Carbon-Dot-Based Thin Film with Responses toward Mechanical Stimulation and Acidic/Basic Vapors

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ABSTRACT: Carbon dots (CDs) as a kind of potential materials have drawn much attention due to their excellent optical properties. However, it is a challenge to fabricate new CDs-based thin films with intelligent responses. Herein, a kind of CDs with mechanical- and basic/acidic vapor-stimulated responsive behaviors was prepared using glutathione as a passivation agent via a one-pot solvothermal reaction. The high solubility of CDs enhanced by glutathione passivation was suitable for the preparation of CDs-based thin film. It is worth noting that the fluorescence of CDs-based poly(methyl methacrylate) (PMMA) thin film can be enhanced under grinding treatment, and it was also sensitive to the presence of ambient acids or bases. These CDs-based films have high stability and excellent mechanical and acid/base responses have great potentials for environmental monitoring.

INTRODUCTION

Carbon dots (CDs) are considered as outstanding fluorescent nanosized carbon materials owing to their excellent fluorescence, good biocompatibility, and high stability.1-3 Various methods have been used to prepare CDs involving arc discharge, thermal decomposition, chemical oxidation, and electrochemical oxidation.4-6 Traditionally, surface passivation is used to improve the properties of CDs. Diamine-terminated poly(ethylene glycol)-passivated CDs were first reported in 2006 by Sun et al.7 Since then, different types of passivation agents for fluorescent CDs preparation have been used, including ethylenediamine,8 urea,9 and polyethylenimine,10 which improve the performances in many aspects, such as fluorescence quantum yield enhancement, fluorescence emission change, and high stability and solubility. Therefore, surface passivation will be applied for the preparation of further new types of CDs. Intelligent CDs, which are of great research interest in the field of nanotechnology, can be used in sensing pH,5,10 metal ions,6,11,12 temperature,13 humidity,14 and biomolecules.15,16 Mechanical-stimuli responsive materials have received extensive attention because of their potential applications in memory devices, security systems, and sensors.17 In 2017, piezochromic CDs with the ability to change color from yellow to blue upon exertion of external pressure that stimulated the transition of electrons between the sp² and sp³ was reported.18 Liu et al. investigated the CDs, and their results showed that the π-conjugated system and carbonyl group induced changes to the fluorescence of CDs with red and blue shifts, respectively.19 Solvent-dependent surface functional group changes are another incentive for mechanical responsive CDs.20 However, CDs-based thin films with intelligent multimode responses, especially mechanical and acid–base responses, have not yet been reported. It is challenging to develop mechanical responsive CDs and their thin films that do not require the exertion of high external pressure.

Herein, we used glutathione as a passivation agent to prepare an intelligent CDs-based thin film with mechanical and acid/base responses. When the CDs-based thin film was ground for 30 min, 40% fluorescence intensity enhancement can be observed. Furthermore, the CDs-based poly(methyl methacrylate) (PMMA) thin film is sensitive to the presence of acidic or basic vapors. Whereas the fluorescence of thin film was quenched by acidic vapor treatment, basic vapor enhanced the fluorescence emission intensity. The CDs and thin films with high stability and excellent mechanical and acid/base responses have great potential for further environmental monitoring.

RESULTS AND DISCUSSION

CDs were prepared through a solvothermal reaction between pyrene-1-butyl acid (PyBA) and glutathione at 180 °C for 4 h. The color of the solution changed from green to brown, and a bright blue fluorescence can be observed. These changes...

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suggest that the substrates were successfully carbonized, and passivation agents are vital in the formation of CDs because it improves their fluorescence and promotes their surface states.

The size and morphology of glutathione-functionalized CDs were investigated using transmission electron microscopy (TEM). Nanosized CDs with a size distribution of 5–40 nm were observed and are shown in Figure 1. High-resolution TEM image showed a 0.24 nm lattice spacing in CDs, which is attributed to the (100) facet of graphite (Figure S1). These results demonstrated that CDs were successfully prepared during the solvothermal process.

The peaks in PyBA at 3450, 1700, and 1450 cm$^{-1}$ are associated with hydroxide (−OH), carboxyl, and C–C double bond (C=) stretching, respectively, as shown in Figure 2. The peaks at 3000 cm$^{-1}$ are associated with carbon–hydrogen bond (C–H) stretching. The IR spectra of the CDs had peaks at 3450 and 3000 cm$^{-1}$, that are associated with −OH, and C–H stretching. Amide condensation was successfully achieved because the carboxyl stretching bond transferred from 1700 to 1653 cm$^{-1}$. The C–N bond was retained in CDs at 1390 cm$^{-1}$, which was also presented in the glutathione sample (Figure 2).

The X-ray photoelectron spectroscopy (XPS) data showed the elements in these CDs were carbon, nitrogen, oxygen, and sulfur with contents of 61.99, 13.4, 23.17, and 1.44%, respectively (Figure 3A, Table S1, and Figure S2). The C 1s spectra can be resolved into three components at 284.6, 286.1, and 288.1 eV, and are assigned to the C–C/C=N, C–N/C−O bond, and carboxyl bond, respectively (Figure 3B). Glutathione was successfully introduced into CDs because of the appearance of N and S doping (Figure 3A and Table S1). Thus, the above-mentioned results demonstrated that CDs were formed from the combination of PyBA and glutathione.

