



Microwave-assisted one-step synthesis of white light-emitting carbon dot suspensions



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ABSTRACT

In this contribution, we demonstrate that an aqueous solution with adjustable fluorescent color, including white light emission, can be achieved by a rapid one-step microwave synthesis method resulting in a mixture of blue-emitting carbon dots (CDs) and the yellow-emitting 2,3-diaminophenazine (DAP). Aqueous mixtures of o-phenylenediamine (oPD) and citric acid (CA) are used as precursors. The resulting product structures are analyzed by FT-IR and NMR spectroscopy and the size of the resulting CDs is determined by atomic force microscopy to be 1.1 ± 0.3 nm. The synthesized solution exhibits two fluorescence emission peaks at 430 and 560 nm, which were found to originate from the CDs and DAP, respectively. The intensity ratio of both fluorescence peaks depends on pH, which is driven by the protonation state of DAP. In consequence, the fluorescence emission color of the CD solution can be tuned precisely and reproducibly from blue to white to yellow by careful control of the pH. Finally, at a pH level of 5.4, at which there is equal blue and yellow emission intensity, a white light emitting solution can be successfully produced in a very fast and simple synthesis procedure.

1. Introduction

In recent years, photoluminescent carbon dots (CDs) have received significant scientific attention due to their high fluorescence, unique optical properties, low toxicity and high biocompatibility [1–5]. CDs prepared by environmentally-friendly processes show similar fluorescence properties and present a promising economical alternative to conventional toxic metal-based quantum dots (QDs) [6]. In consequence, the investigation of CDs were driven forward and different application possibilities were tested [7,8]. The vast majority of CDs emit light in the blue range of the visible spectrum [8]. Therefore, the question arises whether it is possible to create different fluorescent colors by combining CDs with organic fluorophores and, in particular, to create white light for white light-emitting diodes (WLEDs). Semiconductor QDs are currently mainly used for the production of WLEDs. At the moment, there are only two widely-used methods for creating white color emission: the additive RGB method which combines different color-emitting QDs (red, green, blue) to achieve white light and the phosphor method [9]. The RGB method is limited by the fact that it requires challenging processes with toxic substances and shows a poor color rendering index [10]. The phosphor method is based on the

concept that the combination of blue and yellow appear white to the eye and involves combining blue LED light with a yellow phosphor layer [11]. Nevertheless, toxic materials are still needed in this case and waste disposal of heavy metals used in the LEDs must also be considered [12]. The use of CDs as a fluorescent material for WLEDs is a promising solution to this problem [13] and the idea to obtain white light from the combination of a blue and yellow light emitter was adopted. Until now, CDs were mostly used as the blue emitter in combination with rare earth luminescent materials [14,15]. Y. Wang et al. showed that it is possible to achieve white light emitting diodes from CDs produced from microwave synthesis. However white light was only achieved after several processing steps, including mixing the freeze dried CDs with silicone and thermal curing of the mixture [16]. In this work, we describe a white light emitting CD solution synthesized within 10–15 min in a one-step microwave synthesis reaction. The solution consists of nitrogen-doped blue fluorescent CDs and 2,3-diaminophenazine (DAP), a yellow fluorescent dye which were both synthesized simultaneously from mixtures of o-phenylenediamine (oPD) and citric acid (CA). During synthesis, the oPD has two important functions: it behaves as a doping agent to improve the blue fluorescence intensity of the CDs while simultaneously reacting with itself to form

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the yellow emitting DAP. The microwave-assisted approach is a low cost, energy efficient and facile technique with a very short reaction time of only 5–20 min [17–19]. The blue emitting CDs and yellow emitting DAP expose light of the complementary colors and the combination of both emit pure white light. The suspensions exhibiting two emission peaks in the blue and yellow spectral region and the intensity ratio of both peaks and therefore the emission color is a unique function of pH. White light emission was obtained at a preset pH of 5.4. However after synthesis, the color can be switched reversibly to blue or yellow, by setting the pH beneath or above 5.4. Finally, a white light emitting CD solution could be synthesized very quickly and easily, thus demonstrating the mixing abilities of CDs and the simplicity of achieving a white light emitting aqueous solution by microwave synthesis.

2. Experimental section

2.1. CD/DAP solution synthesis

0.144 g of oPD and 0.129 g of CA (both obtained from Carl Roth, Germany) were dissolved in 100 ml ultrapure water, resulting in an oPD:CA molar ratio of 2:1. For getting the white light-emitting combined CD solution, the pH of the mother solution was adjusted from 4.3 to 5.4 by using 0.1 M NaOH. 4 ml of the solution was heated to a temperature of 125 °C for 5 min by a microwave reactor from CEM Discover with a power of 300 W. The reactor was equipped with a reaction tube in an autoclave with a maximum capacity of 80 ml. The product was cooled to room temperature and the remaining solution appeared yellow-orange. The product can be purified with a dialysis membrane with a molecular cut-off of 1000 g/mol (supplied by Spectrum Laboratories Inc., USA). Since DAP is able to pass the dialysis bag, the equilibrium between blue and yellow fluorescence is shifted to blue fluorescence. Therefore the dialysis time should be very short (< 30 min) and the pH of the purified solution must be raised after purification to regain white light. As reference pure DAP solution was synthesized by microwave-treading of a solution of 0.216 g of oPD in 100 ml ultrapure water under the same conditions as for the CD synthesis and the obtained product appeared brightly yellow. The pH of the solution was measured in the range of 6–7. For measuring fluorescence quantum yield (QY), size and photostability of the single CDs, the CD/DAP solution was dialyzed for several hours to remove free DAP.

