Preparation and Characterization of Carbon Nanodots from Natural Polysaccharides and its Application as Photo Sensitizer in Solar Cell

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Abstract: The study explored the utlization of the abundant natural polysaccharides as precursor for carbon nanodots (CNDs) using hydrothermal carbonization and its potential as photosensitizer in solar cell. TEM revealed spherical shape of Cladophora cellulose CNDs (5.79 ±1.60 nm) and crystalline structure (d-spacing of 0.205 ±1.60 nm) indicating graphitic nature. AFM revealed the spherical shape and polydisperse size of the CNDs. FTIR and TOF-SIMs analysis confirmed the presence of hydroxide and carbonyl functional groups on the CND surface. Optical characterization using UV-Vis and Fluorescence Spectroscopy supported the structural and functional group analysis of carbon nanodots suggesting its potential as photosensitizer because it absorbs in the visible region up to 600 nm. The sensitized solar cell fabricated using CNDs as dye replacement showed the potential of CNDs as photosensitizer albeit in lower yields compared to the controls.

Key Words: Carbon nanodots, polysaccharide, cellulose, solar cell

1. INTRODUCTION

Carbon nanodots (CNDs) are newly discovered class of carbon nanomaterials with size below 10 nm. They are referred to as carbon nano lights because they exhibit good solubility and photoluminescence, depending on their size, excitation wavelength, and the surface functionalization (Georgakilas, 2015; Li et al., 2010). There has been much progress in terms of the synthesis, properties, and application of carbon nanodots (Baker and Baker, 2010, Li et al., 2010, Lim et al., 2015, and Roy et al., 2015) since its discovery in 2004. The hydrothermal carbonization method have achieved significant attention owing to its simple set-up and benign way to convert biomass into higher value carbonaceous materials (Wu et al, 2015). It is the objective of this work to characterize and compare the CNDs prepared from different polysaccharide precursors. We report herein the succesful CND synthesis from various polysaccharides and its potential use as sensitizer in solar cell.

2. METHODOLOGY

2.1 Synthesis of CNDs

The following polysacchardies precursors were used: Raw cellulose and cellulose nanocrystal extracted from green algae *Cladophora rupestris*, commercial alpha-cellulose, chitosan and k-carrageenan. Carbon nanodots (CNDs) were prepared by using 2.0 grams of the polysaccharide dispersed in 40 mL distilled water and further agitated by ultrasonication for 15 minutes. The mixture was transferred to a Teflon-lined stainless autoclave (100 mL). The sealed autoclave was placed in an oven at 220 °C for 6 hours. Following cooling, the mixture was subjected to centrifugation at 10,000 rpm for 20 minutes to separate the black solid particle (hydrochar) from the mixture. The yellowish-brown mixture obtained was collected and then dialyzed using a dialysis tube (1000 Da molecular weight cut off) for 24 hours and further purified using 0.2 µm PVDF syringe filter (Whatman) to afford carbon nanodots (CNDs).

2.1 Fabrication of carbon nanodots-sensitized solar cell

Titanium dioxide paste was coated on the conducting surface of the FTO glass using doctor blade method and was sintered at 450 °C in a muffle furnace for 30 minutes. Upon cooling to 80 °C, it was soaked into an aqueous solution of $TiCl_4$, washed with water, then ethanol and dried. This was then immersed in aqueous solution of carbon nanodots. The counter-electrode was prepared by brushing the FTO conducting glass with an alcoholic solution of platinum (Platisol, Solaronix) and then sintered at 450 °C in a muffle furnace for 30 minutes. The CND-sensitized solar cell (open configuration) was prepared by sandwiching the electrolyte solution (Iodolyte AN 50, Solaronix) in between the photoanode and the counter electrode. The cell was secured by attaching two clips at each side of the cell. The same process was used for the fabrication of the positive control DSSC using Ru dye (Ruthenizer 535-bisTBA, Solaronix) and the negative control DSSC without CND or dye. Energy conversion was determinde by electrochemical impedance spectroscopy and AM 1.5 solar cell simulator.

3. RESULTS AND DISCUSSION

The CNDs produced from *Cladophora rupestris* showed nanoparticles with a spherical shape. TEM analysis for CNDs from raw cellulose precursor showed a well dispersed spherically shaped carbon nanodots with an average mean diameter of 5.79 ±1.60 nm (n=100). AFM analysis confirmed the formation of a spherical nanoparticle CNDs.

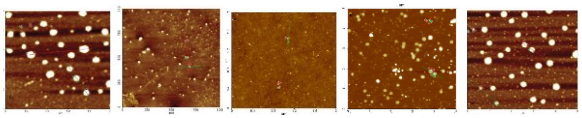

Figure 1. AFM of CNDs from (left to right) Alpha-cellulose, Cladophora cellulose, chitosan, k-carrageenan and cellulose nanocrystals (not the same scale)

