



Tuning optical properties of printable carbon quantum dots using near-field environment



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ABSTRACT

Tuning emission properties of carbon quantum dots (CQDs) is a challenge as limited domain size of sp^2 islands in the CQDs restricts electron mobility in one dimension. The result is the formation of often blue and green light-emitting CQDs. The present manuscript depicts the transformation of CQDs into printable ink material and its utilization in fabricating films with tunable emission properties. Excitation and emission spectra of the CQDs were studied in powder form, aqueous suspension, freely suspended polyvinyl alcohol (PVA) film, printed impressions (PIs) and as thin-films respectively. Analysis of spectroscopic and microscopic data showed a substantial near-field effect in powder, CQD-embedded PVA (PVA-CQD) films and PIs. Light-responsive current-voltage characteristics in PVA-CQD films were explained in the light of interparticle-interaction induced near-field effect.

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1. Introduction

The miniaturization of future light-sensitive devices is limited by diffraction effects due to the wave nature of light. Moreover, the most desirable and challenging aspect is scaling down of the typical size of these optical elements within nano-regime. Researchers are currently looking for sustainable solutions in the area of photonic devices. In this regard, noble metal nanoparticles have shown a path towards the development of nanophotonics. The surface plasmons generated in metal nanoparticles have somewhat facilitated the realization of tuning optical properties within nano-domain. Mulvaney and coworkers have experimentally determined scattering spectra of gold nanorod (GNR) dimers arranged in different orientations [1]. They have shown the presence of plasmon hybridization due to near-field coupling of the nanorods. El Sayed and coworkers have shown that gold nanoparticle (GNP)

assembly can provide alternative concepts in analyte-sensing applications [2,3]. Shear based orientation of GNRs dispersed in a polymer matrix was shown to create dynamic changes in low energy absorption properties in polymer-GNR composite [4]. Bhattacharjee et al. have reported that chain like self assembly of spherical gold nanoparticles can give rise to distinct absorption profile of GNPs compared to their dilute samples [5]. Thus there exist many such published sciences on the near-field effect with metal nanostructures. Such near-field effects are interesting and possess huge potential in future nano-photonic applications.

The disadvantage of metal-based nanomaterials for futuristic photonic devices may be their production cost and adverse environmental impacts. Thus, it is necessary to identify alternative nanomaterials those are abundant, cheap, scalable and eco-friendly, for near-field studies. Carbon quantum dots (CQDs) are currently viewed as promising and environmentally benign nanomaterials as they are composed of carbon, oxygen and nitrogen [6,7]. Investigations on the structure of CQDs reveal the presence of isolated sp^2 islands separated or dispersed in sp^3 matrix [7–9]. The CQDs can be compared with organic nanoparticles composed of molecular aggregates that emit solid-state fluorescence (FL) [10,11]. In recent years, the emission property of CQDs with suitable surface

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functionality has been utilized for various applications [12–22]. Emission properties in CQDs originate from the combination of strong quantum confinement and surface defect sites [8,23,24]. Wen et al. have used ultrafast spectroscopy to establish that the FL of CQDs consists of two spectral overlapped bands that can be ascribed to the intrinsic and extrinsic fluorescence [25,26]. The former is attributed to the sp^2 nano-domains and the later to the surface states [11].

In order to study near-field effects with CQDs, it is important that these nanomaterials can be assembled in a matrix where their interparticle-interactions can be controlled. This is important to achieve a tunable optical response of the assembled materials. As carbon is a hydrophobic material, it is mandatory that the surface of CQDs should be capped with molecules that offer easy dispersion in solvents like water. Polymer-stabilized CQDs and their optical properties of in suspension have been extensively reported with appreciable quantum yield and biological applications [7,27–29]. The origin of the strong emission in polymer-stabilized CQDs is stable surface-trap sites [30–33]. Literature suggests that these surface trap sites create low-lying energy levels and facilitate effective radiative-recombination [8,34,35]. Polymer-passivated CQDs show appreciable quantum yield and enhanced processibility through control over size, crystallinity and surface sites [8,31]. Several authors have reported FL of polymer-passivated CQDs in suspension [7,31,36–39]. Few reports on FL properties in solid state, polymer films and fabricated structures are available [40,41]. De and coworkers have recently reported that polymer-coated CQDs for the fabrication of transparent fluorescent coatings [42]. However, to the best of our knowledge, there is no report on near-field studies of polymer-stabilized CQDs and its effect on the fluorescence and other physical properties of the composite. Moreover, understanding of non-covalent interactions of CQDs with macromolecules like polymer can be an important advancement in the field of tuning the optical properties of CQDs and provide further insight into the origin of optical modulation.

