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Towards versatile photonics based on GaP nanowires decorated with carbon dots

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Abstract. Carbon dots (CDs) exhibit great potential as nanostructures in photonics due to their simple fabrication process, adaptable and effective emission. We used hydrothermal synthesis to fabricate CDs and decorated vertical gallium phosphide (GaP) nanowire array. Through feasible drop-casting deposition technique, we successfully observed efficient luminescence across the nanowires surface using confocal microscopy. Numerical calculations combined with experimental data revealed amplified luminescence through the resonant optical modes of the nanowire, acting as a waveguide. As a result, this study provides insight into the possibility of development of novel photonic devices by decorating optically dense nanowires with CDs to enhance and control over the emission efficiency and propagation.

Keywords: carbon dots, gallium phosphide, nanowires, confocal microscopy, photoluminescence

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На пути к универсальной фотонике, основанной на нитевидных нанокристаллах GaP, декорированных углеродными точками

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Аннотация. Углеродные точки (УТ) отлично подходят в качестве наноструктур, используемых в фотонике, благодаря простому процессу изготовления, адаптируемости и эффективному излучению. Мы использовали гидротермальный синтез для изготовления УТ и декорирования вертикальных массивов нитевидных нанокристаллов (ННК) фосфида галлия (GaP). Используя метод капельного осаждения, мы успешно наблюдали эффективную люминесценцию на поверхности ННК с помощью конфокальной микроскопии. Численные расчеты в сочетании с экспериментальными данными показали усиление люминесценции за счет резонансных оптических мод ННК, работающий как волновод. В результате, данное исследование дает представление о возможности разработки новых фотонных устройств путем декорирования оптически плотных ННК УТ для повышения эффективности и направленности излучения.

Ключевые слова: углеродные точки, фосфид галлия, нитевидные нанокристаллы, конфокальная микроскопия, фотолюминесценция

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Introduction

Among promising photonic materials carbon dots (CDs) became a bright star in the research during the past decade. CDs are unique nanostructures with dimensions below 10 nm, and exhibit extremely low toxicity, chemical stability, and the potential for optoelectronic applications due to efficient light absorption, adjustable emission [1], and nonlinear optical effects [2]. From the biological point of view, CDs combine inexpensive and eco-friendly synthesis procedure.

To achieve the highest possible emission efficiency and control the spectral features of CDs, the crystallinity and composition has to be engineered precisely [3]. This engineering can be derived by accurate tailoring of the CDs synthesis protocols [4]. In order to optimize optical properties, different approaches have been applied recently. In [3], the authors showcased how triangular CDs with a high quantum yield of up to 72% can achieve multicolored narrow bandwidth emission. In addition, the emission efficiency was improved further up to 75.9% through microwave-assisted CD powders and the addition of NaOH [5], as well as via a simple solvothermal method [6].

While striving for the prosperous integration of CDs in photonics and lighting applications, the issue of CDs aggregation negatively affecting the emission effectiveness must be addressed. Controlling the aggregation of CDs can be accomplished through dispersion on suitable nanostructures or strategic molecule assembly. Semiconductor nanowires (NWs) [7] offer numerous benefits for integrating with CDs. Such a hybrid structure can improve optical absorption, enhance transfer of interfacial charge carriers, and effective separation through appropriate bandgap engineering.

GaP epitaxial NWs are well known in terms of low concentration of lattice defects [8] and mechanical strength, large aspect ratio [9], possibility of synthesis on mismatched substrates [10], low absorption and high refractive index in almost all visible and IR spectral range starting from 500 nm [11]. Our study is devoted to study photonic properties of hybrid GaP NWs/CDs structures.

Materials and Methods

Carbon dots were prepared via hydrothermal procedure utilizing the process described in 15]. A mixture of 1.05 g of citric acid (Sigma Aldrich), 340 μl of ethylenediamine (Sigma Aldrich), and 10 ml of distilled water was added to a Teflon beaker inside an autoclave and stirred until the citric acid was dissolved (see Fig. 1 for schematic). The autoclave was subsequently heated in an oven at 200 °C for 5 hours. The resulting reaction products were then filtered through a syringe filter with a pore diameter of 0.22 μm to remove much of the impurities. The filtered solution was dialyzed for 24 hours in a dialysis tube (MWCO 3.5 kDa) to further remove residual unreacted components and low-molecular-weight compounds.

