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Linear and nonlinear optical waveguiding in bio-inspired peptide nanotubes

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ABSTRACT

Unique linear and nonlinear optical properties of bioinspired peptide nanostructures such as wideband transparency and high second-order nonlinear optical response, combined with elongated tubular shape of variable size and rapid self-assembly fabrication process, make them promising for diverse bio-nano-photonic applications. This new generation of nanomaterials of biological origin possess physical properties similar to those of biological structures. Here, we focus on new specific functionality of ultrashort peptide nanotubes to guide light at fundamental and second-harmonic generation (SHG) frequency in horizontal and vertical peptide nanotubes configurations. Conducted simulations and experimental data show that these self-assembled linear and nonlinear optical bio-waveguides provide strong optical power confinement factor, demonstrate pronounced directionality of SHG and high conversion efficiency of SHG $\sim 10^{-5}$. Our study gives new insight on physics of light propagation in nanostructures of biological origin and opens the avenue towards new and unexpected applications of these waveguiding effects in bio-nanomaterials both for biomedical nonlinear microscopy imaging recognition and development of novel integrated nanophotonic devices.

1. Introduction

Biological basic scaffolds such as proteins and peptides have a fundamental property to self-assemble into elongated nanostructures like collagen and amyloid fibrils. These biological nanotubular assembles are the inspiration for the development of a new class of bio-nanomaterials composed of chemically synthesized peptide biomolecules and mimicking natural fibrillar structures and tissues [1].

Overwhelming majority of biological materials possess intrinsic asymmetric structure and demonstrate ferroelectric and related phenomena such as pyroelectric [2], piezoelectric effects [3] and second order-nonlinear optical response [4]. In particular, second harmonic generation (SHG) was investigated in biological collagen fibrils and many other natural bio-tissues including skin, tendon, blood vessels, etc. using new biomedical technique of nonlinear optical microscopy. Recent studies of abnormal collagen assemblies using SHG microscopy opened the avenue for diagnosing of cancer, fibrosis and connective tissue disorders diseases [5].

Asymmetry-based physical properties were also found in bioinspired nanostructures [6]. For example, piezoelectric and SHG were observed in elongated peptide nanotubes [7,8]. In addition, it has recently been exhibited that diphenylalanine (FF) open-end bioinspired peptide nanotubes (PNT) can guide visible light [9,10] similar to waveguiding in natural biological materials such as *Escherichia coli* [11].

The remarkable linear and nonlinear optical properties of bioinspired peptide nanostructures make them good candidates as optical waveguides of biological origin, which could be used in biomedical nonlinear optical microscopy [12,13] and in novel integrated nano-photonic devices.

In this work, these new functional properties of linear and nonlinear light propagation mechanism and waveguiding effects in peptide-elongated nanostructures are studied at both horizontal and vertical nanotubes' configurations by Finite Difference Time Domain (FDTD) method-based numerical simulations along with an experimental research.

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2. Materials and methods

2.1. Sample fabrication

FF-PNT were prepared by dissolving the L-diphenylalanine (FF) peptide (Bachem) in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Sigma Aldrich) at an initial concentration of 160 mg/mL (for vertically aligned ultra-short FF tube like structure). For the preparation of horizontally aligned FF-PNT, the L-diphenylalanine (FF) peptides (Bachem) were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Sigma Aldrich) at an initial concentration of 100 mg/mL, and then diluted to a final concentration of 2 mg/mL in deionized water.

2.2. Environmental Scanning Electron Microscopy (ESEM)

For ESEM measurements, drops of the above solutions were placed onto clean silicon substrates, and then they were dried at room temperature. The samples were coated with palladium–gold and scanned using a JSM JEOL 6300 scanning electron microscope operating at 10–15 kV.

2.3. Two-photon confocal scanning microscopy

The SHG measurements were obtained using a scanning near-field optical microscope alpha300S+, (WITec Co., Germany). A p-polarized Ti:Sapphire femtosecond laser, (Avesta Ltd., Russia) with a power of 360 mW (100 fs, 80 MHz) was used to transmit a laser beam at a wavelength of 800 nm. The laser beam traversed a half-wave plate (AHWP05M-600, Thor Labs) and reached the scanning near-field optical microscope (where it was collected by X20 objective, with a N.A. of 0.4 (ZEISS Ltd.), after passing through a set of mirrors. The PNTs were illuminated by the laser, with a spot size of 1 μm. An area of 70 μm × 70 μm was scanned at a resolution of 7.3 pix/μm. The nonlinear second-order response of the PNT was collected with a ZEISS 60× objective, with N.A. of 0.8. A set of 2 BG39 filters (Schott Ltd.) were placed before a lens that coupled the light from the PNT into a photomultiplier (PMT) detector (H8259-02, Hamammatsu Ltd.). To verify that the PNT transmit light at half the wavelength of the incident laser beam, a long pass filter GG420 (Schott Ltd.) was placed after the BG39 filters to cut the signal below 420 nm.

