Ball-milling treatment of cotton fiber for optimizing its derived carbon quantum dots

Ping Huang¹², Shunjian Xu²*, Yongping Luo², Wei Zhong², Haiyan Fu², Hui Ou² and Meng Zhang¹*¹

¹School of Materials Science and Engineering, Nanchang University, Nanchang 330031, China
²Xinyu Institute of New Energy, Xinyu University, Xinyu 338004, China
*Corresponding author’s e-mail: xushunjian@xyc.edu.cn (S Xu)

Abstract. Due to the physical force of agate balls, many cracks on the surface of cotton fiber are caused by ball-milling treatment. Moreover, ball-milling changes the structure of cotton cellulose from crystalline to amorphous. These factors help increase the contact area of cotton fiber with active water and become more reactive in the hydrothermal process. Finally, ball-milling treatment improves the yield of carbon quantum dots (CQDs), which leads to a 10% increase in the power conversion efficiency of CQDs based quantum dot-sensitized solar cells. Besides, the fluorescence intensity of CQDs is doubled without changing its other characteristics because of the ball-milling treatment. Therefore, ball-milling could be adopted as an effective green method to optimize cotton derived CQDs.

1. Introduction

Owing to the outstanding fluorescent performance, excellent electron transfer capability, abundant surface functional groups, favorable biocompatibility and chemical stability, carbon quantum dots (CQDs) have been widely used in bioimaging, catalysis, sensing and photovoltaic, et al. [1-4] Hydrothermal method is an efficient green method to synthesize CQDs with low cost. [5] Various kinds of biomass products have been used to prepare CQD through this method, such as fruits, plants, vegetables and animal derivatives, et al. [6] Cotton is one of the most widely grown crops in the world, and the content of cellulose in cotton is as high as 98%. Wang et al. [7] firstly prepared fluorescent CQDs from degrease cotton by hydrothermal method for selectively determining chromium ions.

However, cellulose is a large molecule polysaccharide that is insoluble in water under normal conditions, which leads to a low yield of CQDs prepared by hydrothermal method. Cellulose is usually considered as a two-phase material with both crystalline and amorphous phases. It is generally believed that amorphous domains of one material are weaker and more reactive than its corresponding crystalline domains. In the research of the effect of cellulose crystallinity on its hydrolysis, Zhao et al [8] found that reducing crystallinity through ball-milling treatment could effectively accelerate the hydrolysis. Howsmon et al. [9], Ago et al. [10] and Ling et al. [11] have demonstrated that ball-milling could change the structure of cotton cellulose, and achieved the transformation of cotton cellulose from crystalline phase to amorphous phase. Therefore, ball-milling was adopted as a way of pretreatment of cotton to promote the first step of its hydrothermal reaction (namely hydrolysis), which will improve the yield and performance of CQDs.
2. Results and discussion

Figure 1 SEM morphologies of (a) untreated cotton and (b) ball-milled cotton

1 g cotton was subjected to be ball-milled in agate jar with 165 g agate balls at 600 rpm for 8 h. As shown in figure 1, the untreated cotton has smooth fibrous morphology with no more than 10 mm in diameter. After the ball-milling treatment, the gap between the cotton fibers has been greatly reduced due to the physical force of agate balls, although the diameters have not changed much. More importantly, severe cracks have been observed on the fiber surface, which will increase its surface area.

XRD patterns in figure 2 show that the untreated cotton has evident characteristic peaks at 15.3°, 16.7°, 22.9° and 34.6°, which are ascribed to crystalline planes of (110), (110), (200) and (004) for cellulose I, respectively. [11] However, the intensities of these three peaks decrease much when the cotton suffers from ball-milling, indicating that the ball-milling treatment makes some crystalline domains of the cotton change into amorphous domains.

