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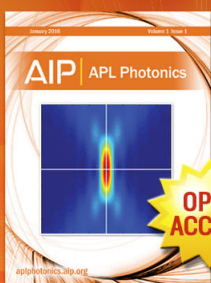
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## Enhanced photoluminescence of Si nanocrystals-doped cellulose nanofibers by plasmonic light scattering

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We report the development of bio-compatible cellulose nanofibers doped with light emitting silicon nanocrystals and Au nanoparticles via facile electrospinning. By performing photoluminescence (PL) spectroscopy as a function of excitation wavelength, we demonstrate plasmon-enhanced PL by a factor of 2.2 with negligible non-radiative quenching due to plasmon-enhanced scattering of excitation light from Au nanoparticles to silicon nanocrystals inside the nanofibers. These findings provide an alternative approach for the development of plasmon-enhanced active systems integrated within the compact nanofiber geometry. Furthermore, bio-compatible light-emitting nanofibers prepared by a cost-effective solution-based processing are very promising platforms for biophotonic applications such as fluorescence sensing and imaging. © 2015 AIP Publishing LLC.

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Polymer nanofibers prepared by electrospinning are cheap, flexible, and bio-compatible platforms for manipulating light at the nanoscale in nanophotonic and biophotonic applications.<sup>1,2</sup> The elegance of electrospinning technique relies on its simplicity and solution-based process in the absence of additional harsh chemicals and precisely controlled environment (pressure, temperature, *etc.*) that are traditionally required for most nanofabrication techniques. Light-emitting active nanofibers doped with semiconductor nanocrystals (NCs)<sup>3,4</sup> or organic dyes<sup>5</sup> have particularly attracted much attention due to their wide range of applications including waveguides,<sup>6–8</sup> light-sources,<sup>9–11</sup> optical sensors.<sup>3,12,13</sup>

It is well-known that plasmonic nanostructures such as Au and Ag nanoparticles (NPs) and nanorods can modify the emission properties of emitters located in their close proximity.<sup>14,15</sup> By carefully designing the material and structure, enhanced emission of NCs coupled to localized surface plasmon resonance (LSPR) of metal NPs has been demonstrated.<sup>16,17</sup> This is also applicable to NCs-doped electrospun nanofibers.<sup>18</sup> However, in order to suppress the non-radiative quenching of emitters coupled to metal surfaces or NPs,<sup>19,20</sup> complex fabrication techniques must be developed capable to accurately control the distance between metal NPs and emitters, which is a very challenging task.

In this work, using the cost-effective electrospinning technique, we demonstrate plasmon-enhanced emission in bio-compatible light-emitting silicon nanocrystals (Si-NCs) doped nanofibers. The combination of water-based hydroxypropyl

cellulose (HPC) polymer precursor and nontoxic Si-NCs emitting in the biological window (650–1300 nm)<sup>21,22</sup> enables the fabrication of all-biocompatible active nanofiber systems for sensing<sup>23</sup> and imaging.<sup>24</sup> Furthermore, we engineer the light-emission properties of the nanofibers by Au-doping them with plasmonic NPs. By performing photoluminescence (PL) spectroscopy of Au-doped nanofibers with and without metal NPs, we demonstrate plasmon-driven PL enhancement by a factor of 2.2 in the absence of non-radiative quenching due to the strong scattering of excitation light by Au NPs in side nanofibers.

Colloidal dispersions of Si-NCs are prepared by the method described elsewhere.<sup>25,26</sup> Si-rich borophosphosilicate glasses (BPSG) were first deposited by co-sputtering Si, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> in an RF-sputtering apparatus. The films were peeled off from the plates and annealed at 1075 °C in a N<sub>2</sub> gas atmosphere for 30 min to grow Si-NCs in BPSG matrices. The Si-NCs were isolated from matrices by dissolving in HF solution (46 wt. %). Isolated Si-NCs were then transferred to water. As reported in our previous work,<sup>27</sup> co-doping B and P enables us to obtain the water-dispersible Si-QDs without organic ligand passivation. In Figure 1(a), we show a photograph of Si-NC dispersion and a transmission electron microscope (TEM) (Tecnai Osiris, FEI) image. Si-NCs are well-dispersed in water, and no agglomerates were observed in the image. The average diameter of Si-NCs estimated by TEM was 3.3 ± 0.9 nm.

