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Polymer carbon dots from plastics waste upcycling

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ABSTRACT

We present the upcycling of plastic waste into photoluminescence polymer carbon dots (C-Dots). The recycling was conducted to the polypropylene (PP) plastic waste using a simple heating process at around its melting point temperatures of 200 °C, 250 °C, and 300 °C. The optical properties and size as well as structure of polymer C-Dots from PP plastic waste are successfully identified. The newly polymer C-Dots from plastic waste recycling have absorption spectra at the 400–435 nm wavelength range. We obtained a very unique rare phenomenon on the emission spectra that it happened two peaks emission wavelengths of 410 nm (3.03 eV) and 440 (2.83 eV). Polymer C-Dots from PP plastic waste has an average particles size of ~15 nm (200 °C), ~11 nm (250 °C) and ~8 nm (300 °C). The alteration of the optical properties—absorption spectra and emission spectra—as well as particle size of polymer C-Dots are caused by structural change of PP plastic waste due to heating process in recycling process. During the heating process on PP plastic waste, the carbon chain binds oxygen from the environment and forms C=O carbonyl group on the wave number 1638 cm^{-1} which is the main constituent of Polymer C-Dots. Recycling of PP plastic waste into polymer C-Dots has a huge potential to be used as materials for photocatalyst, bioimaging as well as sensors in optoelectronic materials. Furthermore, the result of this study has a role as real action in term of environmental conservation and it answers how to overcoming the problem of plastic waste.

1. Introduction

Plastic is a modern product invented in the 20th century. Plastic becomes very popular object used in dailylife due to it performs superior properties such as lightweight, waterproof, strong and excellent insulator material (North and Halden, 2013). The immense use and best-selling of plastics have resulted to direct impact of plastics waste that leading to the critical environmental issues. Plastics made from polymer seeds which are extremely difficult to decompose naturally (Kunwar et al., 2016). Plastics waste and its management are still complicatedly faced by most of countries in the world because of inadequate technology in order to manage it (Xanthos and Walker, 2017; Miandad et al., 2017).

Plastics are produced using heating process of polymer seeds consisting arranged and united long chains of carbons (Sharuddin et al., 2016). Various types of plastics classified based on their base material such as polyethylene (—C_2H_4)n (PE), polypropylene (—C_3H_6)n (PP), polystyrene (—C_8H_8)n (PS), polyvinyl chloride (—C_2H_3Cl)n (PVc) and other polymer seeds. In general, all of these plastics comprising carbon chains with an abundance of about 62.6–92.2% carbon compound (Zhuo and Levendis, 2014; Nkwachukwu et al., 2013). The existence of carbon chains within polymer seeds—polyethylene glycol (PEG), polyacrylic acid (PAA), polyvinyl alcohol (PVA) and other polymeric species—have been used as the base material for the synthesis of a new material from carbon families called C-Dots (Zhou et al., 2017; Tao et al., 2017; Zhu et al., 2015; Li et al., 2015).

C-Dots have very unique optical properties where it has fluorescence, tiny particle size (< 10 nm) and low toxicity. Those properties make this material has been widely used in fields of bio-imaging in biomedicine, photocatalyst for environmental pollutant decomposition, sensors and solar cells on optoelectronic field (Hong et al., 2015; Aji et al., 2016; Li et al., 2015; Maiaugree et al., 2015; Wang et al., 2014a). C-Dots can be formed by polymerization and carbonization processes using heating treatment of polymer seeds or other carbon from natural resources such as mangosteel peel, flowers, papaya, garlic, and vegetables (Aji et al., 2017; Han et al., 2017; Wang et al., 2016; Zhao et al.,

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2015; Wang et al., 2014b). The carbon chains undergo rearrangement in the polymerization and carbonization processes to form C-Dots particles. Generally, the presence of abundant carbon chains in plastic waste is highly potential to be a novel source of carbon to produce C-Dots material. This study aims to recycle plastic waste into photoluminescence materials of C-Dots. Enhancing the value of plastic waste is vitally important action in term of environmental conservation and it is one of the answers in overcoming the issues of plastic waste by now and in the future.

2. Experiment

C-Dots nanoparticles were uniquely produced from plastic waste bag material—polypropylene (PP)—using heating process at temperature T = 200 °C, T = 250 °C and T = 300 °C for 20 min. A small piece 0.5 g of heated plastic waste was added by 10 ml of ethanol solution as a dispersant solution of C-Dots nanoparticles. The optical properties of colloidal C-Dots nanoparticles were observed by measuring the absorption spectrum using spectrofluorometer UV-Vis Fluostar Omega BMG Labtech in room temperature. Another optical property spectrum emission of fluorescence was measured using a spectrophotometer photoluminescence Cary Eclipse Spectro-flourometer MY14440002 with wavelength excitation 365 nm. Functional group of C-Dots chemical bonding was determined by transmitting spectrum analysis from the Fourier transform infrared measurement using FTIR spectrophotometer Perkin Elmer Spectrum Version 10.03.06. While the size of C-Dots nanoparticles in colloidal solutions was estimated using the Hitachi TEM system HT7700.

