ACS Sustainable Chemistry & Engineering

Letter

Cite This: ACS Sustainable Chem. Eng. 2018, 6, 4510−4515

pubs.acs.org/journal/ascecg

Converting Waste Papers to Fluorescent Carbon Dots in the Recycling Process without Loss of Ionic Liquids and Bioimaging Applications

Yoon Jeong,[†,§] Kyunghwan Moon,[†,§] Soohyun Jeong,[†] Won-Gun Koh,[*,‡] and Kangwon Lee[*,†,⊥]

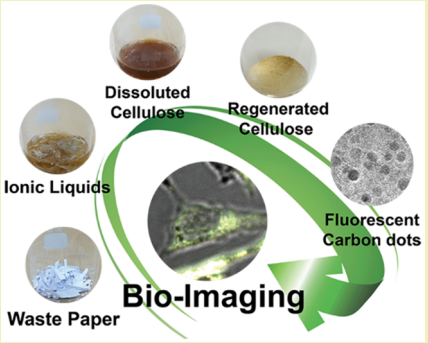
[†]Program in Nanoscience and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Seoul 08826, Republic of Korea

[‡]Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Republic of Korea

[⊥]Advanced Institutes of Convergence Technology, Gyeonggi-do 443-270, Republic of Korea

Supporting Information

ABSTRACT: Recycling is a fascinating topic in academia due to the environmental and economic benefits in industries. In this paper, we report on the method to recycle cellulose waste papers using a green (eco-friendly) approach based on ionic liquids (ILs) where the regenerated cellulose was converted to carbon dots (CDs). The addition of waste papers to the IL, 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), disrupted the chemical arrangement of cellulose and completely dissolved the waste paper under microwave irradiation. Subsequent cellulose regeneration by an additional antisolvent, absolute ethanol, was carried out to recover IL and obtain cellulosic materials' units from waste papers. Furthermore, we report a practical strategy to fabricate CDs under microwave-assisted irradiation. The CDs made by the regenerated cellulose (RC-CDs) were characterized by using analytical and spectroscopic techniques, such as transmission electron microscopy (TEM) and X-ray diffraction (XRD). Finally, we confirmed that RC-CDs exhibited low cytotoxicity, which suggests RC-CDs acts as a promising fluorescent probe for bioimaging.



KEYWORDS: *Paper waste, Cellulose, Recycled materials, Ionic liquid recovery, Carbon dot, Bioimaging*

INTRODUCTION

There is a growing interest in paper recycling, because cellulosic products have been widely used and recycled in many industrial fields. Due to economic and environmental benefits, paper recycling rates have increased by nearly 20% within the last few decades.[1−3] However, down-graded waste papers, which have been recycled several times, might not be recyclable due to fiber damage and decreased cellulose molecular weight during the process.[4−6] A number of research groups have endeavored to convert lower quality waste paper into valuable products.[7−9] In this regard, waste papers typically containing 90−99% cellulose derivatives can be worthy candidates for recycled, value-added product production.

Ionic liquids (ILs), such as organic and organoelement salts, have recently gained attention in both academia and industry for their ability to dissolve cellulose derivatives like fiber, papers, and membranes.[10−13] Compared to conventional solvents, ILs are environmentally friendly and more effective alternatives due to the chemical and thermal stability, miscibility, and negligible vapor pressure over a wide temperature range with a nonflammable nature.[12−14] These unique properties make IL ideal solvents for many applications. Most notably, ILs can be easily recovered and recycled after dissolving cellulose through a simple purification step with consistent, strong cellulose dissolving capacity.[15,16] Small hydrogen bond acceptors, chlorides found in ILs, play important roles in cellulosic dissolution by penetrating the cellulose structure and destroying a wide range of hydrogen bonds. Due to their efficiency and ease of recovery, ILs have huge potentials in cellulose processing.

Carbon dots (CDs) have been spotlighted as multipurpose nanomaterials that hold many advantages like broad excitation spectra, tunable emission spectra, stable photoluminescent (PL), good water solubility, and cytocompatibility.[17,18] CDs can be produced from any carbon-abundant materials[19] and several previous studies have demonstrated a method to fabricate carbon materials from cellulosic resources with ILs, such as grass, straw, ligneous materials, and even waste.[20,21] However, there are two major problems: the physicochemical resistance of cellulose and the extraction of IL from the synthetic process. Intra- and intermolecular hydrogen bonds in cellulose cannot be easily broken down under relatively mild carbonization conditions. In addition, IL should not be consumed in the conversion process and the high cost of IL is one of the main obstacles for its practical utilization.[22] Thus, separating IL from cellulose to demonstrate IL's economic feasibility is vital.

