



Fabrication of Si–Ag “wire-cap” nanostructures for metal-enhanced fluorescence

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ABSTRACT

We demonstrate a convenient nanotechnology to modulate Si–Ag “wire-cap” nanostructures for metal-enhanced fluorescence by self-selective electroless plating on Si. Optimized coupling between Ag caps and organic emitter can be achieved by altering the bending degree of the Si nanowires resulting in significantly enhanced local electric field intensity. The enhanced photoluminescence from the organic emitter coupled Si–Ag “wire-cap” nanostructures derives from the excitation of localized surface plasmons between the Ag nanocaps and also the energy transfer effect in the surface plasmon resonant coupling between the organic emitter and Ag caps. Our technique has potential applications in biochemical sensors and light emitters.

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1. Introduction

Metal-enhanced fluorescence, which can be used to engineer the spectral properties of fluorophores [1], offers promise in a myriad of applications including surface-enhanced cellular fluorescence imaging [2,3], light emitting diodes [4], and single-molecule studies [5]. Experiments have confirmed the importance of overlapping between the localized surface plasmon resonance energy of the surface configuration and emission energy [1,6,7]. The type, shape, height, and density of the surface nanostructures determine the degree of enhancement [8]. In order to explore the cause and mechanism, experiments have been conducted carefully to often exclude other possible factors which may contribute to the enhancement such as reflection from the metallic nanostructures, emission from the metallic nanostructures themselves, increased absorption of light in photoluminescence (PL) enhancement, and quenching of defect emission. Although the exact mechanism is still debatable, it is generally agreed that the effects of metallic colloids interacting with fluorophores can be understood by the formation of metal interstitial sites. These interstitial sites, so-called “hot spots” or “hot junctions” in the nanostructures, consist of two or more coupled particles or nanostructured surfaces with closely spaced features, and there are highly concentrated

electromagnetic (EM) fields associated with the strongly localized surface plasmon resonance [6,9].

In this paper, we report the synthesis of Si–Ag “wire-cap” nanostructures by a promising technique involving self-selective electroless plating [10]. The superiority of this design is that the surface topography of the Ag caps on the tips of Si nanowires (SiNWs) will change along with the bending of nanowires. The bending degree is altered by the length of the SiNWs and can be controlled by simply immersing the Si wafer into the HF/AgNO₃ solution for an appropriate etching time. Considerable enhancement of the PL from the organic emitter poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) on Si–Ag “wire-cap” nanostructures is observed. Moreover, the light emission properties of MEH-PPV can be tailored by coupling to resonance-tuned Si–Ag “wire-cap” nanostructures.

2. Materials and methods

Commercial single-side polished Si wafers (p-type, B-doped silicon (100)) were cut to 2 × 2 cm² squares. They were immersed in a solution containing HCl, H₂O₂, and H₂O with a volume ratio of 1:1:6 at 70 °C and treated ultrasonically for 10 min to remove any trace of heavy metals and organic species. This was followed by etching in a diluted aqueous HF (10 wt%) for 10 min. The silicon wafers were then etched in a 5.0 mol/L HF solution containing 0.02 mol/L of silver nitrate at 50 °C for different periods of time. The container was a conventional

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Teflon-coated stainless steel vessel. After etching, the silicon wafers were rinsed with de-ionized water and air dried. The thick Ag dendrites covering the silicon wafer were detached before microstructural investigation. The silver dendrites could be easily stripped by a tweezer because they were loose and easily peeled. The morphology of the samples was determined on an FEG JSM 6335 field emission scanning electron microscope (SEM).

MEH-PPV was chosen as the organic emitter because its optical property is well understood and has been widely applied to optoelectronic devices. The MEH-PPV powders were dissolved in a tetrahydrofuran (THF) solution to a concentration of 0.2 mg/mL at room temperature and then coupled to the Si–Ag “wire-cap” nanostructures by means of the drop coating of the solution onto the sample. The PL spectra were acquired on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer.

3. Results and discussion

Self-selective electroless plating has been demonstrated to be a simple and effective method to produce functional one-dimensional nanomaterials [10]. The technique which is based on conventional electroless plating utilizes the base substrate and surface metal deposition to produce the desired functional nanostructures. In the Si–AgNO₃–HF system, the holes injected from the silver ions are consumed by an oxidation process and deposition can occur without an externally applied bias. We have demonstrated that Ag protects the silicon underneath from etching during the process of self-selective electroless plating on Si and the SiNWs capped with Ag nanoclusters acting as the cathode are eventually formed at the expense of etching of the surrounding Si acting as the anode [11]. The lengths of Si–Ag “wire-cap” nanostructures depend on the etching time, as show in Fig. 1. It can be observed