2.2. Characterization

For recording UV-Vis absorption spectra, a Cary 100 (Varian) spectrometer with a range from 200 to 800 nm was used. Fluorescence spectra were measured in a wavelength range from 300 to 800 nm using a Jobin-Yvon photoluminescence spectrometer (Horiba, Japan). All absorbance and fluorescence spectra were recorded at room temperature using quartz cuvettes with a path length of 10 mm. Fluorescence quantum yields (QY) were determined using the slope method described by Jones et al., Do et al. and Zheng et al. using quinine sulfate dissolved in 0.5 M H₂SO₄ as a standard (Sigma-Aldrich, America, QY: 54.6%) [20–22]. The QY was calculated using the following equation (1):

$$\phi_x = \phi_s \left(\frac{G_x}{G_s} \right) \left(\frac{n_x}{n_s} \right)^2 \quad (1)$$

where ϕ is the QY, G is the slope determined by the fitted line in a plot of the integrated fluorescence intensity versus absorbance at the excitation wavelength, n is the refractive index, and subscripts x and s refer to the sample and the standard, respectively. For the white emitting solution at pH 5.4 the QY was calculated to 5.4%.

The Fourier transformed infrared (FT-IR) spectra were recorded using a “Digilab FTS3100” FT-IR spectrometer. The samples were

prepared by being pressed to discs with KBr. The height of the CDs was determined using a MultiMode SPM “NanoScope 3” (Digital Instruments/Veeco, Germany) atomic force microscope (AFM). For the measurement, NSC15/ALBS cantilevers (frequency 325 kHz, spring constant 46 Nm⁻¹ and nominal tip radius < 10 nm) were used in the tapping mode. In order to prepare CDs samples for AFM size measurements, the CD/DAP solution was dialyzed for several hours and the CD solution was dropped on a clean Mica sheet (Plano, Germany) and dried at room temperature. The ¹H NMR spectra were measured using a JEOL ECX 400 MHz spectrometer with a DMSO-*d*₆-inset as internal standard. The deuterated solvent was CDCl₃. For size characterization of the particles in solution, sedimentation velocity experiments at 55 000 rpm for 36 h at 25 °C were conducted in an analytical ultracentrifuge (AUC) “Optima L-90 K” (Beckman Coulter, USA) equipped with a multi wavelength (MWL)-detector. The related background information can be found in the literature [23]. The photostability of the CDs and DAP solutions was measured by using a 365 nm UV-lamp from Consort VL-6.L with the power of 24 W.

3. Results and discussion

3.1. Characterization of the synthesized CD/DAP structures

It has been previously shown, that CA is able to react with α,β -diamines to form fluorescent CDs of high QY [24,24–26]. There is much debate in the literature about the structure of CDs and their origin of fluorescence emission. The carboxylic acid groups of CA undergo condensation reactions with the amino groups of the α,β -diamines, resulting in the formation of polyamides. Crosslinking, dehydration and irreversible carbonization of these polymer structures at temperatures > 200 °C leads to formation of sp² and sp³ hybridized carbon cores containing pyridinic and pyrrolic nitrogen [24,25,27–33]. It was shown that the QY of CDs increases with the amount of pyridinic nitrogen [31]. It is also proposed that CA is capable of ring closure upon reaction with several α,β -diamines such as oPD resulting in a corresponding pyridone derivate [24,25]. Accordingly, the formation of a fluorescent 2-pyridone species, a low-molecular fluorophore (Fig. 1(a)) and the associated reaction mechanism was proposed (Fig. S1(a)) [24,26,34,35]. Moreover CA undergoes a pyrolytic polycondensation reaction leading to formation of carbon cores consisting of small graphene oxide like units (Fig. 1(a)) [28]. The low-molecular fluorophores can then be attached or integrated into the carbon core [26,30,35]. The group of Fang et al. proposed that the pyridone-molecules are connected covalently to the CD surface due to condensation reactions, providing the CDs new energy levels and producing an intrinsic PL signal [25]. In summary, blue-emitting CDs consist of an aromatic carbon skeleton formed by CA condensation, fluorophores located on the CD surface and/or fluorescent centers in the core (Fig. 1(a)) [24,26,36–38]. The dominant fluorophore structure is not only depending on the starting materials but also on reaction conditions: at low reaction temperatures and/or short reaction times low-molecular pyridone-like fluorophores seem to be the dominant fluorescence mechanism of CDs [30]. In this case the CDs exhibit high QY, the fluorescence spectrum is excitation-wavelength independent and the CDs are susceptible to photobleaching [24,30,34,35]. In contrast the fluorescence of CDs synthesized under harsher conditions is ascribed more to the carbon core. In that case excitation-wavelength dependent fluorescence spectra are observed for wavelengths > 380 nm and the QY is mostly < 20% [30,38]. Reasons for the excitation-wavelength dependent fluorescence spectra, quantum confinement as well as trap or molecular states on the surface are proposed and discussed [30]. If oPD is used as starting material besides CA the reaction mechanism is even more complex than discussed above as solutions of the free base oPD are susceptible to dimerization (or even polymerization) under oxidizing conditions (such as in the presence of air) [39]. This reaction is accelerated by light due to the photo-induced formation of oxygen

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