Received: January 23, 2018
Revised: February 13, 2018
Published: February 21, 2018

DOI: 10.1021/acssuschemeng.8b00353
ACS Sustainable Chem. Eng. 2018, 6, 4510−4515

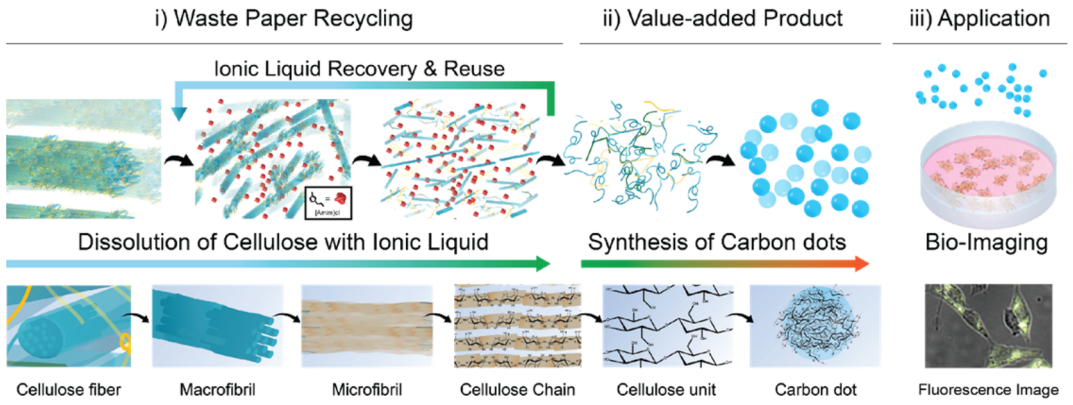


Figure 1. Schematic illustration. (i) Methods for recycling both waste paper and ILs; (ii) the production of carbon dots from regenerated cellulose; (iii) application for bioimaging.