FT-IR analysis revealed that most functionalities from the precursor are retained on the carbon nanodots such as the hydroxide stretching (3410 cm^{-1}), C-H stretching (2920 cm^{-1}), O-H stretching (1627 cm^{-1}), C-O stretching (1220 and 1160 cm^{-1}) and C-H rocking vibration of carbohydrates (985 cm^{-1}) (Sucaldito and Camacho, 2017) suggesting that the carbon nanodots contain hydrophilic functionalities, which also accounts for the good water solubility of CNDs. The FTIR spectra of the chitosan-derived CNDs exhibited characteristic absorption bands of O-H stretching overlapping N-H stretching vibrations of amine group in the region of 3400-3170 cm^{-1} and C-H stretching at 2910 cm^{-1}. The N-H bending at 1592 cm^{-1} is characteristic of the amide III C-N stretch, suggesting the presence of amino-containing functional groups. The FTIR spectra of the carrageenan derived CNDs exhibited characteristic absorption bands at 1174 cm^{-1} and 1068 cm^{-1} assigned as O-S-O symmetric vibration and bridge -O, stretching, respectively. The band at 889 cm^{-1} and 852 cm^{-1} refers C–O–SO_3^- on C-6 of galactose residue and O-SO_3^- stretching, respectively. TOF-SIMS data of cellulose-based carbon nanodots shows the ions in the surface of the carbon nanodots indicating the presence of hydrophilic functional groups in the form of hydroxides (OH-) and carbon-based oxides (O-). The TOF-SIMs spectroscopic analysis of the heteroatom-containing carbon nanodots prepared from chitosan shows the presence of nitrogen-containing ions such as cyano (CN^-), nitro (NO_2^-), and nitrogen oxides (CNO^-, $C_3N_2O^-$) on the surface of the CNDs. CNDs obtained from carrageenan on the other hand showed the presence of the precursor functional groups such as SO_3^-, SO_4 and SO_4H-

indicating the retention of the precursor functional groups in the CNDs.

The CNDs exhibit UV-vis absorption from 190 to 400 nm. Absorbance peak around 250-300 nm was attributed to π-π* complex electron transition on the surface due to π conjugated aromatic system and n-π* transition of the carbonyl and other oxygen-containing compounds (Wu et al., 2015). The as-prepared carbon nanodot solutions under daylight show colors ranging from pale yellow (Cladophora cellulose CNDs), to yellowish-brown color (carrageenan and alpha-cellulose CNDs) to brown color (CNC and chitosan CNDs). All polysaccharide CNDs produced viewed under UV light showed green luminescence.

The current-voltage characteristics of CND-SSCs were measured under dark and illuminated conditions. In dark condition, the basic solar cell structure with the donor component, acceptor component, cathode, and anode showed a property characteristic of a diode and no current is generated. However, upon light illumination, the current-voltage curve shifted upward and the solar cell generates current. The performance of carbon nanodots sensitized solar cell from different polysaccharide sources was determined using standard AM 1.5 simulated sunlight (100 mW/cm^2). The curves show the current-voltage profile of CNDs prepared from different polysaccharide assembled with Iodolyte AN 50 (electrolyte). The power conversion efficiency (%PCE) shows that among the carbon nanodots-sensitized solar cell (CND-SSC) fabricated; the one made from CNC precursor has the highest efficiency at 0.0176%, although very low as compared to the positive control reported efficiency of CND-SSC from literature. This can be can be attributed to the observed fluorescence properties of CNDs (Zhang et al., 2015). Fluorescence emission, in a way serves as a charge recombination pathway, greatly affecting the utilization of photo-excited electron for energy generation, lowering efficiency of CND-SSCs. Another possible explanation could be the effectivity of adsorption of the carbon nanodots into the surface of TiO$_2$-coated conducting glass (photo anode). The size and tendency to form aggregates/cluster during the CNDs storage as well as during the soaking step of the photo anode can influence the effectivity of adsorption of CNDs into the TiO$_2$-coated conducting glass since large and aggregated particles will not penetrate easily into the nanoporous surface of the TiO$_2$. Chitosan CNDs tend to have relatively high %PCE compared to other solar cells prepared. Although as expected, the typical surface functionality present on the surface of carbon nanodots, which is carbonyl and hydroxide functional group, the nitrogen-containing polysaccharide precursor tend to be less prone to clustering/aggregation. Comparison of the solar cells prepared in this study with the efficiencies reported from the literature showed lower yields. Nonetheless, it followed similar trends that overall performance of the DSSC can be based on the effective adsorption of CNDs into TiO$_2$-coated conducting glass (photo anode). This is due to the anchoring of functional groups present and the stability of carbon nanodots in aqueous solution (resistance to particle aggregation) to effectively bind to the surface of TiO$_2$.

4. CONCLUSIONS

Carbon nanodots were prepared from various polysaccharide precursors using hydrothermal carbonization to afford colloidal solution of carbon nanodots, separated from larger hydrochar components. The AFM analysis showed spherical shapes with size ranging from 10 nm to 77 nm TEM analysis of Cladophora cellulose CNDs showed smaller average diameter of 5.79 nm (±1.60) compared to AFM analysis due to deconvolution effect. Structural and surface functionalities of carbon nanodots showed retention of functionalities (FT-IR) upon hydrothermal carbonization of the polysaccharide precursors. Carbon nanodots showed that CNDs have UV absorbances at 250-300 nm attributed to conjugated sp^2 carbons and carbonyl functionalities. The colloidal CNDs from various polysaccharide precursors were then successfully used as photo sensitizer for solar cell affording low yield but demonstrated its potential as a photosensitizer.

5. ACKNOWLEDGMENTS

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