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Mn(II)-coordinated Fluorescent Carbon Dots: Preparation and Discrimination of Organic Solvents

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A B S T R A C T

Herein, we prepared a Mn(II)-coordinated carbon dots (CDs) with fluorescence and MRI (magnetic resonance imaging) bimodal properties by a one-pot solvothermal method and separated via silica column chromatography. The quantum yield of the CDs increased greatly from 2.27% to 6.75% with increase of Mn(II) doping, meanwhile the CDs exhibited a higher MR activity (7.28 $mM^{-1}s^{-1}$) than that of commercial Gd-DTPA (4.63 $mM^{-1}s^{-1}$). In addition, white light emitting CDs were obtained by mixing the different types of CDs. Notably, these CDs exhibited different fluorescence emissions in different organic solvents and could be used to discriminate organic solvents based on the polarity and protonation of the solvents.

1. Introduction

Carbon dots (CDs) have drawn much attention due to their various fascinating advantages, which include tunable fluorescence, excellent photo- and chemical-stability, low toxicity, and favorable biocompatibility [1–5], which have been applied in biological sensing and imaging [6–11]. However, their usage remains challenging due to few methods available for fluorescence enhancement and functionalization [12].

Metal-enhanced fluorescence has emerged as an efficient way to improve the fluorescence properties of CDs. Zhang et al. found that the fluorescence of CDs could be enhanced via a metal-enhanced fluorescence process using silver island films [13]. CDs with excellent fluorescence can also be obtained by doping with ZnO or ZnS, as shown by Sun et al. [14]. Wang et al. prepared Mn(II)-coordinated CDs that exhibited yellow emission and could be used for the discrimination of volatile organic compounds [15]. Thus, metal-enhanced fluorescence has been shown to be an efficient way of improving the optical properties of CDs [16,17] and the use of Mn(II) ions as a doping source is regarded as an excellent archetype for the investigation of doping effects [18,19].

Further, magnetic resonance imaging (MRI) has been widely used and exhibited an excellent collaboration ability with fluorescence imaging [20]. Many kinds of fluorescence/MR bimodal CDs have been prepared using gadolinium as MR unit. However, gadolinium ions are highly toxic because of calcium channels inhibition [21,22]. Mn(II) ions exhibit low toxicity and have been reported as an efficient contrast agent for MRI [23], which would be a good choice to CDs for building new fluorescence/MR bimodal probes [24]. Therefore, the design of a CDs coordinated with Mn(II) ions for fluorescence enhancement and obtaining MR activity is highly desired.

Solvothermal method as a novel and simple method has become a mature technology for preparing nanomaterials. For example, Zhang et al. prepared PS@ZnO nanoparticles by two steps of fabrication of polystyrene (PS) spheres and fabrication of PS@ZnO in ethanol [25], and they also demonstrate a double-phase method for synthesizing the blue emitting ZnO nanoparticles that are stable in aqueous solutions [26]. Not only for semiconductor nanomaterials, solvothermal method is mostly preferred because of its simplicity, controlled reaction conditions, and cost-effectiveness for the preparation of CDs. Herein, we prepare Mn(II)-coordinated CDs (Mn-CDs) with fluorescence and MR bimodal properties via the one-pot solvothermal reaction of a mixture of *p*-phenylenediamine, ethanol, and $MnCl_2 \cdot 4H_2O$ at 180 °C for 4 h. We found that the fluorescence intensity and quantum yeild of the resulting CDs (Mn-CDs) were enhanced, and the quantum yield of the CDs

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increased greatly from 2.27% to 6.75%, meanwhile the CDs exhibited a higher MR activity (7.28 $mM^{-1}s^{-1}$) than that of commercial Gd-DTPA (4.63 $mM^{-1}s^{-1}$). The product could be separated by silica gel column chromatography into four fractions that emitted different colors from red to blue, which were denoted as CDs-1, CDs-2, CDs-3, and CDs-4, respectively. We found that the fluorescence emission of the CDs blue-shifted with the increase of particle size. After the characterization of X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP), Mn(II) was found to be centered on the yellow emitting CDs-2, which had high fluorescence and excellent magnetic resonance properties. White light-emitting CDs obtained by mixing CDs, had CIE coordinates of (0.37, 0.35). Notably, the white light emitting CDs showed solvent-dependent fluorescence emission, which can be used for the discrimination of organic solvents. Therefore, these Mn(II)-coordinated CDs can be used for rapid identification of organic solvents. This work not only offers a simple, cost-effective method of synthesizing fluorescence/MRI bimodal CDs with excellent fluorescence properties for the discrimination of organic solvents, but also promotes the development of metal-coordinated CDs in general (Scheme 1).

