

Synthesis of Nitrogen and Phosphorus doped carbon dots and study of their photoluminescence in the solid state

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Summary:

In this work, the solid-state photoluminescence of different carbon dot types was examined. The carbon dots were synthesized solvothermally with variations in dopant species and solvent. Incorporation of heteroatoms such as nitrogen and phosphorus altered the optical properties of carbon dots. For photoluminescence measurements, thin films of carbon dots were prepared on Si/SiO₂ substrates using spin coating.

Keywords: carbon dots, doping, photoluminescence, solid state

Introduction

Carbon dots (CDs) is a class of carbon nanomaterials with sizes less than 10 nm, which has attracted widespread attention due to its excellent optical properties, biocompatibility and low cost of synthesis. Doping of CDs with heteroatoms like nitrogen, phosphorus, sulfur and boron can lead to modification of their properties, including their photoluminescence [1]. Another factor that influences the optical properties of CDs is the solvent used during synthesis or in which they are dispersed [2]. While photoluminescence of CDs has been extensively studied in solution-form, strategies to control solid-state photoluminescence of CDs are still in development, mainly due to challenges that arise from aggregation-caused quenching [3].

In this work, the photoluminescence of various types of CDs in the solid state was investigated. CDs doped with nitrogen (N), phosphorus (P) or co-doped with nitrogen and phosphorus (NP), were prepared by a solvothermal method. Ultrapure water and glycerol were used as solvents. The novelty of this work lies in the

combination of the precursor materials used for the synthesis of CDs and the study of their photoluminescence in the solid state.

Materials and Methods

CDs with different types of doping were solvothermally synthesized by varying the precursor materials. Citric acid was used as source of carbon, while urea and phosphoric acid were used as sources of nitrogen and phosphorous, respectively. Specific amounts of each precursor material were dissolved in ultrapure water or glycerol, and the mixture was transferred to a Teflon-lined stainless-steel autoclave, where heating was applied. The solution obtained was purified by centrifugation and filtration. Thin films of the various CDs were prepared by spin coating on Si/SiO₂ substrates. Then, the substrates were heated on a hotplate to evaporate the solvent. The names of the samples indicate their doping type. The samples N-CDs-1, P-CDs-2 and NP-CDs-1 were prepared by using ultrapure water as solvent while P-CDs-1 glycerol was used as solvent.

The optical, structural and morphological properties of the CDs were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), ultraviolet-visible (UV-Vis) spectrometry and Fourier-transform infrared (FT-IR) spectrometry. The photoluminescence (PL) spectra of the thin films were collected, after laser excitation 355 nm.

Results

Representative SEM images of the thin films prepared from the samples P-CDs-1 and NP-CDs-1 as well as EDS spectrum for NP-CDs-1 are presented in Fig. 1. The thin film of P-CDs-1 is uniformly spread on the surface of the Si/SiO₂ substrate. On the other hand, the thin film of NP-CDs-1 exhibits a patterned surface morphology with 3D texture, which could be attributed to the co-existence of two different dopants.

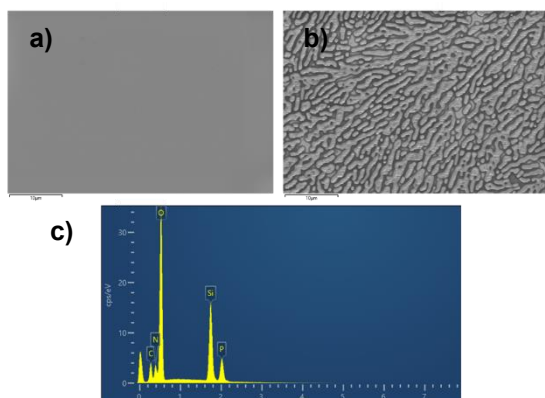


Fig. 1 SEM image of the thin films prepared from the sample (a) P-CDs-1 and (b) NP-CDs-1 captured at 20 kV and x2500 magnification, and (c) EDS spectrum of sample NP-CDs-1.

The UV-Vis spectra of the different types of CDs are presented in Fig. 2. It is observed that all types of CDs strongly absorb light in the UV region. A primary peak at 199-232 nm is present in all the samples and is attributed to π - π^* electronic transitions of C=C bonds. Moreover, a secondary peak at 262-336 nm is present in N-CDs-1, P-CDs-1 and NP-CDs-1. This peak is attributed to n- π^* electronic transitions of C=O or C=N bonds.

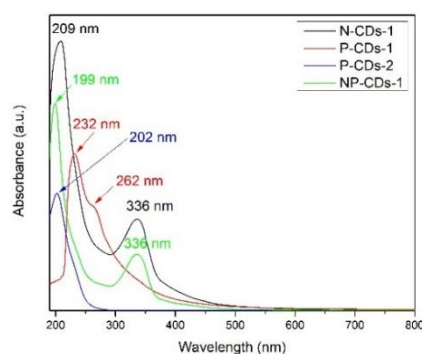


Fig. 2 UV-Vis spectra of the different types of CDs.

The PL spectra of the different types of CDs after excitation with a 355 nm laser are shown in Fig. 3. Photoluminescence is observed in all the samples by exhibiting broad peaks. The samples N-CDs-1, P-CDs-2 and NP-CDs-1 emit mainly light in the region of blue-green color with peaks at 467 nm, 462 nm and 490 nm, respectively.

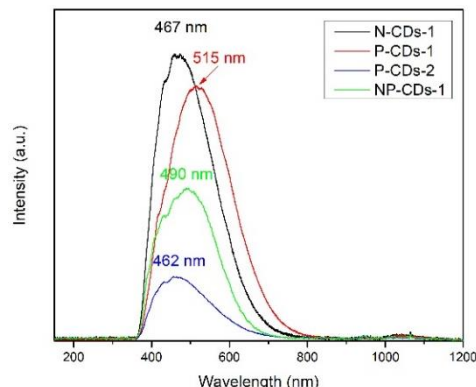


Fig. 3 PL spectra of the different types of CDs at an excitation wavelength of 355 nm.

The sample P-CDs-1 emits mainly light in the region of green-orange color with a peak at 515 nm. Moreover, down-conversion is observed in all samples, since irradiation with a UV-laser at 355 nm leads to emissions with higher wavelength, between 462 nm and 515 nm. This could be explained by the presence of various surface states and defects in the structure of CDs.

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