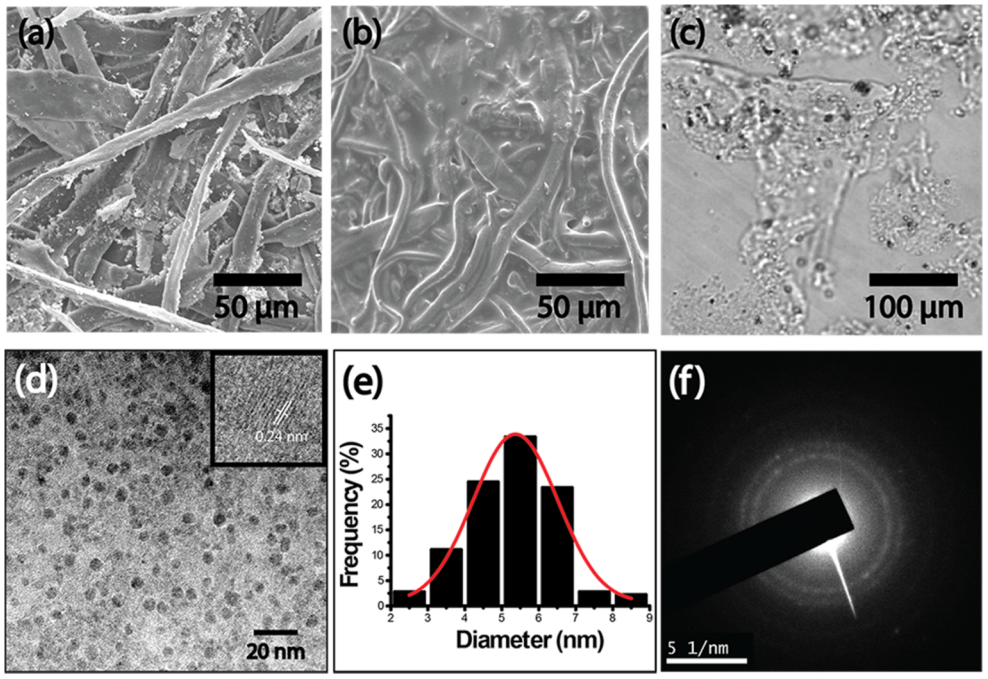


Figure 2. Physico-chemical properities. Scanning electron micrograph (SEM) images of waste paper (a) before (left) and (b) after (right) dissolution and regeneration from the ionic liquid [Amim][Cl]. (c) Optical microscopic image of waste papers dissolved in the ionic liquid. (d) HR-TEM image of the RC-CDs and inset shows the lattice fringes of an individual CD. (e) The distribution histogram of particle size analysis from the HR-TEM images. (f) Corresponding selected-area electron-diffraction (SAED) pattern image.

In this paper, we report a novel practical and promising approach to render CDs from waste papers without consuming IL in an eco-friendly way. Using the microwave-assisted pyrolytic method, waste paper was effectively regenerated and converted to a value-added product, which is regenerated cellulose based CDs (RC-CDs). To the best of our knowledge, this work is it is the first report of the CD synthesized from cellulosic materials without consuming ILs by recycling. This study also demonstrated the potential use of RC-CDs as promising fluorescent probes for bioimaging.

RESULTS AND DISCUSSION

The dissolution of waste papers was conducted through microwave-assisted pyrolysis (at 700 W maximum power for 2−3 s cyclic pulses) due to the rapid and efficient heating process by "microwave dielectric heating effects". A lot of handy, up-to-date dissolving technologies based on microwave heating were reported to improve yield and make controlled heating possible.[10,12,23]

We illustrate the entire process from the degradation of cellulosic materials to the synthesis of CDs in Figure 1. The IL ([Amim][Cl]) has been reported to completely dissolve cellulosic materials at temperatures from 80 to 110 °C.[24] To avoid overheating, we carried out the reaction with intermittent heating, in which the vial was heated and cooled repeatedly until a viscous, homogeneous solution was observed. The process of dissolving cellulose wastes was confirmed though microscopic images to ensure complete dissolution of the waste. During the dissolution process by IL, we observed the surface morphology and cellulose structure to change significantly. Subsequently, the cellulose fibers were fused with one another, displaying relatively homogeneous textures, as shown in SEM images (Figure 2a,b) Furthermore, a microscopy photograph observed by the optical microscope

DOI: 10.1021/acssuschemeng.8b00353
ACS Sustainable Chem. Eng. 2018, 6, 4510−4515

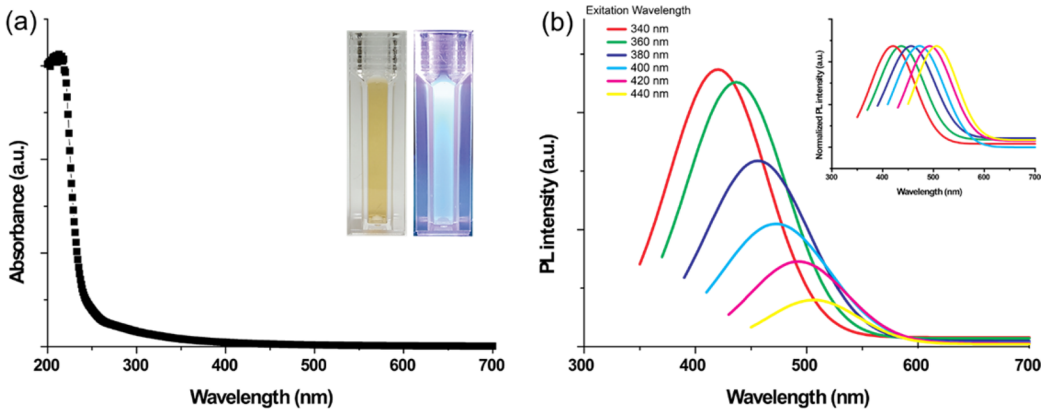


Figure 3. (a) Absorption spectra of RC-CDs. Inset: optical images under daylight (left) and 365 nm UV light (right). (b) Excitation dependent emission PL spectra of RC-CDs at different wavelengths, increasing from 340 to 440 nm with 20 nm increments. Inset: normalized PL emission spectra.

shows the structure of cellulose fibers become dissociated and ruptured in the IL solution (Figure 2c). This can be explained by the depolymerization of the crystalline−amorphous fibers while breaking the hydrogen-bonding network. Cellulose harbors specific chemical arrangements, β-anhydroglucose units with dominant hydroxyl groups, and has the ability to form extensive intra- and intermolecular hydrogen bonds.[25] The higher basicity of ILs can weaken and break inter- and intramolecular hydrogen bonds in the cellulose, causing dissolution. Hence, IL plays a pivotal role in the dissolution of the cellulose structure where the crystalline structure and the amorphous structure are repeated.

