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# Fluorescent carbon nanoparticles: electrochemical synthesis and their pH sensitive photoluminescence properties<sup>†</sup>

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Highly fluorescent carbon nanoparticles were synthesized directly from ethanol by a one-step sodium hydroxide-assisted electrochemical treatment. These nanoparticles could emit bright and colorful photoluminescence covering the entire visible spectral range and had excellent up-conversion fluorescent, stable ionic, long fluorescence lifetime and pH-sensitive photoluminescence properties.

## 1. Introduction

In recent years, various forms of carbon nanomaterials such as fullerenes, carbon nanotubes, nanodiamonds and other carbon nanomaterials have been rapidly developed not only for their scientific interest but also for many technological applications.<sup>1-9</sup> The emergence of fluorescent carbon nanoparticles (FCNPs) also has great potential application in the fields of nanobiotechnology and nanocatalysis.<sup>10-16</sup> Compared with traditional fluorescent semiconductor quantum dots and organic dyes, FCNPs possess excellent properties, such as chemical inertness, high photostability against photobleaching and blinking, and can be modified easily.<sup>11,12</sup> In particular, brighter fluorescence (i.e., increased fluorescence quantum yield) is observed after passivation by covalent binding of organic groups.<sup>15</sup> In addition, FCNPs are biocompatible, small in size and low in molecular weight, and have low toxicity, making them superior to quantum dots. 11,13

To date, a lot of routes for preparing FCNPs have been reported, including chemical oxidation of arc-discharge single-walled carbon nanotubes (SWCNTs),<sup>10,14</sup> laser ablation of graphite,<sup>15–17</sup> electrochemical oxidation of graphite or multiwalled carbon nanotubes (MWCNTs),<sup>18–20</sup> thermal oxidation of suitable molecular precursors,<sup>21–24</sup> supported routes,<sup>25</sup> vapor deposition of soot,<sup>11,26</sup> proton-beam irradiation of nanodiamonds<sup>27,28</sup> or microwave methods<sup>29</sup> and so on. However, these methods usually involve complex processes, expensive precursors, high energy loss or severe synthetic conditions, which are unlikely to be extended significantly or not an environmental-friendly process in the near future. Consequently, the convenient, green, low energy loss and large scale fabrication of FCNPs is the urgent challenge in nano-technology and nanochemistry.

Recently, we have reported water-soluble fluorescent carbon quantum dots (CQDs) cutting from graphite rod under alkaliassistance.<sup>30</sup> which can be size-controlled and have excellent fluorescent properties. However, we find that the loss of graphite rod after electrochemical treatment is not equal to the amount of the as-prepared CQDs, the amount of fluorescent carbon product is larger than the loss amount of graphite. We speculate that the extra carbon products come from ethanol. In this paper, we study and prove that these extra carbon products derive from the ethanol. Meanwhile, we report a facile and green method to prepare FCNPs by a one-step electrochemical treatment of ethanol under sodium hydroxide assistance, and the formation mechanism of FCNPs is also investigated. Compared with the FCNPs or CQDs prepared using other methods, including our own previous work, the present approach is much simpler, more economic and easier to be controlled or separated. Further extensive research will be carried out on physical properties. These FCNPs also have excellent water-solubility, strong visible emission, and up-conversion photoluminescence (UPL), stable ionic, pH-sensitive and long fluorescence lifetime properties.

## 2. Experimental

### 2.1 Materials and preparation of FCNPs

All the chemicals were purchased from Sigma-Aldrich and Beijing Chemical Reagent (Beijing, China), and were used as-received. In a typical experiment, 8.0 g sodium hydroxide was added to a mixed solution of 200 ml ethanol and 10 ml deionized water to form a clear solution. Then the solution

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Downloaded by Brown University on 13 January 2013 Published on 16 September 2011 on http://pubs.rsc.org | doi:10.1039/C1NJ20575G was given an electrochemical treatment for 4 h at room temperature (cell potential: 25–40 V). Pt rods (diameter of about 0.2 cm) were used as an anode and a cathode, respectively, the reference electrode was not used. We succeeded in synthesizing FCNPs with a current intensity in the range of 200–260 mA cm<sup>-2</sup>. After that, the raw solution was given a dialysis treatment using a semi-permeable membrane (MWCO 14000) to remove the non-fluorescent deposit. After filter treatment, the obtained solution became brown, implying the formation of FCNPs. The conversion per pass of FCNPs is 3–4%.