2.4. Numerical simulations

Finite Difference Time Domain (FDTD) method-based optical simulations are performed to study the linear and nonlinear waveguiding effects in FF peptide nanostructures. We used commercially available FDTD Solutions software from Lumerical (Lumerical Solutions, Inc. http://www.lumerical.com/tcad-products/fdtd/). In order to improve simulation accuracy and reduce required computational resources, the non-uniform computational mesh was used in all simulations.

3. Results and discussion

Linear aromatic diphenylalanine (FF) peptide, which is the core motif of Alzheimer-amyloid protein, is self-assembled into open-end hexagonal nanotubes (FF-PNT) [14,15] and can be fabricated either in vertical- or horizontal-modes. Vertically-aligned FF-PNT are formed by fast evaporation of a solution containing FF monomers dissolved in the organic solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) [14]. Horizontally-aligned FF PNT are formed by dehydration of aqueous solution that contains FF monomers [15]. Fig. 1 depict an Environmental Scanning Electron Microscopy (ESEM) images of FF PNT, prepared by us in accordance with techniques [14,15] one in vertically-mode (Fig. 1a) and the second in horizontally-mode (Fig. 1b). Note that both images show similar FF-PNT morphology: hollow-core and hexagonal shape of their shell.

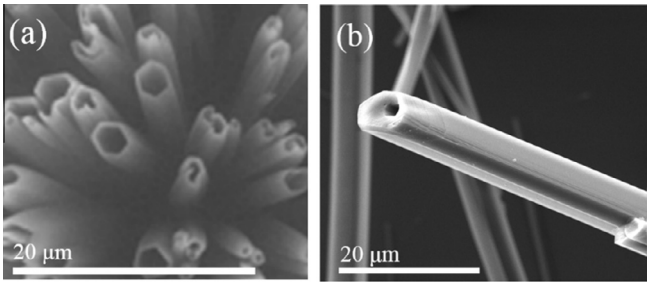

Fig. 1. ESEM image of (a) vertically aligned FF PNT, and (b) horizontally aligned FF PNT.

As was already reported in previous study [16], FF PNT have asymmetric nanoscale crystalline structure (C_6 for FF nanotube [17]), which allows observation of fundamental physical properties such as piezoelectricity [7], linear electrooptical, and nonlinear optical effects [8]. It is thus expected that FF PNT can also generate and guide light having second-harmonic frequency.

Once defining the configuration of the FF PNT, we can simulate the linear and nonlinear waveguiding property in vertically and horizontally alignments. Both configurations were measured in nonlinear optical microscopy originally aimed for analyses of biological tissues [5].

We begin with horizontally aligned FF PNT, placed on a glass substrate. This structure is shown in the top of Fig. 2. We examined the linear and nonlinear waveguiding properties as a function of the incident beam's angle. The simulated structure consists of 40 μm-long hexagonal peptide tube deposited on glass (SiO_2) substrate. The thickness of the tube walls is 200 nm. The guided optical modes in the tube were excited by linearly polarized ($E_x \neq 0, E_y = E_z = 0$) Gaussian beam (wavelength of 800 nm) focused on the tube's end.

The waist radius of the focused beam was 2 μm. The refractive indices of the FF-tube and the glass substrate at wavelength 800 nm are 1.66 and 1.45, respectively. The value of the refractive index of phenylalanine residues was already discussed in the work [18]. In all our simulations, the refractive index does not have an imaginary value, i.e. we did not simulate possible losses.

For the nonlinear waveguiding property, we used the second-order nonlinear optical susceptibility of FF-PNT ($\chi^{(2)} = 24$ pm/V) that was experimentally obtained in our previous work [8]. In addition, we simulated the case of perfect phase-matching condition (i.e., $n_\omega \sim n_{2\omega}$), a reasonable assumption for ultra-small interaction volume [4]. The dimensions that were used for simulating the FF PNT were obtained from experimental data (Fig. 1), which relies both on ESEM (presented in Fig. 1), and Kelvin Probe Force Microscopy (KPFM) images [19]. It should be stressed that in contrast to propagation of light generated by photoluminescence (PL) in FF PNT that was already reported [9,10,20], here we simulate the propagation of the modes, excited by the incident beam itself.

The linear and nonlinear waveguiding of the horizontally aligned FF PNT are presented in Fig. 2. The color maps in Fig. 2 show the two dimensional distributions of the electric field intensity $|E|^2$ of the guided modes. It can be observed that in horizontally aligned FF PNT, the light with fundamental wavelength at 800 nm propagates within the hexagonal shell of the nanotube, with maximum value at the uppermost surface, as the incident beam angle increases. The cross-section images explicitly show that the modes

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