We have recently reported conducting properties of single polymer-passivated CQDs where the presence of polymer on the surface of the CQDs helps to create low lying energy states and facilitate high mobility of electrons [43,44]. Herein, we report tunable optical properties of polymer-stabilized CQDs in various forms like powder, aqueous suspension, free-standing polymer films and printed impressions (PIs). All the samples were thoroughly characterized and the reason for tunability in emission characteristics was studied. Light responsive properties of CQDs in suspended polymer films were also investigated.

2. Experimental section

2.1. Materials

Citric acid (99.7%) was purchased from Himedia Chemicals. Poly (sodium 4-styrene sulfonate, 99.8%, M.W. 70,000) (PSS) and 8-Anilino-1-naphthalenesulfonic acid (1,8-ANS) were purchased from Sigma-Aldrich and they were used as received without further purification. Polyvinyl Alcohol (PVA) (Sigma-Aldrich, M.W. 1,46,000–1,86,000, 98–99% hydrolyzed) was used for preparation of CQD-embedded PVA (PVA-CQD) film. Poly (dimethyl diallyl ammonium) [PDDAC] (Aldrich, M.W. 100 kDa) was used for layer-by-layer self-assembly. Methanol, acetone, hydrogen peroxide, sulphuric acid and ammonia were purchased from Loba Chemie and used without purification. Dialysis membranes were purchased from Himedia. Milli-Q water was used in all experiments. All the measurements were performed at room temperature (25 °C) unless otherwise mentioned.

2.1.1. Synthesis of CQDs

CQDs were synthesized in a one step pyrolysis process from citric acid where PSS has been taken as a stabilizer and was reported in our previous publications [33]. 3 g of anhydrous CA and 0.5 g of PSS were dissolved in Milli-Q water followed by evaporation at 80 °C until the dry powder was obtained. The powder was kept in a vacuum desiccator for further removal of moisture. The powder was pyrolyzed for 2 h at 200 °C in a tubular furnace. Finally, the brownish-black powder was obtained which was used in experiments. Purification of PSS-passivated CQDs (PSS-CQDs) was done by dialyzing aqueous suspension by snake-skin dialysis membrane.

2.1.2. Preparation of PVA-CQD film

Polymer solution (3 wt %) was prepared with PVA by slowly dissolving 3 gm of polymer in 100 ml of water. Solution was kept under stirring for one day at 70 °C. A clear PVA solution was obtained. PVA-CQD films were prepared with different CQD loading ranging from 10 to 200 mg of powder CQDs. 10 ml of purified powder CQDs (10 mg) aqueous suspension was dissolved in 10 ml of PVA solution and stirred overnight. Later, the solution was poured in a Petri dish with uniform thickness and diameter. The Petri dish was kept on water bath to evaporate out excess water followed by drying in vacuum oven. A free standing PVA-CQD film was obtained. Similarly, few more PVA-CQD films were made with 30 mg, 50 mg, 80 mg, 140 mg and 200 mg CQDs respectively. The films were named as 10 F, 30 F, 50 F, 80 F, 140 F and 200 F respectively depending on CQD loading and the same has been mentioned in the present manuscript. Optical studies of the film were performed using spectrofluorometer and UV–Vis spectrometer using solid-state accessories. A piece of PVA-CQD film (1 cm × 1 cm) was clamped between two IC connectors and current was recorded at a voltage regime of –3 V to 3 V. Thicknesses of the films was 0.56 mm. I-V data were recorded with Keithley 2450 source meter unit. Solar simulator from ABET Technologies was used for illuminating the samples to study light harvesting property of PVA-CQD samples.

2.1.3. Preparation of spin-coated glass slide for EPI fluorescence microscopy

Glass slides were washed with soap water and then sonicated several times with double distilled water. Similar procedure was adopted for washing with acetone. After that the slides were treated with a mixture of water, ammonia and hydrogen peroxide in a ratio of 5:3:1 for 30 min followed by washing with Milli-Q water. Slides were dried purging nitrogen gas. Before spin coating, slides were kept under UV (long wavelength) light for 1 h. After UV exposure, the glass slides were spin coated with 0.1 wt % aqueous CQD suspensions at 1500 rpm for 100 s by Laurel spin coater. Spin coated glass slides were characterized by AFM and EPI fluorescence.

2.2. Steady-state and time-resolved spectroscopic measurements

Steady state absorption measurements were done with Shimadzu UV-spectrophotometer using 10 mm path length quartz cuvettes. All the steady state measurements in solutions were carried out using HORIBA Jobin Yvon Fluorimax-4 fluorimeter. An aqueous suspension of CQDs (0.01 wt %) was taken for all the measurements to keep the absorption value minimum as to avoid inner filter effect. The experiments were carried out at pH 2.0, 4.0, 7.0 and 9.0, where pH was controlled using HCl and NaOH solutions. All the CQD stock solutions were prepared depending on their water-dispersion abilities. Fluorescence spectra were recorded by 10 mm path length quartz cuvette in the region from 355 nm to

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