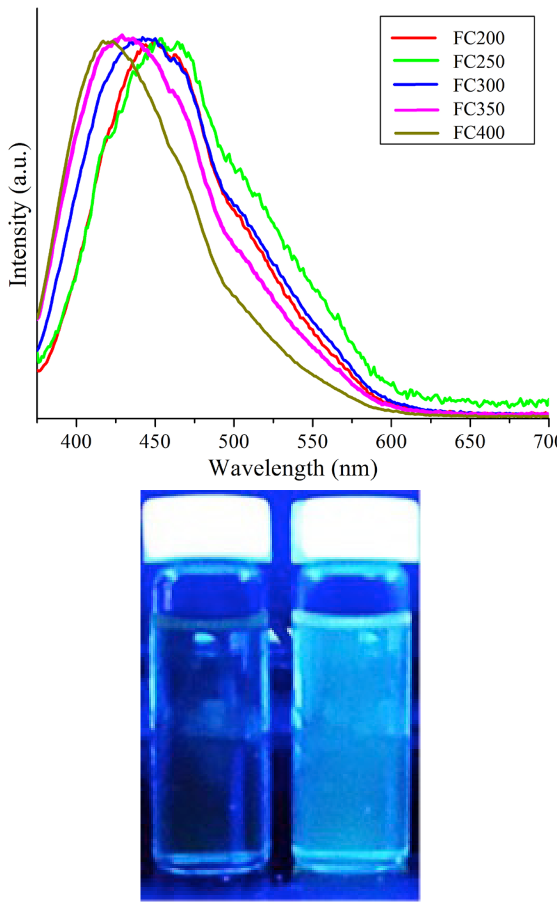

Fig. 2. (a) Emission Spectra of FC; (b) photograph images of water (left) and FC 300 (right) under 254 nm UV light.

The peak is mainly addressed to a three-dimensional confinement of electrons on nano-sized carbon. The photoluminescence (PL) emission spectra of fluorescent carbon are recorded in the wavelength range from 355 nm to 700 nm as shown in Fig. 2b. The difference in emission wavelength is attributed to the different carbon macromolecular structure of bamboo leaves. The pattern of the PL emission spectra is quite similar - the difference is not greater than about 5 nm. The UV-Vis and PL spectra verify the phenomenon of circular absorption and photon emission occurring at the carbon dots. FC 300 has a PL emission around 460 nm and produces a pale blue fluorescence under the portable UV lamp. This finding is in full correspondence with the data reported in ref. [9]

The particle size distribution of fluorescent carbon FC 300 is confirmed by AFM. The corresponding image and particle size distribution histogram is showed in Fig. 3. Based on the AFM image in Fig. 3a, fluorescent carbon FC 300 has quite homogenously dispersed particles. Fig. 3b shows a limited particle size distribution of 1nm -11 nm. The dominant distribution is observed at 3 nm.

a)

b)

