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Facile synthesis of carbon nanodots with surface state-modulated fluorescence for highly sensitive and real-time detection of water in organic solvents

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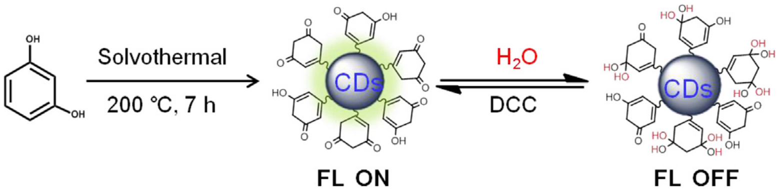
HIGHLIGHTS

- The CDs were synthesized by one-step solvothermal method using resorcinol as the only presusor.
- A simple fluorescent assay for water in organic solvents was developed by changing the surface states of the CDs.
- This assay is capable of water determination in spirit samples in both solution and solid-state paper test strips.
- This assay bears advantages including rapidity, simplicity, lost cost, good sensitivity, selectivity, and reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

In our study, the carbon nanodots (CDs) were synthesized by one-step solvothermal method using resorcinol as the only presusor. The obtained CDs contained abundant unsaturated oxygen-containing groups resulting from the surface oxidation. A novel, simple, and real-time fluorescent assay for the detection of water in various organic solvents was thus established by reducing the surface oxidation states. Excellent reversibility can be readily achieved by the external stimulus water and N,N′-dicyclohexylcarbodiimide (DCC). The water-induced sensitive (limit of detection = 0.006%, v/v, in ethanol) and ultrafast (<1 s) response in emission properties was capable of water determination in spirit samples in both solution and solid-state paper test strips.

1. Introduction

The presence of water can adversely affect many chemical reactions by impeding not only the yield of chemicals but also their activities and uses. Besides, the control of its content in organic solvents is essential for many practical applications such as environmental monitoring, food processing and pharmaceutical manufacturing, in which water is generally identified as a common contaminant and impurity [1]. Therefore, it is very important to establish a simple, fast, and reliable analytical strategy for accurate quantification of water in organic solvents not only in synthetic

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laboratories but also for industrial applications.

Generally, Karl Fischer titration is the most broadly used method for the detection of water [2–4]. However, such approach requires specialized instruments, well-trained personnel and relatively lengthy assays. Moreover, the use of toxic and expensive chemical reagents, undesirable side reactions and interferences from other common co-existing species are usually encountered [5]. These disadvantages seriously prevent it from being a universal method. Fluorescence-based systems for water detection have attracted much attention as the alternatives to Karl Fischer titration because of their significant advantages involving operational simplicity, high sensitivity, low cost and rapid response as well as their capability of remote and in situ monitoring [6]. To date such water sensors are mainly restricted to organic molecules [6–17]. Despite great successes, many of them failed to detect water content at very low levels (<1% v/v) and cannot be readily recovered and reused. In addition, they are significantly influenced by environmental factors such as the change of polarity or pH of the sensing media [8,18,19], and only applied in a very limited number of specific organic solvents depending on their solubility.

Recently fluorescent nanomaterials have gained increasing importance in achieving water detection benefitting from rapid analysis, easy miniaturization and facile recovery [20–31]. Although each of these methods possesses their own features, most are based on the effect of O–H oscillators or water-induced aggregation/disaggregation mechanism [23,24,26–31]. Therefore, it is still very critical to develop novel materials using unusual sensing mechanism for robust detection of water in organic solvents more simply, selectively and sensitively. Carbon nanodots (CDs) as an emerging fascinating carbon nanomaterial have attracted rapidly growing interest in recent years [32]. Owing to their excellent water dispersibility, tunable optical property, chemical- and photostability, low cost and good biocompatibility, the CDs have been used as potential candidates in numerous applications including bioimaging [33], catalysis [34], optoelectronics [35], and particularly sensing [36,37], due to the unique fluorescent properties caused by the quantum confinement and surface effects.