Due to the high price of IL, recovery and reutilization of IL is important in the process of regeneration. ILs can be recycled by evaporation, pervaporation, ionic exchange, salting out, and reverse osmosis.[12] By adding absolute ethanol as an antisolvent, both regenerated cellulose and ILs can be obtained. Separating IL from a mixture of IL and cellulose was achieved by a stronger interaction of antisolvent with ILs than cellulose. Recycling IL for reuse was repeated several times (Figure S2). The recovered IL yield was determined as the weight percent from the recovered IL amount in the previous cycle. The result demonstrated that all recovery yield percentages for IL were over 96.9 ± 1.2% on average, indicating that the recovery process was highly reproducible. It is important to note that the recovered IL, when compared to pure IL, still preserved high dissolution efficiency. Therefore, the recovered ILs do not require any further purification steps to remove other impurity elements.

After recovering IL from the cellulose dissolution process, we could obtain regenerated cellulosic materials. Then, these regenerated materials were converted into carbonaceous materials according to the method detailed in the experimental section. The morphology and size of RC-CDs synthesized from the regenerated cellulosic materials are shown in Figure 2d,e. The TEM images clearly displayed that the RC-CDs are spherical with a narrow size distribution for RC-CD diameters that are well dispersed and ranging from 2 to 9 nm (an average diameter of 5.37 ± 0.09 nm). The results of DLS data and ζ-potential measurements of RC-CDs provided further analytical understanding of the particle size and surface potential, as shown in Figure S3. DLS measurements revealed that the size of RC-CDs near 2−3 nm (by number and volume) were dominant. The ζ-potential was determined to be −39.6 mV, which indicates a negative charge on the RC-CD surface, providing steric barriers to prevent RC-CD agglomeration for stable dispersion in aqueous solutions.

The lattice fringes were measured as 0.24 nm and correspond to the (100) graphite facet in the high resolution TEM (HR-TEM) image (Figure 2d inset). Furthermore, the selected-area electron-diffraction (SAED) result corresponded to the high crystallinity and displayed a ring pattern with interplanar lattice spacing of 0.24 nm, which agrees with the (100) lattice spacing of graphite (Figure 2f). Moreover, the X-ray diffraction (XRD) pattern in (Figure S4a) displayed a single broad peak centered at 22°, which is attributed to highly disordered carbon atoms corresponding to the graphite lattice spacing. From the FT-IR spectra (Figure S4b), the revealed broad peak of the spectrum at around 3400 cm^{-1} were attributed to the stretching vibration of large residual O—H groups in regenerated cellulose and RC-CDs. Meanwhile, the peaks observed at 2961 and 1401 cm^{-1} were assigned to the bending vibrations and the stretching vibrations of C—H groups, respectively. Besides, the peak for C═C and C═O at 1644 cm^{-1} associated with the stretching vibration suggests the formation of graphitic domains during carbonization under microwave irradiation. These characteristics suggest both graphitic and amorphous carbon phases for the sp2 and sp3 hybridized carbon structures at various ratios.[26]

Though the comprehensive mechanism of CD formation is still unclear, it has been proposed that various consecutive chemical reactions including hydrolysis, condensation, polymerization, and carbonization between carbon precursors lead to spherical carbon materials.[27] The synthetic process of CDs from cellulosic materials' units is needed to clarify which chemical reactions are involved. It is important to note that pretreatments (e.g., IL, enzyme, acid) are required for the overall general procedure, because it increases the surface area and disintegrates the cellulosic fibril structures, which are then suitable for the conversion process.[28,29] In our study, we provide examples of the pretreatment and conversion process for value-added products.