#### 2.2 Characterization methods

All solid samples were dried under vacuum at 60 °C for 8–10 h before the measurement. The Fourier Transform Infrared (FTIR) spectrum of FCNPs was obtained with a Varian Spectrum GX spectrometer. The PL study was carried out on a Horiba Jobin Yvon (FluoroMax 4) Luminescence Spectrometer and an optical fluorescent microscope (Leica DM4500B), while UV-visible spectra were obtained with an Agilent 8453 UV-VIS Diode Array Spectrophotometer. The transmission electron microscopy (TEM) image was obtained with a FEI/ Philips Techal 12 BioTWIN TEM. The X-ray photoelectron spectra (XPS) were measured by a Kratos AXIS UltraDLD photoelectron spectroscope. The fluorescence lifetimes of the FCNPs were measured by a FluoroLog 3-211-TCSPC.

## 3. Results and discussion

#### 3.1 Characterization of FCNPs

Fig. 1a shows the TEM image of the obtained FCNPs, from which we can see that these small FCNPs are well dispersed and their diameters are in the range of 3–7 nm. The size histogram (Fig. 1, inset) is provided to prove that the FCNPs are well dispersed. The lower right corner of Fig. 1 shows high-resolution TEM (HRTEM) images of FCNPs with a lattice spacing of around 0.26 nm, which agrees well with



**Fig. 1** (a) Typical TEM image of FCNPs, the inset shows the particle size distribution of FCNPs. (b) Digital photograph of FCNPs solution in sunlight. (c) Digital photograph of FCNPs solution with UV lamp (365 nm, center) illumination. (d–g) Fluorescence microscopy images of FCNPs under different excitations: for 360 nm, 390 nm, 470 nm, and 540 nm, respectively. (h) PL spectra of FCNPs with UV and visible light excitations.

the  $\langle 111 \rangle$  spacing of carbon. Particularly, the present FCNPs can freely disperse in water with transparent appearance without further ultrasonic dispersion (Fig. 1b), so they are called "water-soluble FCNPs". The FCNPs solution is very stable, and there is no nanoparticle precipitation within 6 months. Even at a very dilute concentration, the FCNPs solution can emit bright blue-green light when it is irradiated using a UV lamp (365 nm). This bright blue-green fluorescence of FCNPs is strong enough to be easily seen with the naked eye (Fig. 1c). Furthermore, the FCNPs were investigated under a fluorescent microscope, and different emission colors were found in the same sample. Typical specimen for an optical microscope was prepared by placing a drop of the solution on a cover glass and evaporating the water. Fig. 1d-g exhibit the corresponding fluorescent microscopy images of CNPs at different excitation wavelengths (at 360 nm, 390 nm, 470 nm, and 540 nm excitations, respectively) in the same sample: blue, cvan, yellow, and red. This kind of ultra small sized CNPs with strong and stable PL would offer great potential for a broad range of applications, including as light-emitting diodes (LEDs) and bio-sensors, and in biomedical imaging.

To further explore their optical properties, the PL spectra of the obtained FCNPs were assessed. Fig. 1h gives the typical PL spectra of FCNPs with visible PL emission by excitation from 300 nm to 650 nm. The corresponding visible emissions of CNPs covering the blue-to-red wavelength range can all be obtained in the same sample under UV and/or visible excitations. The maximum fluorescence emission intensity can be obtained when excited at 450 nm. The fluorescent emission peaks shift to longer wavelength with increasing the excitation wavelength.

The FCNPs not only have excellent PL in the visible range, but also exhibit strong UPL property. Fig. 2a shows the PL spectra of FCNPs excited by long wavelength light (from 700 to 1000 nm) with the up-conversion emissions located in the range from 400 to 700 nm. Similar to previously reported carbon dots,<sup>16</sup> this UPL property of FCNPs should be attributed to the multiphoton active process. Additionally, the excitation wavelength changed from 800 to 950 nm, the upconverted emission peaks shifted from 517 to 554 nm. Remarkably, Fig. S1 (ESI<sup>†</sup>) shows the linear relationship between Em and Ex, and these results are similar to previous reports. The shifting between the energy of upconverted emission light (Em) and excitation light (Ex) was almost unchanged, about 0.90 eV. Compared with the carbon nanoparticles prepared using other methods,<sup>14–29</sup> the FCNPs prepared in this paper with an electrochemistry method are relatively inexpensive and



**Fig. 2** (a) The UPL spectra of FCNPs. (b) UV-vis absorption spectrum of FCNPs, and the inset shows the enlarged graph from 200 nm to 400 nm.

have excellent PL properties, such as strong PL in the visible range and excellent UPL property. These results suggest that FCNPs may be applied as a powerful energy-transfer component in photocatalyst design for applications in energy and environmental issues.