To prepare the precursor of electrospun nanofibers, we first dissolved HPC in DI water and then added Si-NC solution to the polymer solution, followed by stirring for about 1 h to obtain a homogeneous mixture solution containing

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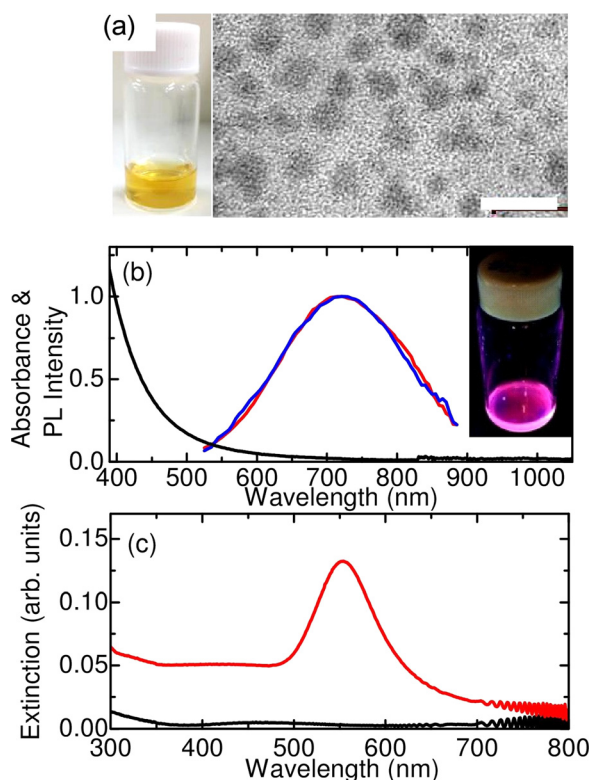


FIG. 1. (a) Photograph of colloidal dispersion and TEM image of Si-NCs (Scale bar: 10 nm). (b) Absorbance (black) and normalized PL spectra of Si-NCs in water (red) and planar HPC film (blue). The excitation wavelength is 488 nm. Inset: Photograph of HPC solution (45 wt. %) containing Si-NCs under UV excitation. The color of the emission appears pink due to the contribution of the weak blue emission from the HPC polymer under UV excitation. (c) Extinction spectra of single- (black) and Au-doped (red) HPC films.

45 wt. % HPC and 0.8 mg/ml Si NCs. Photoluminescence spectra were measured using a monochromator (Oriol Cornerstone 260, Newport) and photomultiplier tubes (Oriol 77348, Newport). The excitation source was 488 nm line of an Ar ion laser (Spectra Physics, 177–602). Figure 1(b) shows absorbance and normalized PL spectra of Si-NCs in water (red) and in the HPC solution (blue). In the inset, we show a photograph of HPC solution containing Si-NCs under UV light excitation, exhibiting bright red luminescence. The Si-NCs in HPC solution exhibit a broad PL peaked at 710 nm, which is identical to that observed for Si-NCs in water.

Plasmonic NPs and Si-NCs co-doped (Au-doped) polymer solution was prepared by directly adding concentrated Au NPs (70 nm diameter) synthesized by a seeded growth method to the mixture solution. The concentration of the final mixture solution was 45 wt. % HPC with 0.8 mg/ml Si-NCs and 1.2 mg/ml Au NPs. In the following, we refer to the sample doped with both Si-NCs and Au NPs as Au-doped sample, and to that doped with Si-NCs alone as single-doped sample. In Figure 1(c), we plot the extinction spectra of single- (black) and Au-doped (red) HPC films prepared by spin-coating mixture solutions. In the Au-doped HPC film, the extinction peak originating from LSPR of Au NPs is clearly observed around 550 nm. The slight increase of extinction at a wavelength shorter than 400 nm observed in both spectra is due to the absorption of Si-NCs. We notice that in this

wavelength range, the absorption (and scattering) of the HPC host film is negligibly small compared to that of Au NPs.