To support this point, a simple comparison experiment was carried out using regenerated cellulose powders obtained from the recycling process and a shred of paper as the controlled precursor. The CDs made by regenerated cellulose exhibit fluorescence (approximately, PL quantum yield of up to 6%). However, it was found that there is no clear fluorescent signal under a 365 nm UV irradiation from the aliquots of the

DOI: 10.1021/acssuschemeng.8b00353
ACS Sustainable Chem. Eng. 2018, 6, 4510−4515

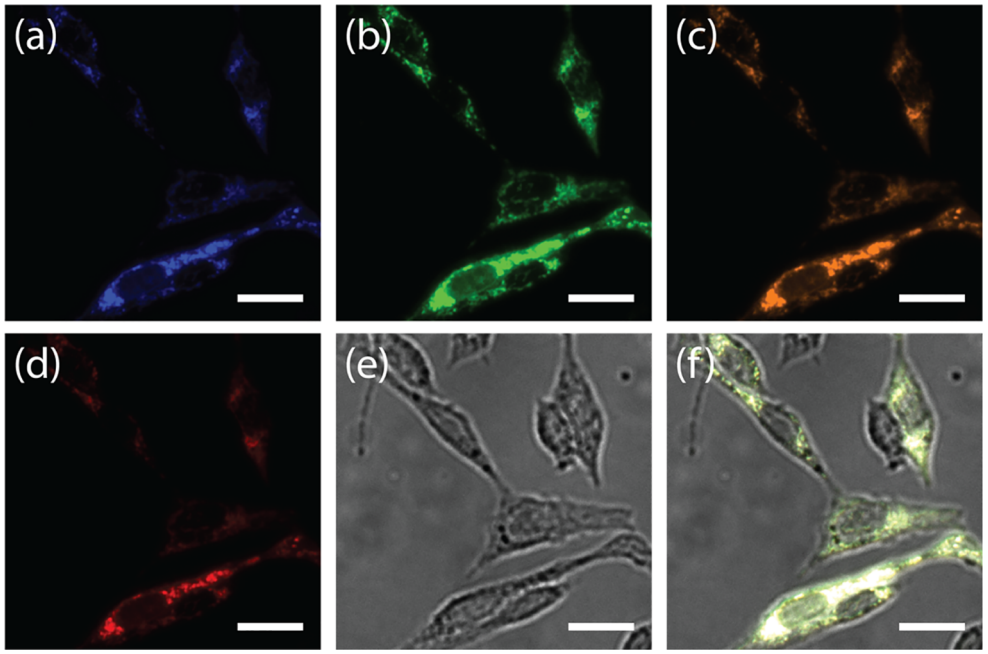


Figure 4. Fluorescence microscope images of C6 Cells incubated with the RC-CDs at excitation wavelengths of (a) 364 nm, (b) 488 nm, (c) 553 nm, and (d) 595 nm (e) bright field (f) merged images. Scale bars: 50 μm.

solution from the controlled precursor. This indicates that the decomposition of the cellulose structure should be conducted beforehand in order to synthesize CD from the waste paper (and/or cellulosic materials). In other words, the degradation process is indispensable to convert waste papers into CDs.

Most papers, such as the A4 white office paper, already contain various unknown fluorescent materials. Interestingly, we observed that these kinds of waste can show bright emission lights shifted to different wavelengths by a simple microwave irradiation process.(Figure S5) The emission shift might result from certain complex chemical reactions involved in various fluorescent chemicals. Although clarification is needed, this implies that fluorescent chemical removal steps might proceed when fabricating CDs from the used waste paper. In this experiment, we only used the filter paper, which does not contain fluorescent chemicals to circumvent this problematic issue.

It has been reported that CDs have unique optical properties because they possess both the broad absorption band and the excitation-dependent PL behavior.[18,27] To understand the optical properties of generated RC-CDs, we provide the UV visible absorption and photoluminescence (PL) spectra in Figure 3. The RC-CDs showed blue fluorescence under 365 nm UV irradiation (inset Figure3a). The absorption spectrum of CDs showed an intense peak at 225 nm, which can be ascribed to n−n* transitions of aromatic C═C bonds and the absorption extends into the visible region of the spectrum. Furthermore, absorption shoulders at about 270−300 nm were assigned to $\pi-\pi^*$ transition of C═C bonds and $n-\pi^*$ transition of the C═O bonds to functional group at the surface.[30,31] In Figure 3b, where PL emission spectra were shown, red-shifted spectra were observed by gradually changing the excitation wavelength from 340 to 440 nm. This phenomenon is in agreement with various CDs' PL spectra, which might be attributed to the surface state of fluorescent carbon-based materials.[17] Until now, several mechanisms have been proposed regarding these optical properties: quantum confinement, surface energy traps, formation of aromatic structures, and recombination of excitons.[32−34] However, the optical property origins of CDs are still in debate and have not yet been fully understood.