Fig. 2b depicts the typical UV-vis absorption spectrum of FCNPs. The absorption band peaked at the 240–300 nm region, and the inset shows the enlarged graph of this characteristic absorption peak. This absorption band represents the typical absorption of an aromatic  $\pi$  system, which is similar to that of polycyclic aromatic hydrocarbons.<sup>31</sup>

Meanwhile, the XPS result indicated that the FCNPs contain mainly carbon and oxygen (Fig. 3a), and no observable impurities were detected. These results indicate that these small FCNPs are pure and exhibit excellent water-solubility, strong PL emission. Furthermore, the FTIR spectrum (Fig. 3b) was acquired to determine the surface functional groups of the obtained FCNPs. The peaks around 3400, 3000 and 1600  $\text{cm}^{-1}$ correspond to the vibrations of C-OH, C-H, and C=O bonds. The asymmetric and symmetric stretching vibrations of C–O–C ( $\sim$ 1300 cm<sup>-1</sup> and  $\sim$ 1200 cm<sup>-1</sup>) in the carboxylate groups were also detected.<sup>17,29</sup> The FTIR results indicate that the surface of FCNPs is full of hydrophilic groups: hydroxy and carboxylic groups. Similar to the earlier reports,<sup>21,32</sup> we speculate that these hydrophilic groups may be due to the oxidation of the obtained carbon nanoparticles under electrochemical conditions, and the introduction of such functional groups is the crucial factor for the origin of the FCNPs' PL. The presence of O-rich groups makes the FCNPs soluble in aqueous medium and provides additional advantages for further functionalization meeting various requirements. Apart from the solubility of FCNPs in aqueous medium, the obtained FCNPs can also be well dispersed in common organic solvents such as acetone and acetonitrile, which facilitates the applications in non-aqueous phase and organic devices as demonstrated below for fabrication of photovoltaic cells.33

The quantum yield of the FCNPs with yellow emission was estimated to be about 4% by calibrating against fluorescein as a reference.<sup>9,34,35</sup> The as-prepared FCNPs also show good photostability, *e.g.* the PL properties and appearance remained unchanged after long time (>4 days) UV illumination and being stored for several months (>6 month) in air at room temperature. Based on the above-mentioned results, we expect that the present FCNPs are superior to metal-based QDs in terms of high stability, ease of use, low cost, and environmentalfriendliness. Consequently, this kind of FCNPs should offer great potential for a broad range of applications, including in biomedical imaging and photocatalysis, and as bio-sensors.<sup>36,37</sup>



**Fig. 3** (a) XPS spectrum of the FCNPs. (b) FTIR spectrum of FCNPs.



**Fig. 4** (a) Fluorescence intensity of the FCNPs in NaCl aqueous solution against ionic strength. (b) The graph of fluorescence intensity *vs.* pH value.



Fig. 5 Fluorescence lifetime of carbon nanoparticles prepared from ethanol by electrochemical synthesis.

Moreover, we investigated the influence of ionic strengths and pH on the fluorescence intensity of FCNPs (Fig. 4a and b). The results showed that the fluorescence intensity of the CNPs did not change even in aqueous solution with a high ionic strength (2 M NaCl). The pH value of the solution had some effects on the photoluminescence of the CNPs. And the PL emission spectra (excitation at 550 nm) of FCNPs were collected under different pH conditions at 25 °C. As shown in Fig. 4b, under strongly acidic or alkaline conditions, the photoluminescence is nearly completely quenched, whereas the FCNPs had the strongest emission intensity when the solution pH value was 7.0. Interestingly, the fluorescence intensity decreased significantly when the pH was out of this value. When the pH of the system was adjusted back to the range of 6.0 to 8.0, the fluorescence intensity of the CNPs became high again. Such a pH range (6.0-8.0) is similar to the physiological pH environment (pH 7-8), so this result makes the FCNPs with excellent fluorescence properties good candidates for potential biological applications and for use as pH sensors.

