

Size-dependent one- and two-photon fluorescence of acetonitrile-derived carbon dots

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Carbon dots (CD) – carbonaceous luminescent nanoparticles – are increasingly employed in bioimaging, fluorescent sensing, photocatalysis, and light emitting devices [1–3]. Photoluminescence mechanisms of CD are versatile and include contributions from the quantum confinement effects, surface groups and defects, heteroatoms and organic molecular fluorophores in their structure [4, 5]. In addition to linear excitation luminescence of CD can be excited by nonlinear absorption of ultrashort laser pulses. Nonlinearly excited luminescence of CD is important for fluorescent imaging and photocatalysis. Previous works demonstrated that characteristics and mechanism of nonlinear luminescence of CD can be different from luminescence excited by linear absorption [6].

There is a demand for tailoring optical properties of CD for various applications. The nanoparticle size is the key morphological parameter, affecting optical properties of carbon dots and this size can be controlled with synthetic procedures or size separation techniques. Given diverse absorption and luminescence mechanism of CD the effect of the size is not straightforward and can vary for different types of carbon dots. This effect can also elucidate the mechanism of CD luminescence [7].

Previously we demonstrated that femtosecond pulsed laser synthesis in liquid medium is a viable method for production of CD from simple organic precursors [8, 9]. It is instructive to analyze the relation between the size and optical properties of laser-synthesized CD. For this purpose we chose carbon dots obtained by laser synthesis from acetonitrile [9]. Acetonitrile carbon dots were polydisperse colloidal nanoparticles with diameters in the nanometers range. We used dialysis of CD's aqueous solution in 2 and

10 kDa dialysis containers to separate the sample into three fractions: “small” or CD-1, “medium” or CD-2 and “large” or CD-3 (Fig. 1a). Then chemical composition and optical properties of the fractions were analyzed in comparison with the original sample.

Elemental analysis and infrared microscopy revealed that the three fractions had elemental content and chemical groups similar to the original CD sample. All the fractions exhibited broad and featureless absorption spectrum spanning the ultraviolet (UV) and visible range and bright visible fluorescence. Their fluorescence was multicomponent and its emission maxima shifted from deep blue to yellow spectral region with increase of the excitation wavelength. The strongest fluorescence intensity was emitted under excitation at 340–350 nm with peak emission intensity at 420–430 nm. The fluorescence lifetime was within nanoseconds range.

Carbon dot size influenced optical properties of CD: larger size led to stronger broadband visible and near-UV absorption, red shift of excitation and emission spectra, stronger green fluorescence, shorter fluorescence lifetimes and exerted effect of opposing directions on quantum yields of different components of heterogeneous photoluminescence emission. Size-dependent shifts of excitation and emission peaks were too small (< 0.12 eV) to support quantum confinement effects in CD. We explain the influence of the nanoparticle diameter with a number of effects, including size-dependent shifts of CD's energy levels, accumulation of nanographene domain and resonance energy transfer in large carbon dots.

Carbon dots emitted visible fluorescence excited by two-photon absorption of femtosecond laser pulses of the near-infrared range. Two-photon fluorescence (TPF) spectra were excitation-dependent and shifted to longer wavelength with increase of the excitation laser wavelength. TPF spectra were always broader and redshifted

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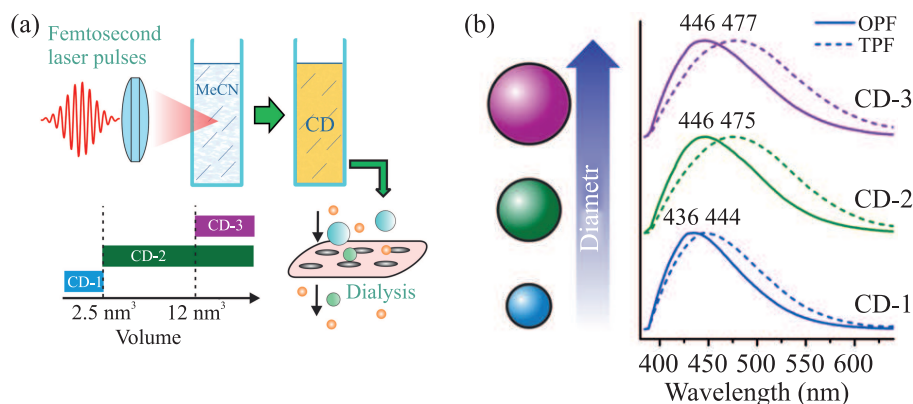


Fig. 1. (Color online) (a) – Laser synthesis of carbon dots and their separation into fractions by dialysis. (b) – Comparison of spectra of one-photon (OPF – solid lines) and two-photon (TPF – dashed lines) excited fluorescence of the fractions in ethanol. OPF was excited by femtosecond laser pulses centered at 360 nm, TPF – by pulses at 720 nm

compared with one-photon fluorescence (OPF) spectra, excited at doubled frequency (Fig. 1b). The magnitude of difference between TPF and OPF was larger for carbon dots of larger diameters. TPF lifetimes were always shorter than OPF lifetimes.

We explain the difference between TPF and OPF characteristics with heterogeneity of CD emission, which can be represented as a sum of emission of diverse fluorescence centers, having different excitation and emission spectra. Variation in one- and two-photon absorption cross-section leads to varied contributions from different centers in the OPF and TPF spectra. Centers with emission spectra shifted to longer wavelengths make larger contributions to the TPF, which results in broadening and red shift of TPF spectra.

In conclusion, we analyzed optical properties of the size fractions of acetonitrile-derived carbon dots. Although quantum confinement effects for this type of carbon dots were discarded, the nanoparticle size still exerted considerable influence on their absorption and luminescence characteristics. We found a systematic difference in spectra and lifetimes of one- and two-photon fluorescence, and showed that it can be explained with a simple model of heterogeneous emission.

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