Figure 2 XRD patterns of cotton

Figure 3 (a) UV-Vis spectra of CQDs (inset: photo of CQDs under natural light), (b) J-V curves of CQDs based QDSCs
Take 300 mg cotton into the Teflon reactor with 300 μL ethanol amine and 35 mL ultrapure water. Then the reactor was put into the over and kept the temperature at 200 ℃ for 15 h. After centrifugation at 1000 rpm for 30 min and filtration with 0.22 μm membranes, the reaction solution was dialyzed for 24 h. Whereafter, the obtained CQDs were keep in the refrigerator at 4 ℃ for later use. Here, the CQDs prepared using the untreated cotton and ball-milled cotton are labeled as CQD-U and CQD-B, respectively. Figure 3(a) show the UV-Vis spectra of CQDs. Both CQDs exhibit a large absorption before 400 nm, with diminution to visible range. Three absorption peaks at around 240 nm, 285 nm and 345 nm appear in both CQDs. The peaks before 300 nm are attributed to π→π* transition of aromatic hydrocarbon, while the last peak corresponds to n→π* transition of C=O bond. [12] It is noted that the absorption of CQD-B is larger than that of CQD-U all over the scale. The possible reason is that the cotton fiber broken by agate balls has a larger contact area with active water, and thus increases the hydrolysis of the cotton fiber, which greatly improves the yield of CQDs. The photos of CQDs under natural light in inset of figure 3 show that the color of CQD-B is much darker than that of CQD-U, which is a good proof of the above speculation. The results of the transmittance spectra are consistent with that of the absorption spectra.

In view of their good light absorption performance, the synthesized CQDs were used as sensitizers in quantum dot-sensitized solar cells (QDSCs). The TiO2 photoanode, Pt counter electrode and I-/I3- electrolyte were prepared as the previous report [13]. Then the photoanode was immersed in the CQD solution for 24 h to get the sensitized photoanode. Finally, the QDSC was assembled by pouring the electrolyte between the counter electrode and the sensitized photoanode. J-V curves of QDs based QDSCs are present in figure 3(b) under simulated illumination of AM1.5 G. The effective irradiating area was 0.16 cm2. The short-circuit current density (Jsc), open-circuit voltage (Voc) and fill factor (FF) of QDSC based on CQD-U and CQD-B are 1.05 mA/cm2, 0.63V, 0.61 and 1.19 mA/cm2, 0.63V, 0.61 respectively, which makes the power conversion efficiency (PCE) of CQD-B based QDSC (0.46%) is 10% higher than that of CQD-U based QDSC (0.42%). The improvement of PCE mainly comes from Jsc, owing to the increasing concentration of CQD solution with ball-milling treatment.

Besides, the photoluminescence (PL) of the CQDs are explored for more application. As shown in figure 4, CQD-B shows the same rules as CQD-U. When the excitation wavelength increases from 270 nm to 410 nm, the emission intensity of CQD increases first and then decreases, and reaches the highest at the excitation wavelength of 350 nm. Meanwhile, the emission wavelengths exhibit obvious red shift. Most notably, the maximum emission intensity of CQD-B is twice as high as that of CQD-U, indicating that ball-milling treatment could enhance the PL intensity of CQDs. This is verified by the photos of CQDs under UV light of 365 nm in inset of figure 4. Ball-milling treatment will provide an important optimization method for the application of cotton derived CQDs in bioimaging.

![Figure 4](image-url) PL spectra of (a)CQD-U and (b)CQD-B (insets: photos of CQDs under UV light of 365 nm)
3. Conclusion
Due to the physical force of agate balls, many cracks on the surface of cotton fiber are caused by ball-milling treatment, which will increase its contact area with active water in the hydrothermal process. XRD pattern indicates that ball-milling treatment facilitate the transformation of cotton cellulose from crystalline phase to amorphous phase, while amorphous domains are weaker and more reactive than its corresponding crystalline domains. Based on the above-mentioned reasons, ball-milling treatment greatly improves the yield of CQDs, which makes the light absorption of CQD-B larger than that of CQD-U all over the scale. This helps increase the PCE of CQDs based QDSC by 10%. Furthermore, ball-milling treatment doubled the PL intensity of CQDs, which provide an important optimization method for the application of cotton derived CQDs in bioimaging.

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