Vertical nanowires were grown on a Si (111) substrate using molecular beam epitaxy (MBE) in the Veeco Gen III unit via the vapor-luquid-solid (VLS) mechanism with Ga droplets serving as catalysts. The resulting NWs were approximately 30 μm long and 200 nm thick without sufficient tapering. To fabricate the CDs/GaP NW hybrid structures, aqueous solution of CDs was drop-casted onto the vertical NWs. The resulting sample was analyzed using scanning electron microscopy (SEM) and confocal luminescent microscopy. For numerical simulation of the emission of a single hybrid NW structure the finite-difference-time-domain (FDTD) method was used (Ansys Lumerical Software). In the modeling, a single NW was represented as a hexagonal prism with a height of 5 μm, vertically oriented on the Si substrate. The boundary conditions, perfectly matched layer (PML), were chosen to simulate waves propagation to the infinite space. Mesh spatial step was 4 nm. The simulations were performed for the three diameters: 200, 150, and 80 nm. As a hexagonal prism diameter circumscribed circle diameter was chosen. CDs photoluminescence was simulated using 3 equidistant dipole sources providing Gaussian emission in a spectral range of 500-650 nm.

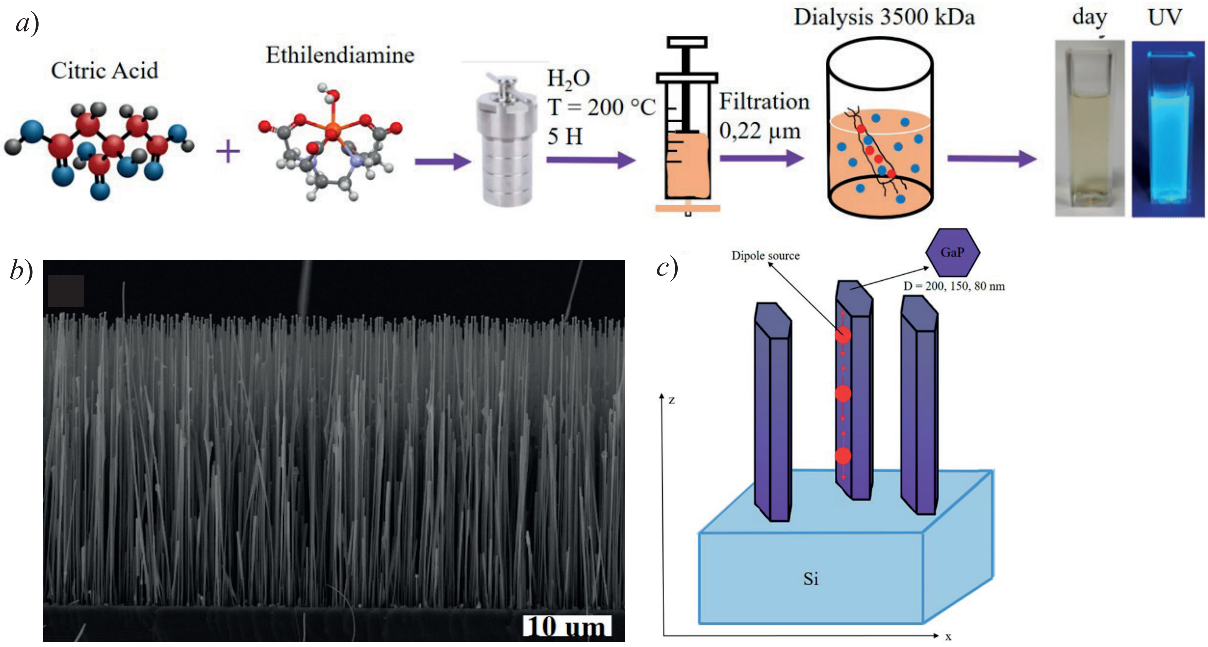

Fig. 1. Schematic of the CD's synthesis (*a*), SEM image of the as-synthesized vertical GaP NWs on the Si substrate (111) (side-view) (*b*), model geometry for the numerical simulation (*c*)

Results and Discussion

SEM images of the sample after CDs deposition demonstrate an interesting phenomenon: NWs form bundles (see Fig. 2). Bundling occurs due to the surface tension of the water and it is retained due to the large length of the NWs.