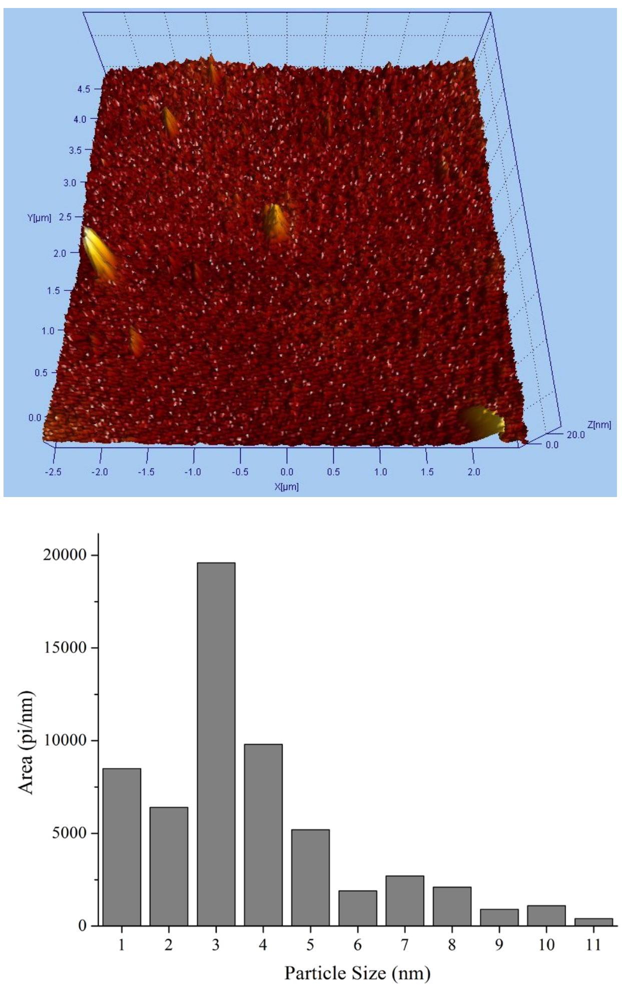

Fig. 3. (a) AFM Image of FC 300 (b) Particle size distribution of FC 300 histogram.

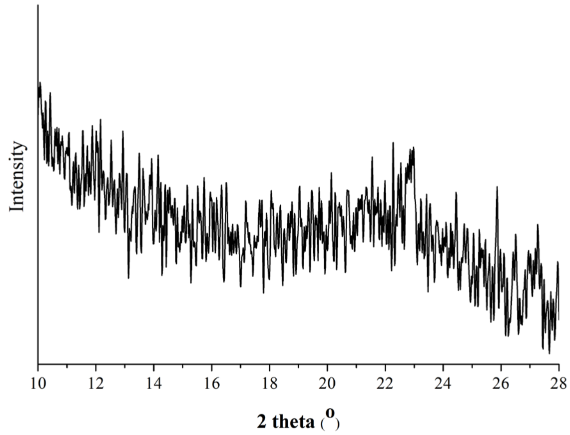

Fig. 4. XRD pattern of FC300.

The XRD pattern of FC300 is shown in Fig. 4. FC 300 is amorphous and a broad peak is observed in the 2θ range of 18° - 26°. The FC 300 structure is quite similar to that of the graphitic structure based on JCPDS26-1076. The FC 300 particle size is determined in the broad amorphous peak region by the Scherer equation and is found equal to 0,244 nm.

The functional groups of FC 300 are analyzed by FTIR spectroscopy. The FTIR spectrum of FC 300 is shown in Fig. 5. Peaks are outlined at 3431.38 cm^{-1}, 2852.81 cm^{-1} and 1415.8 cm^{-1}. They are assigned to O-H, C-H, and C=O. The hydroxyl and carbonyl groups in FC300 indicate that the fluorescent carbon contains graphene quantum dots [10] and graphene oxide [11]

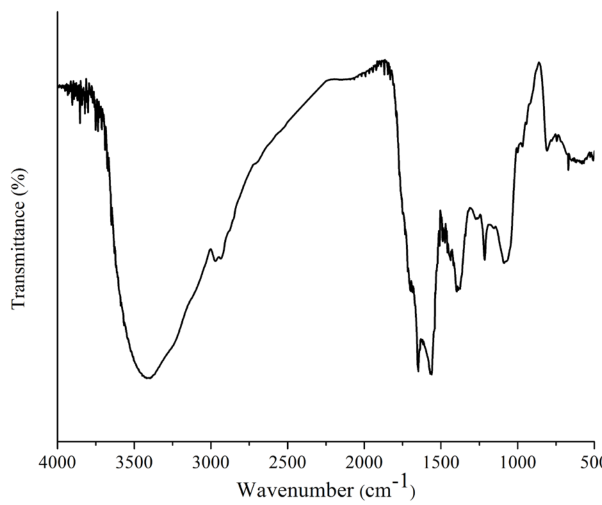

Fig. 5. FTIR Spectrum of FC300.

CONCLUSIONS

Fluorescent carbon is successfully synthesized by partial oxidation of local bamboo leaves. The sample obtained at 300^0C has the optimum solubility. It shows PL emission at 460 nm and has blue fluorescence. Its particles show a dominant distribution at 3 nm. The presence of carboxylic and hydroxyl groups is verified. This fluorescent carbon has the potential of a bio-imaging agent due to its optical properties. It can be also used as a drug transport material because of the size of the resulting carbon dots.

Acknowledgements

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