The fluorescence lifetimes of the FCNPs were measured by time-correlated single photon counting, with excitation and emission wavelengths of 370 and 520 nm (Fig. 5). The lifetime is 6.74 ns which is the longest lifetime among most of the reported CNPs.<sup>38</sup> This feature indicates that the FCNPs could be a potential excellent fluorescent probe.

#### 3.2 The formation mechanism of FCNPs

Since the FCNPs were obtained directly from ethanol, we envision that the formation mechanism of FCNPs is as follows (see Fig. 6): (1) the decomposition of ethanol; (2) the polymerization of carbon substances formed in the prior step;



Fig. 6 Schematic growth model for FCNPs.

(3) the growth of carbon substances formed in step (3); (4) the oxidation process of grown carbon substances. It is known that ethanol can be decomposed into carbon substances under low-temperature hydrothermal conditions.<sup>32</sup> An electrochemical synthesis is achieved by passing an electric current between two or more electrodes separated by an electrolyte. By definition, the synthesis takes place at the electrode-electrolyte interface. Electrochemical synthesis takes place close to the electrode within the electric double layer, which has a very high potential gradient of  $10^5$  V cm<sup>-1</sup>. Under these conditions, the reactions often lead to products which cannot be obtained in a chemical synthesis. Meanwhile, an electrochemical synthesis is an oxidation or a reduction reaction. By fine-tuning the applied cell potential, the oxidizing or reducing power can be continuously varied and suitably selected-a luxury not afforded by chemical synthesis.<sup>39</sup> So in this paper, we consider that the ethanol also can be broken into carbon substances and these carbon substances can be obtained after polymerization, growth and oxidation process. In the absence of ethanol, no FCNPs were observed, indicating that the FCNPs were formed by the decomposition of ethanol. Additionally, similar to previous reports the carbon nanotube can be obtained from ethanol<sup>32,40</sup> and also FCNPs can be derived from carbon nanotubes after chemical oxidation,<sup>10,14</sup> we think that the carbon substances can be obtained from ethanol. On the other hand, the FCNPs can be synthesized by electrochemical oxidation of graphite or multiwalled carbon nanotubes (MWCNTs),<sup>18-20</sup> thermal oxidation of suitable molecular precursors.<sup>21-24</sup> So the carbon substances also can be oxidized into FCNPs after dc electrochemical oxidation. Our experiments also indicated that a NaOH aqueous solution with high concentration was essential for the formation of the FCNPs. There were no FCNPs detected by the TEM observations when the reactions were conducted in aqueous solutions with low NaOH concentration. We propose that the role of high concentration NaOH during the formation of CNPs is most likely as a chemical activation agent to activate ethanol. Under the present electrochemical conditions, the activated ethanol becomes easy to decompose into element carbon and other products. The C with active surfaces is probably preferential for the polymerization and growth of FCNPs under the electrochemical conditions. However, the true role of NaOH in the formation of FCNPs is not clear. A detailed study is required to understand the mechanism of the FCNPs. The current intensity also is a key factor for the formation of FCNPs, only when the current reached a critical intensity (e.g. 200 mA cm<sup>-2</sup>, 2 h), the FCNPs can be obtained.

In comparison to the synthesis of FCNPs reported before, our approach is a facile and green method, the monodisperse FCNPs were obtained in ethanol solution, and no toxic reagents were used. The synthetic procedure involves none of the toxic organic solvents, initiators, or surfactants. This ensures that the as-prepared nanoparticles are nontoxic enabling their use in biochemistry or biodiagnostics, and so on.

#### 4. Conclusion

In summary, the method reported herein provides a new, convenient, low energy loss and green method to prepare a large amount of FCNPs by one step sodium hydroxide-assisted electrochemical treatment of ethanol, further, the present method may provide a promising and practical approach for the large-scale fabrication of nanosized fluorescent carbon materials. These FCNPs exhibit stable and strong visible emission (quantum yield  $\sim 4\%$ ) and excellent UPL properties. Combining free dispersion in water (without any surface modifications) and attractive PL, stable ionic, pH-sensitive and long fluorescence lifetime properties, this kind of FCNPs should serve as a promising candidate for a new type fluorescence marker, fluorescent probe and in related biomedical applications.

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