To confirm RC-CDs as bioimaging applicable, we conduced CCK-8 assays to evaluate the cytotoxic effects of RC-CDs to C6 cells. No obvious toxic effects were observed on C6 cells after 24 h of exposure. This demonstrated that the RC-CDs have very low cytotoxicity (Figure S6). Meanwhile, 10% of DMSO used as a positive control showed acute cytotoxic effects. Even when the concentration of RC-CDs was up to 1 mg/mL, the cells' viability was over 90%. As shown in Figure 4, we have performed *in vitro* cellular uptake assay in the C6 cells. After incubation with C6 cells for 24 h, the RC-CDs taken by the cells could be observed and readily detected under a fluorescence microscope like most CDs reported by certain scientists.[35,36] Without surface modification or the target moiety attachment to deliver RC-CDs into specific regions in cells, they can be localized in the cytoplasm. However, based on the fluorescence microscope images, we found the agglomeration of RC-CDs inside the cells more localized in the peri-nuclear region. Even though this phenomenon needs future work to validate localization mechanisms, we hypothesize that this is connected with various cellular behaviors like vesicular transport and interaction with sequestering proteins involving continual ingestion and internalization of solute and fluids.[37,38] Therefore, we postulate that RC-CDs that have multicolor emission profiles and localization in peri-nuclear regions have great potential to be used in biolabeling or bioimaging.

CONCLUSION

We demonstrated a practical and eco-friendly synthesis of CDs while waste paper recycling and recovering IL processes. The waste paper was effectively converted into CDs without IL loss. The obtained RC-CDs exhibit typical excitation-dependent emission. When treated to C6 cells, they show specific localization at the peri-nuclear region of the cytoplasm.

DOI: 10.1021/acssuschemeng.8b00353
ACS Sustainable Chem. Eng. 2018, 6, 4510−4515

Therefore, fabricating CDs while recovering both waste paper and IL is advantageous for the waste recycling process, which could be further applicable to biotechnologies using fluorescence properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b00353.

Detailed experimental methods and additional results (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*K. Lee. E-mail: kangwonlee@snu.ac.kr, Phone: 82-31-888-9145.

*W.-G. Koh. E-mail: wongun@yonsei.ac.kr, Phone: 82-2-2123-5755.

ORCID

Won-Gun Koh: 0000-0002-5191-2531

Kangwon Lee: 0000-0001-5745-313X

Author Contributions

§These authors equally contributed to this work

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Bio & Medical Technology Development Program of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (grant no. NRF-2016R1D1A1B03932220, NRF-2016M3A9B4919711, and NRF 2009-0093823).

■ REFERENCES

(1) Pivnenko, K.; Eriksson, E.; Astrup, T. F. Waste paper for recycling: Overview and identification of potentially critical substances. *Waste Manage.* **2015**, *45*, 134−42.

(2) Ghinea, C.; Petraru, M.; Simion, I. M.; Sobariu, D.; Bressers, H. T. A.; Gavrilescu, M. Life Cycle Assessment of Waste Management and Recycled Paper Systems. *Environ. Eng. Manage. J.* **2014**, *13* (8), 2073−2085.

(3) Yeon, J. O.; Kim, K. W.; Yang, K. S.; Kim, J. M.; Kim, M. J. Physical properties of cellulose sound absorbers produced using recycled paper. *Constr. Build Mater.* **2014**, *70*, 494−500.

(4) Merrild, H.; Damgaard, A.; Christensen, T. H. Recycling of paper: accounting of greenhouse gases and global warming contributions. *Waste Manage. Res.* **2009**, *27* (8), 746−53.

(5) Rahman, M. O.; Hussain, A.; Basri, H. A critical review on waste paper sorting techniques. *Int. J. Environ. Sci. Technol.* **2014**, *11* (2), 551−564.

(6) Villanueva, A.; Wenzel, H. Paper waste - Recycling, incineration or landfilling? A review of existing life cycle assessments. *Waste Manage.* **2007**, *27* (8), S29−S46.