In order to create active nanofibers by electrospinning, the HPC mixture solution was poured into 10 ml Syringe (diameter 18.94 mm) fitted with a 20 gauge stainless steel needle. The syringe was then transferred to an infusion syringed pump (Braintree scientific) with the needle connected to the positive terminal of a high power voltage source (Gamma high voltage). Controlled by the syringe pump, the precursor (45 wt. % HPC solution) was pushed continuously to the needle tip with a flow rate of 0.4 ml/h. Driven by the high voltage (18 kV) established in the Taylor cone between the nozzle and metal plate collector, the precursor was ejected from the nozzle creating HPC nanofibers after solvent evaporation. The charged HPC nanofibers are neutralized at the collector (kept 20 cm from the nozzle), where they form random networks of nanofibers. Figure 2(a) shows a representative scanning electron microscope (SEM) image of the electrospun HPC nanofibers Au-doped with Si-NCs and with Au NPs. The average diameter of the nanofibers is 249 nm with the standard deviation of 31 nm. The nanofibers form a relatively uniform film with a thickness of 7.6  $\mu\text{m}$  measured by cross-section SEM analysis. We confirmed the same morphology (i.e., thickness and diameter) of both single- and Au-doped nanofibers films. In Figure 2(b), we show a TEM image of the Au-doped system, which demonstrates doping with 70 nm Au NPs within the nanofiber. The TEM image demonstrates that the Au NPs are incorporated into the nanofibers without forming aggregates at this doping concentration. The density of Au NPs (i.e., number of NPs per unit volume) is estimated from TEM analysis to be  $\sim 10^{13} \text{ cm}^{-3}$  in good agreement with the concentration of the precursor solution. The high-resolution TEM image of the nanofiber in

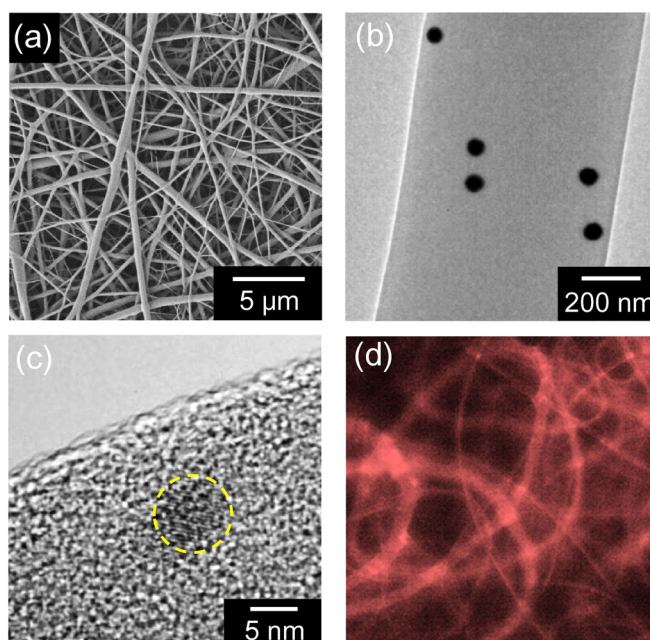


FIG. 2. (a) SEM image of electrospun HPC nanofibers doped with Si NCs and Au NPs. (b) TEM image of Au-doped nanofibers. (c) High-resolution TEM image showing a Si NC doped in a nanofiber. (d) Microscope PL image of Au-doped nanofibers (excited at 430 nm).



Figure 2(c) shows an incorporated Si-NC with lattice fringes corresponding to {111} planes of the Si crystal. Figure 2(d) shows a PL image of Si-NCs Au-doped nanofibers obtained by an optical microscope with excitation at 430 nm. Since only the PL signal from Si-NCs (red to near-IR range) is collected by filtering the excitation light, the image clearly demonstrates that Si-NCs are homogeneously incorporated within the nanofiber network.