3. Result and discussion

Fig. 1 shows the result of plastic waste recycled by heating treatment around of polypropylene's melting point temperature. A simple analysis has been conducted to observe the formation of C-Dots polymer by radiating ultraviolet light (UV) to the sample. The analysis indicates that the sample of heated plastic waste shows the natural photoluminescence. This shows the natural characteristic of the C-Dots polymer (Zhou et al., 2017; Lu et al., 2017). The observed photoluminescence indicates of electron transition within sample of recycled plastic waste. In this case, heating process provides alteration properties of plastic waste. This alteration as polymerization process leads to rearrange the carbon chains of plastic.

Heating treatment alters the optical properties absorption and spectra width of PP plastic waste as shown in Fig. 2. The absorption spectra are observed in wavelength range of 340–550 nm. This absorption region represents the mechanism of electron transition in the orbital $n \rightarrow \pi^*$ that happen on C═O binding (Lu et al., 2017; Niu et al., 2014). The mechanism of electron transition within C-Dots polymer is the transfer of electrons in a fully-charged orbital state by the High Occupied Molecular Orbital (HOMO) electrons to the lowest Unoccupied Molecular Orbital (LUMO). The electron transition process requires a minimum energy of band gap energy. The estimation of band gap energy can be obtained from the analysis of absorbance spectrum. Polymer C-Dots have band gap energy of ~2.8 eV at temperatures T = 200 °C, ~3.05 eV at temperatures T = 250 °C, and ~3.45 eV at temperatures T = 300 °C. The heating temperature has very influential in the formation of C-Dots polymers. During the heating process the carbon chain bond undergoes polymerization of the carbon chains forming a new functional group. The higher of heating temperature the greater number of carbon chains breaks out and forming tiny particles size and increase the C-Dots polymer energy (Zhang et al., 2015). Particle size of the C-Dots polymer is estimated from the TEM image shown in Fig. 3. The C-Dots particle size of PP plastic waste recycling is below the order of < 20 nm. The polymer C-Dots obtained at a temperature of 200 °C has an average particle diameter distribution at ~15 nm. While the plastic waste recycling at temperature 250 °C and 300 °C has a particle size distribution at ~11 nm and ~8 nm, respectively.

Emission spectra polymer C-Dots from plastic waste recycling are shown in Fig. 4. Emission spectra of the C-Dots polymer has two main emission peaks: wavelength 410 nm (3.03 eV) and 440 (2.83 eV) nm. In addition, an emission peak happened at a wavelength of 465 nm (2.67 eV). Analyzing the maximum wavelength of the emission spectra shows that the emitted energy during the recombination process is greater than the absorbed energy during the absorption process as shown in Fig. 2. The electronic transition is occurring from the inter orbital of the fully-charged orbital by the HOMO electron to the orbital empty electron LUMO. An interesting phenomenon was observed in this research because it is very rare to obtain a phenomenon with two emission peaks for fluorescence materials. This phenomenon is known as stimulated emission where there are two electron emissions that undergo recombination process due to photons from UV rays absorbed by C-Dots polymer.

The heating temperature affects the photoluminescence intensity of C-Dots where the higher the heating temperature the lower the luminescence intensity. This is related to the arrangement of monomers which construct the arrangement in form of H and J-aggregates. (Sharma et al., 2017). J-aggregates have a head-to-tail monomer arrangement whereas H-aggregates have a parallel arrangement of monomers (Varughese, 2014). The absorbance spectrum of H band will have blue shift to the smaller wavelength and J-aggregate shifts red band to the large wavelength. Both H and J-aggregate have several different characteristics such as peak intensity of J-aggregate absorption spectrum has increased while the increasing the number of exciton pairs. H-aggregates will decrease the intensity of absorption as the number of exciton pairs decreases. While the emission intensity of J (H)

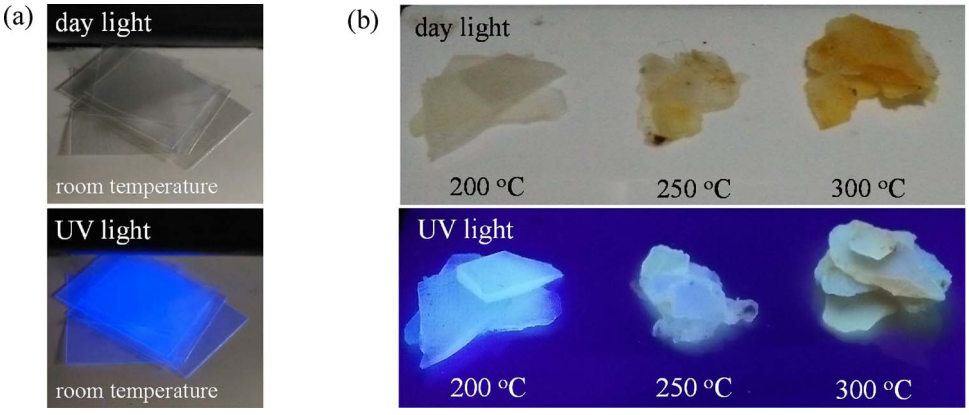

Fig. 1. (a). pieces of PP plastic waste in day light (upper-left image) and under UV light (lower-left image), and (b). pieces of heated PP plastic waste in day light (upper-right image) and under UV light (lower-right image).