(7) Suriapparao, D. V.; Vinu, R. Bio-oil production via catalytic microwave pyrolysis of model municipal solid waste component mixtures. *RSC Adv.* **2015**, *5* (71), 57619−57631.

(8) Won, K.; Kim, Y. H.; An, S.; Lee, H. J.; Park, S.; Choi, Y. K.; Kim, J. H.; Hwang, H. I.; Kim, H. J.; Kim, H.; Lee, S. H. Glucose Oxidase/Cellulose-Carbon Nanotube Composite Paper as a Biocompatible Bioelectrode for Biofuel Cells. *Appl. Biochem. Biotechnol.* **2013**, *171* (5), 1194−1202.

(9) Liu, Z.; Ho, S. H.; Sasaki, K.; den Haan, R.; Inokuma, K.; Ogino, C.; van Zyl, W. H.; Hasunuma, T.; Kondo, A. Engineering of a novel cellulose-adherent cellulolytic Saccharomyces cerevisiae for cellulosic biofuel production. *Sci. Rep.* **2016**, *6*, 24550.

(10) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose [correction of cellose] with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124* (18), 4974−5.

(11) Zhang, H.; Wu, J.; Zhang, J.; He, J. S. 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose. *Macromolecules* **2005**, *38* (20), 8272−8277.

(12) Zhu, S. D.; Wu, Y. X.; Chen, Q. M.; Yu, Z. N.; Wang, C. W.; Jin, S. W.; Ding, Y. G.; Wu, G. Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chem.* **2006**, *8* (4), 325−327.

(13) Zhang, S.; Zhang, J.; Zhang, Y.; Deng, Y. Nanoconfined ionic liquids. *Chem. Rev.* **2017**, *117* (10), 6755−6833.

(14) Isik, M.; Sardon, H.; Mecerreyes, D. Ionic liquids and cellulose: dissolution, chemical modification and preparation of new cellulosic materials. *Int. J. Mol. Sci.* **2014**, *15* (7), 11922−11940.

(15) Sun, N.; Rahman, M.; Qin, Y.; Maxim, M. L.; Rodriguez, H.; Rogers, R. D. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Green Chem.* **2009**, *11* (5), 646−655.

(16) Montalbo-Lomboy, M.; Grewell, D. Rapid dissolution of switchgrass in 1-butyl-3-methylimidazolium chloride by ultrasonication. *Ultrason. Sonochem.* **2015**, *22*, 588−599.

(17) Wang, Y.; Hu, A. Carbon quantum dots: synthesis, properties and applications. *J. Mater. Chem. C* **2014**, *2* (34), 6921−6939.

(18) Namdari, P.; Negahdari, B.; Eatemadi, A. Synthesis, properties and biomedical applications of carbon-based quantum dots: An updated review. *Biomed. Pharmacother.* **2017**, *87*, 209−222.

(19) Zhu, S.; Song, Y.; Zhao, X.; Shao, J.; Zhang, J.; Yang, B. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. *Nano Res.* **2015**, *8* (2), 355−381.

(20) Liu, S.; Tian, J.; Wang, L.; Zhang, Y.; Qin, X.; Luo, Y.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. Hydrothermal Treatment of Grass: A Low-Cost, Green Route to Nitrogen-Doped, Carbon-Rich, Photoluminescent Polymer Nanodots as an Effective Fluorescent Sensing Platform for Label-Free Detection of Cu (II) Ions. *Adv. Mater.* **2012**, *24* (15), 2037−2041.

(21) Liu, R. L.; Gao, M. P.; Zhang, J.; Li, Z. L.; Chen, J. Y.; Liu, P.; Wu, D. Q. An ionic liquid promoted microwave-hydrothermal route towards highly photoluminescent carbon dots for sensitive and selective detection of iron(III). *RSC Adv.* **2015**, *5* (31), 24205−24209.

(22) George, A.; Brandt, A.; Tran, K.; Zahari, S. M. S. N. S.; Klein-Marcuschamer, D.; Sun, N.; Sathitsuksanoh, N.; Shi, J.; Stavila, V.; Parthasarathi, R.; Singh, S.; Holmes, B. M.; Welton, T.; Simmons, B. A.; Hallett, J. P. Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. *Green Chem.* **2015**, *17* (3), 1728−1734.