To investigate the effect of Au NP-doping on the light emission of Si-NCs, we performed PL excitation (PLE) spectroscopy for single- and Au-doped nanofiber samples using a tunable (340 nm–2200 nm) optical parametric oscillator (SpectraPhysics Inspire) pumped by a Ti:sapphire laser (MaiTai HP SpectraPhysics, 82 MHz repetition rate) using an average power of 2.5 mW. The samples are directly irradiated by a focused excitation beam without waveguiding excitation.<sup>7</sup> In Figures 3(a) and 3(b), we show the PL spectra of single- and Au-doped nanofibers excited at 490 and 545 nm, respectively. We measured the PL spectra at 5 different excitation spots, and calculated the average PL intensity and error bars. When excited at 490 nm, which is detuned from LSPR of Au NPs, both the single- and Au-doped nanofibers samples show comparable PL intensity (within the error bars). Figure 3(c) shows the measured PL decay traces of single- (black) and Au-doped (red) nanofiber detected at 720 nm using the excitation by the Ar laser beam (488 nm), which has been modulated with an acousto-optic modulator at a frequency of 1 kHz. The decay curves are

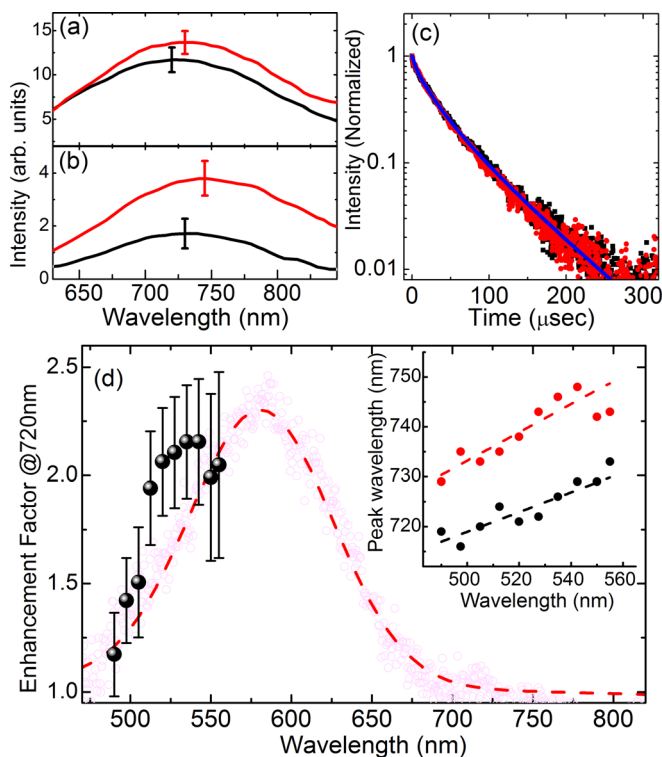


FIG. 3. PL spectra of single- (black) and Au-doped (red) nanofibers excited at (a) 490 and (b) 545 nm. PL peak wavelength of single- (black) and Au-doped (red) nanofibers as a function of excitation wavelength. (c) PL decay curves of single- (black) and Au-doped (red) nanofibers detected at 720 nm with the fitting curve (blue). (d) PL enhancement factors (black) as a function of excitation wavelength. Red dashed curve shows the scattering spectrum of Au-doped nanofibers. Inset: PL peak wavelength of single- (black) and Au-doped (red) nanofibers excited at different wavelengths.

well-fitted by a stretched exponential decay function,  $I = I_0 \exp[(-t/\tau)^\beta]$ , where  $\tau$  is the effective lifetime and  $\beta$  is the stretching parameter. The same  $\tau$  (32  $\mu$ s) and  $\beta$  (0.74) are obtained for both samples, and almost identical to that of Si-NCs doped in a HPC film (i.e.,  $\tau = 31 \mu$ sec and  $\beta = 0.77$ ), which indicates that there is no significant change in the decay time of Si-NCs by electrospinning. Moreover, the comparison between single- and Au-doped nanofibers demonstrate that the spontaneous decay rate of Si-NCs is not affected by the Au-doping with Au NPs, consistent with the large average distance between Si-NCs and Au NP (i.e., precluding near-field interactions).