Herein, we reported a simple approach for the preparation of cost-effective and highly photoluminescent CDs by using the solvothermal treatment of resorcinol via one-pot synthesis. As illustrated in Scheme 1, the as-prepared CDs emitted strong yellow-green fluorescence in organic solvents, and the unsaturated oxygen-containing groups (e.g., carbonyl groups) emerged on the surfaces of the CDs mainly resulting from the oxidation of phenolic hydroxyl groups in resorcinol. When trace amount of water is present in organic solution of the CDs, it would unexpectedly cause strong fluorescence quenching by changing the CDs surface state through the hydration of the carbonyl groups to form a gem-diol species, thus enabling the CDs to be directly exploited as the label-free fluorescent sensing platform for the detection of water. Interestingly, by subsequently introducing N,N′-dicyclohexylcarbodiimide (DCC), a dehydration agent, the turn-off fluorescence was greatly recovered due to the removal of water molecule from the surfaces. We also demonstrated that the CDs can serve as a general agent for the detection of water in a variety of organic solvents such as methanol, DMF, acetonitrile, and DMSO. Finally we successfully achieved visual detection of water content in spirit samples with the CDs-coated test strips.

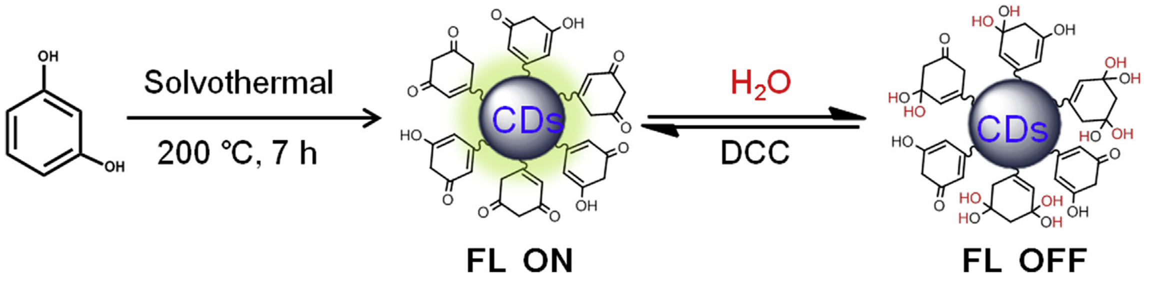
2. Experimental

2.1. Reagents and materials

Resorcinol, pyrocatechol, hydroquinone, N,N′-dicyclohexylcarbodiimide (DCC), Quinine sulfate were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Dialysis bag (retained molecular weight 3500 Da) was obtained from Shanghai Green bird Science & Technology Development Co. (Shanghai, China). Dimethyl formamide (DMF), methanol (MeOH), acetone, dimethyl sulfoxide (DMSO), dichloromethane (DCM), toluene, methanol, trichloromethane ($CHCl_3$), petroleum ether (PTE), carbon tetrachloride (CCl_4), ethylene glycol (EG), acetonitrile (ACN), ethyl acetate (EA), isopropanol (IPA), n-hexane and all other chemicals (analytical-reagent grade) were acquired from Shanghai Qinxi Technology Co. Ltd. (Shanghai, China). In order to rule out the effect from the minimal amount of water in organic solvents, the solvents were dried before use. For example, to obtain anhydrous DMSO, the CaH_2 powder was introduced to the commercial DMSO under vigorous stirring for 12 h, and then the solvent was evaporated under reduced pressure purged with nitrogen. Finally, 4 Å molecular sieves were added for long-term use. Ultrapure water (18.2 MΩ cm^{-1}) was used throughout the experiments.

2.2. Instruments and measurements

Transmission electron microscopy (TEM) was conducted on a JEOL-model 2100 F instrument with an accelerating voltage of 200 kV. Fluorescence spectra are recorded on an F-4600 fluorescence spectrophotometer (Hitachi, Japan) with a slit width of excitation set at 2.5 nm and emission set at 5.0 nm. UV-vis absorption spectra are obtained on a Shimadzu-2550 UV-vis spectrophotometer (Shimadzu, Japan) using a 1.0 cm quartz cell. Infrared spectra were taken with KBr pellets on a Nicolet 5700 FTIR spectrometer (Nicolet, America). X-ray photoelectron spectroscopy (XPS) data were measured by ESCALAB250Xi photoelectron spectrometer (Thermo Fisher Scientific, USA). Raman spectrum was recorded using Horiba-Jobin, Lab Ram HR spectrometer. The as-prepared samples were characterized using X-ray diffraction (XRD, Panalytical) utilizing Cu Ka radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. The zeta potential measurement was carried out at room temperature (90Plus PALS, PRODUCTS).



Scheme 1. Schematic illustration of fluorescence detection of water in organic solvents by altering the surface states of the CDs.

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