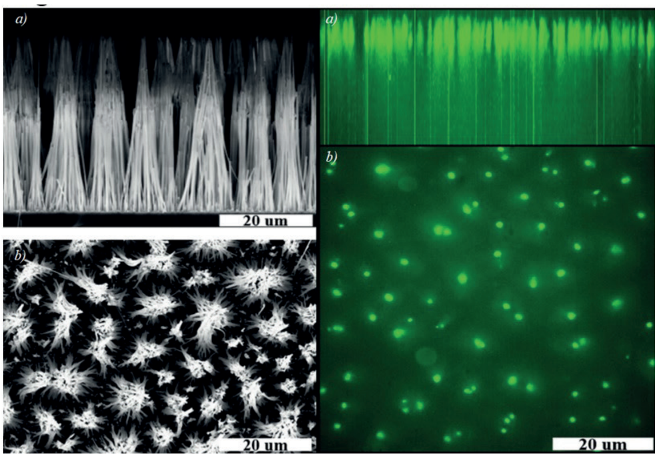

Fig. 2. Cross section (*a*), and plane view (*b*) SEM images and confocal luminescent images of the fabricated sample

Fabricated hybrid structures demonstrate photoluminescence centered at a wavelength of 538 nm under 478 nm laser excitation. The most intense luminescence is observed at the tips of the bundles formed by the NWs. Such a phenomenon could be explained by the waveguiding properties of the GaP NWs with cross-section diameter of about 200 nm. PL from the CDs is coupled with the wire's guided mode, and the resulting radiation is most efficiently scattered at the structure's end facet and defects. Therefore, the most intense signal collection occurs at these specific locations, as further supported by numerical simulations of the individual NWs.

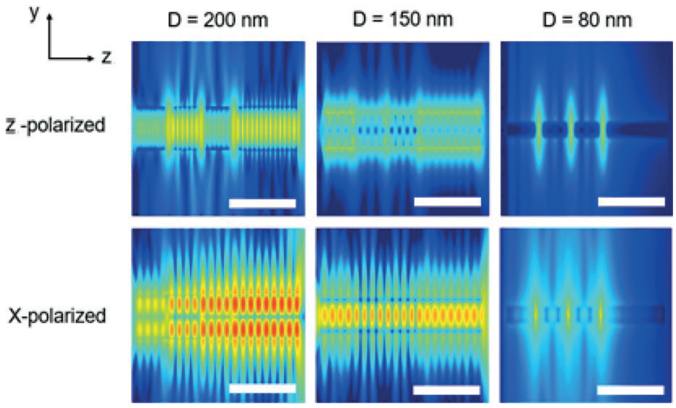

Fig. 3. Fourier images of PL of CDs on GaP NW modeled by three dipole sources with a wavelength of 538 nm. The scale bar is 2 μm

Calculated electric field distribution images (see Fig. 3) demonstrate stronger field localization for thicker NWs. Also, standing waves formation which occurs due to NW Fabry-Perot resonant properties is more evident in the thicker wires. When diameter is insufficient to support the guided modes (80 nm), standing wave is not supported. So, the simulation results demonstrate that for the efficient guiding of the CDs' PL promoting efficient emission at the NW edge, the NWs should possess large diameter (> 150 nm).

Conclusion

We demonstrated that hybrid structures fabricated by a simple drop-cast deposition of CDs over the vertical GaP NWs exhibit efficient luminescence. Due to the waveguiding nature of NWs, the highest photoluminescence intensity is observed experimentally at the edge of the structure. Numerical simulation is then used to demonstrate effects of the NW diameter on the coupling of the CDs emission with the NW guided modes. We demonstrate that the guiding efficiency is the matter of the NW diameter. The results indicate that such a hybrid system can be used to amplify and defectively outcouple the CDs emission in future photonic devices.

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