On the contrary, when we excite the systems at 545 nm, the PL intensity of the Au-doped nanofibers is enhanced by approximately a factor of 2 compared to the one of single-doped nanofibers. To better understand the origin of the measured PL enhancement, we study the PL enhancement spectrum (the PL intensity ratio of Au-doped to single-doped nanofibers). Figure 3(d) shows the enhancement factors of the PL of Si-NCs and the scattering spectrum of Au NPs doped nanofibers. The scattering spectrum of Au-doped nanofibers (red curve in Figure 3(d)) is obtained from the dark-field scattering measurements with the optical microscope using 100 W tungsten halogen lamp. We find that the PL enhancement factor strongly depends on the excitation wavelength and that its trend follows the scattering spectrum of Au NPs in the nanofibers. The PL enhancement in a generic system of emitters (of identical density) can originate from several factors: the modifications of (a) excitation efficiency; (b) extraction efficiency of emitted light; and (c) quantum efficiency (i.e., emission rate) of the emitters. The separation between the extinction peak of Au NPs (at 550 nm shown in Figure 1(c)) and the emission peak of Si-NCs (at 720 nm) allows us to exclude significant enhancement of the extraction efficiency at the emission wavelength. Moreover, due to the large average distance between Si-NCs and Au NPs, we did not observe sizable modifications of the PL decay times of Si-NCs in both samples. Therefore, we can deduce that the measured PL enhancement originates from the plasmon-enhanced light scattering, which increases the effective excitation efficiency of Si-NCs due to the redistribution and trapping of light inside the Au NPs doped nanofibers. The presence of strongly scattering Au NPs in the nanofibers leads to an increase of the absorption rate of the pump inside the Si-NCs doped samples. Our data demonstrate that the Au-doping of Au NPs in active nanofibers significantly enhances the emission of Si-NCs in the absence of non-radiative quenching, which limits the performance of alternative active systems coupled to plasmonic NPs in the near-field.<sup>19</sup>

In the inset of Figure 3(d), we show the PL peak wavelength of single- and Au-doped nanofibers as a function of excitation wavelengths, demonstrating the red-shift with increasing excitation wavelength. This behavior is commonly observed in an ensemble of Si-NCs.<sup>28,29</sup> Due to the size distribution of Si-NCs, only larger Si-NCs with smaller optical bandgap energies can be excited when the excitation wavelength is close to the PL wavelength.<sup>28,29</sup> In addition, we observe a small red-shift between single- and Au-doped samples across the overall excitation wavelength range. This can be explained by photon re-absorption in the presence of

an inhomogeneous population of Si-NCs dispersed inside nanofibers (i.e., the emission from small Si-NCs is re-absorbed by the larger Si-NCs). Since the scattering spectrum of Au NPs overlaps with the shorter wavelength side of the PL spectrum, the emission from the smaller Si-NCs is strongly scattered by the Au NPs and efficiently re-absorbed at lower energy by the larger Si-NCs in the nanofibers. This leads to the slight red-shift of the PL observed in the Au-doped samples.

In conclusion, we developed active light-emitting HPC nanofibers doped with Si-NCs and Au NPs. By performing time-resolved PL and PLE measurements, we demonstrate that Au-doped nanofibers give rise to enhanced PL by a factor of 2.2 in the absence of non-radiative quenching of the Si-NCs emission due to plasmon-enhanced scattering of pump radiation from Au NPs to Si-NCs inside the nanofibers. Our findings provide not only an alternative concept for the plasmon-enhanced PL but also a unique opportunity for bio-compatible active platforms that leverage cost-effective and largely scalable processing with Si-NCs light emission for biophotonics applications.

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