The UV absorption spectra and fluorescence emission spectra were investigated to determine the optical properties of glutathione-functionalized CDs. An absorption peak at 320 nm was presented on the UV absorption spectra and was assigned to the transition of n−π* (Figure S3). The results suggested that the heteroatoms were doped into the CDs, which were comparable to the XPS results (Figure 3). The glutathione-functionalized CDs exhibited an excitation-dependent emission behavior by changing the emission from 460 to 560 nm upon 360–500 nm excitations that were comparable to other studies on CDs (Figure 4A). These CDs exhibited good solubility (Figure 4B) and high fluorescence emission (Figure 4C) with a fluorescence quantum yield of 36.8% (Figure 4C). The universality of the functional strategy was explored using another biothiol cysteine as a passivation agent. A light-blue fluorescence emission can be observed in the cysteine-passivated CDs solution (Figure S4). This demonstrated that biothiols are effective passivation agents for PyBA-based carbon materials.

CDs-PMMA thin films were prepared via a drop-coating process. The transparent film had a blue emission upon 365 nm excitation (Figure 5A). The mechanical responsive ability of CDs-based films was investigated. The thin film was divided into two parts, which were denoted as the experimental group and control group, respectively (Figure 5B). The experimental group was treated with grinding. The ground film exhibited a 40% intensity enhancement in comparison to the control group as shown in the fluorescence emission spectra of the films presented in Figure 5C. The results demonstrated that the CDs-based thin film is sensitive to external mechanical stimulation. The possible mechanism is attributed to the stacking structure alteration among CDs. Upon grinding treatment, the stacking structure of CDs was changed and led to fluorescence enhancement, which was similar to other organic molecules with mechanochromism. The fluorescence enhancement suggests that these CDs can be potentially used for various mechanical applications.

Further, these CDs-based films are sensitive to acidic/basic vapors. A film was divided into three parts to investigate and explore the influence of basic or acidic vapors on the films (Figure 5D). The film treated with basic vapor had a higher fluorescence intensity in comparison to the untreated film. However, the treatment of the film with acidic vapor exhibited
a quenching phenomenon as shown in Figure 5E, and the fluorescence emission spectra of CDs-based films are presented in Figure 5F. Similar results can be observed in the reproducibility test (Figure S5). Therefore, these CDs-PMMA thin films have a multiresponsive ability as their fluorescence intensity changes upon mechanical stimuli or exposure to bases or acids.

**CONCLUSIONS**

In summary, we developed a kind of mechanical-stimulated responsive fluorescent CDs using the solvothermal reaction between PyBA and glutathione. Glutathione functionalization improved the solubility and fluorescence properties of the CDs. We also developed a dual-responsive CDs-PMMA thin film whose fluorescence intensity was changed upon mechanical stimulation and exposure to basic or acidic vapors. The dual-responsive thin films have great potential and may be used for the fabrication of new intelligent CDs in the future.

**EXPERIMENTAL SECTION**

**Chemicals.** Pyrene-1-butyric acid (PyBA), L-glutathione, cysteine, and poly(methyl methacrylate) (PMMA) were purchased from J&K Co. (Beijing, China). N,N-Dimethylformamide (DMF) was obtained from Tianjin Concord Technology Co., Ltd. (Tianjin, China). Deionized water was used in the experiment. The above-mentioned chemicals are used without any further purification.

**Instrumentation.** The morphological characterization of mechanical and acid/base responsive CDs was focused on transmission electron microscopy (TEM) using a JEOL JEM-2100 instrument. To study the solvothermal process, a Bruker Vector 22 spectrophotometer was used to investigate the functional groups of PyBA, glutathione, and mechanical and acid/base responsive CDs, and the detection scale was in the range of 400–4000 cm⁻¹. Furthermore, X-ray photoelectron spectroscopy (XPS) characterization including full width and high-resolution data were collected to study the surface functional groups of mechanical and acid/base responsive CDs, using an instrument of Thermo Scientific ESCALAB250 Xi. The optical characterization consisted of a UV–vis absorption spectrum and fluorescence emission spectra. UV–vis absorption spectrum of mechanical responsive CDs in a range of 200–800 nm was recorded using an Agilent Carry 100 UV–vis spectrometer. The wavelength-dependent emission of CDs-based thin films with mechanical and acid/base responses was performed by a FS920P Edinburgh fluorescence spectrometer.

**Preparation of Glutathione-Functionalized CDs.** Briefly, 34 mg of pyrene-1-butyric acid (PyBA) and 30.7 mg of glutathione were dispersed in 10 mL of the N,N-dimethylformamide solution. The mixture was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave (30 mL), followed by solvothermal reaction at 180 °C for 4 h. The brown solution was filtrated by a 0.22 μm membrane. Finally, the glutathione-functionalized CDs were obtained. To prove the versatility of this solvothermal method, cysteine substituted...
for glutathione was used as a passivation agent to synthesize cysteine-functionalized CDs in a similar process.

Preparation of CDs-Based Thin Film. PMMA (0.1 g) and 0.8 mL of CDs solution were dispersed in 10 mL of DMF solution and heated for 1 h. Then, the homogeneous solution was doped on glass and dried in air at 50 °C. Finally, the thin film was obtained by peeling from a glass matrix.

Characterization of Responses Toward Acidic/Basic Vapors. The CDs-based thin film was placed in an inverted sealed beaker to investigate the fluorescence responses in acidic or basic conditions for 1 h, respectively. Acetic acid was used as the source of acidic vapor, and basic vapor was from ethylenediamine. The fluorescence emission spectrum was collected by a FS920P Edinburgh fluorescence spectrometer.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00465.

High-resolution TEM image of CDs, XPS data of CDs, UV–vis spectra of glutathione-functionalized CDs, the bright-field image and fluorescence image of cysteine-functionalized CDs, and fluorescence images of the thin film with vapor treatment (PDF).

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Notes
The authors declare no competing financial interest.

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