2. Experimental

2.1. Materials

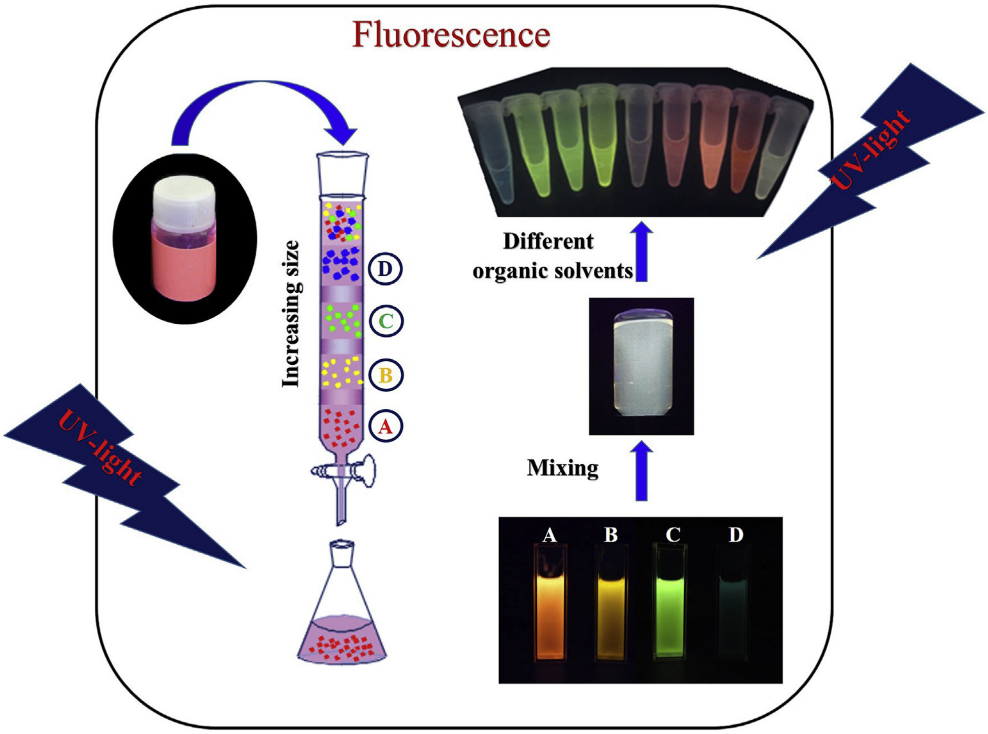
P-phenylenediamine was purchased from J&K Co., Beijing, China. Ethanol, methanol, n-propanol, n-butanol, petroleum ether, dichloromethane, tetrahydrofuran, N, N-dimethylformamide, petroleum ether and $MnCl_2·4H_2O$ were obtained from Tianjin Chemical Co. Ltd. All of the reagents were used without any further purification.

2.2. Synthesis of Mn-CDs

Mn-CDs were prepared according to a previously CDs method with fine modification [27]. Briefly, 0.2 mmol of *p*-phenylenediamine and 0.4 mmol $MnCl_2·4H_2O$ were added into 10 mL ethanol and stirred for 20 min. Then, the mixture was transferred into a poly(tetrafluoroethylene) (Teflon)-lined stainless steel autoclave and heated at 180 °C for 4 h. The supernatants containing Mn-CDs were collected after centrifugation at 11000 rpm for 10 min. Four kinds of Mn-CDs with different fluorescence color were obtained via silica column chromatography separation using a mixture of petroleum ether and ethyl acetate as the eluent, and were denoted as CDs-1, CDs-2, CDs-3 and CDs-4, respectively.

2.3. Instruments

TEM experiments were performed using a Tecnai 20 high resolution transmission electron microscope operating at an accelerating voltage of 200 KeV. The X-ray photoelectron spectra (XPS) were recorded using Thermo SCIENTIFIC ESCALAB250 Xi. The UV—Vis absorption spectra were recorded with an UV—visible Agilent cray 100 spectrometer with a quartz cuvette. Infrared (IR) spectra were obtained with a Bruker Vector 22 spectrophotometer by using KBr pellets for solid samples from 400-4000 cm^{-1} at a resolution of 4 cm^{-1}. The fluorescence spectra were measured on an Edinburgh Instruments FS920P spectrometer. The inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using Optima 7300 V of Perkin Elmer. The magnetic resonance (MR) detections were performed with a 1.2 T MR imaging system (Huantong, Shanghai, China) according to a T_1 detection program. X-ray diffraction patterns were taken on a Rigaku-Dmax 2500 diffractometer using Cu Ka1 radiation.



Scheme 1. Schematic representation of Mn-CDs for the discrimination of organic solvents.