(23) Possidonio, S.; Fidale, L. C.; El Seoud, O. A. Microwave-assisted derivatization of cellulose in an ionic liquid: An efficient, expedient synthesis of simple and mixed carboxylic esters. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48* (1), 134−143.

(24) Wang, H.; Gurau, G.; Rogers, R. D. Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, *41* (4), 1519−37.

(25) Sahin, H. T.; Arslan, M. B. A study on physical and chemical properties of cellulose paper immersed in various solvent mixtures. *Int. J. Mol. Sci.* **2008**, *9* (1), 78−88.

(26) Qu, S.; Wang, X.; Lu, Q.; Liu, X.; Wang, L. A biocompatible fluorescent ink based on water-soluble luminescent carbon nanodots. *Angew. Chem., Int. Ed.* **2012**, *51* (49), 12215−8.

(27) Lim, S. Y.; Shen, W.; Gao, Z. Carbon quantum dots and their applications. *Chem. Soc. Rev.* **2015**, *44* (1), 362−381.

(28) Hassanzadeh, S.; Aminlashgari, N.; Hakkarainen, M. Microwave-assisted recycling of waste paper to green platform chemicals and carbon nanospheres. *ACS Sustainable Chem. Eng.* **2015**, *3* (1), 177−185.

(29) Huang, Y.-B.; Fu, Y. Hydrolysis of cellulose to glucose by solid acid catalysts. *Green Chem.* **2013**, *15* (5), 1095−1111.

(30) He, G.; Shu, M.; Yang, Z.; Ma, Y.; Huang, D.; Xu, S.; Wang, Y.; Hu, N.; Zhang, Y.; Xu, L. Microwave formation and photoluminescence mechanisms of multi-states nitrogen doped carbon dots. *Appl. Surf. Sci.* **2017**, *422* (Supplement C), 257−265.
(31) Meiling, T. T.; Cywiński, P. J.; Bald, I. White carbon: Fluorescent carbon nanoparticles with tunable quantum yield in a reproducible green synthesis. *Sci. Rep.* **2016**, *6*, 28557.
(32) Sun, Y.-P.; Zhou, B.; Lin, Y.; Wang, W.; Fernando, K. S.; Pathak, P.; Meziani, M. J.; Harruff, B. A.; Wang, X.; Wang, H.; et al. Quantum-sized carbon dots for bright and colorful photoluminescence. *J. Am. Chem. Soc.* **2006**, *128* (24), 7756−7757.
(33) Baker, S. N.; Baker, G. A. Luminescent carbon nanodots: emergent nanolights. *Angew. Chem., Int. Ed.* **2010**, *49* (38), 6726−6744.
(34) Fu, M.; Ehrat, F.; Wang, Y.; Milowska, K. Z.; Reckmeier, C.; Rogach, A. L.; Stolarczyk, J. K.; Urban, A. S.; Feldmann, J. Carbon dots: a unique fluorescent cocktail of polycyclic aromatic hydrocarbons. *Nano Lett.* **2015**, *15* (9), 6030−6035.
(35) Cao, L.; Wang, X.; Meziani, M. J.; Lu, F.; Wang, H.; Luo, P. G.; Lin, Y.; Harruff, B. A.; Veca, L. M.; Murray, D.; et al. Carbon dots for multiphoton bioimaging. *J. Am. Chem. Soc.* **2007**, *129* (37), 11318−11319.
(36) Zhu, S.; Meng, Q.; Wang, L.; Zhang, J.; Song, Y.; Jin, H.; Zhang, K.; Sun, H.; Wang, H.; Yang, B. Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging. *Angew. Chem.* **2013**, *125* (14), 4045−4049.
(37) Ruan, G.; Agrawal, A.; Marcus, A. I.; Nie, S. Imaging and tracking of tat peptide-conjugated quantum dots in living cells: new insights into nanoparticle uptake, intracellular transport, and vesicle shedding. *J. Am. Chem. Soc.* **2007**, *129* (47), 14759−14766.
(38) Chou, L. Y.; Ming, K.; Chan, W. C. Strategies for the intracellular delivery of nanoparticles. *Chem. Soc. Rev.* **2011**, *40* (1), 233−245.

DOI: 10.1021/acssuschemeng.8b00353
ACS Sustainable Chem. Eng. 2018, 6, 4510−4515