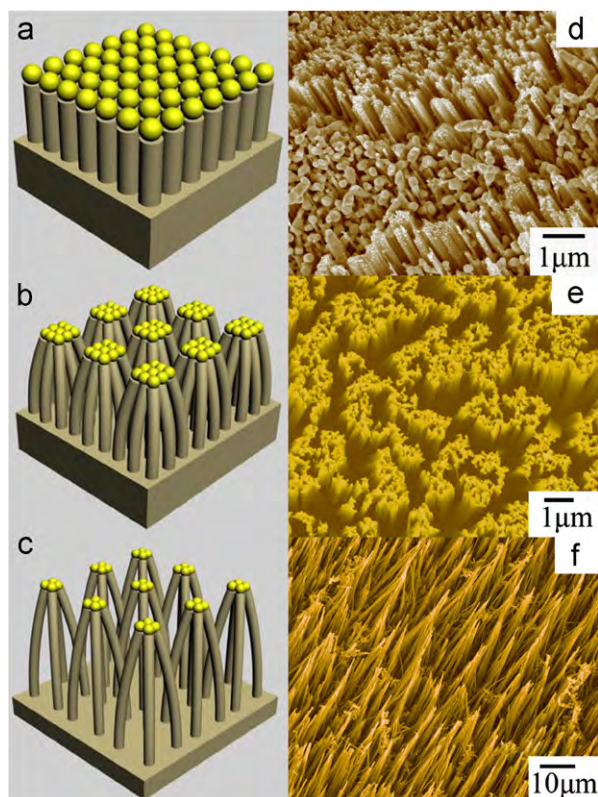


Fig. 1. Schematic illustration (a–c) and corresponding SEM images (d–f) of Si–Ag “wire-cap” nanostructures formed under different etching time: (a, d) 10 min, (b, e) 40 min, (c, f) 60 min.

that the Ag nanoclusters with diameters in the range of 100–300 nm are embedded in the SiNWs and tiny Ag nanoclusters are attached to the apexes and walls of the SiNWs, forming Si–Ag “wire-cap” nanostructures (see Fig. 1(d)). Longer SiNWs with Ag nanoclusters produced by etching for a longer time such as 40 (see Fig. 1(e)) or 60 min (see Fig. 1(f)) are not as rigid as those produced by etching for 10 min (see Fig. 1(d)) and can sometimes be bundled together. It is noted that bending of the nanowires leads to agglomeration of the Ag nanoclusters subsequently altering the gaps between individual caps and this is schematically illustrated in Fig. 1(a–c). This phenomenon can be understood as being due to the irregular shape of nanowires. The center of gravity of each individual nanowire is not aligned with that of other nanowires. The longer nanowires which are off axis to gravitation will bend more, and eventually the torque leads to bending and agglomeration of the nanowires. The van der Waals attraction among the atoms may also play a part in this effect [12].

It has been demonstrated that the EM field can be significantly enhanced in the vicinity of nano-scale metallic particles. The mechanism of enhancement can be explained by localized surface plasmons. Localized surface plasmons are charge density oscillations confined to metallic nanostructures. Excitation of localized surface plasmons by light with a wavelength where resonance occurs results in strong light scattering, appearance of intense surface plasmon absorption bands, and enhancement of the local EM fields [6]. The frequency and intensity of the surface plasmon absorption bands are characteristic of the type of materials and are highly sensitive to the size, size distribution, and shape of the nanostructures [13].

In order to evaluate the fluorescence-enhancing capability of Si–Ag “wire-cap” nanostructures, we first compare the PL spectra of the MEH-PPV coupled 40 min etched sample and MEH-PPV coupled SiNWs without Ag caps. The PL spectra of MEH-PPV coupled samples are shown in Fig. 2 with the same acquisition time of 0.1 s acquired by excitation with the 500 nm line of a Xe lamp. To make sure that the MEH-PPV is soaked deep into the SiNWs, the fluorescence spectra are measured 24 h after MEH-PPV is added on the samples. The peak intensity of the PL spectrum of the MEH-PPV coupled Si–Ag “wire-cap” nanostructures is about 7 times higher than that of the MEH-PPV coupled SiNWs without Ag caps. SiNWs without Ag caps are obtained by simply treating the Si–Ag “wire-cap” nanostructures ultrasonically for 3 min and 20 min to remove the Ag caps. It can be readily understood that the sample ultrasonically treated for 3 min contains more silver particles than the other one. According to Fig. 2(b) and (c), we can observe that the PL intensity of (b) is much weaker than that of (a) and a little stronger than that of (c),

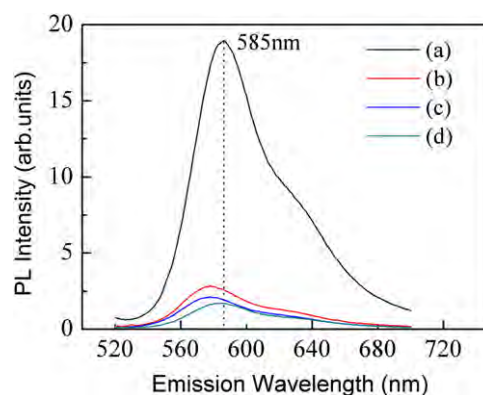


Fig. 2. Comparison of PL spectra of the MEH-PPV coupled Si–Ag “wire-cap” nanostructures (a) and MEH-PPV coupled SiNWs (b, c, d). Sample (b) and (c) are treated ultrasonically for 3 min and 20 min respectively and Sample (d) is cleaned with HNO₃ solution to remove Ag particles on it.

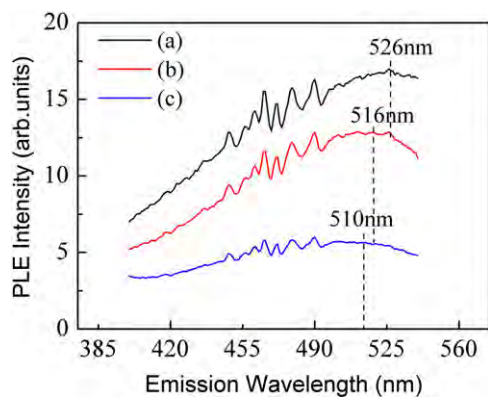


Fig. 3. PLE spectra of MEH-PPV coupled Si-Ag “wire-cap” nanostructures (a) and MEH-PPV coupled SiNWs (b, c). Spectra (b) and (c) show samples treated by ultrasonic wave for 3 min to partly remove the Ag particles and immersed in HNO₃ solution for 20 min to totally removed the Ag particles respectively. (The etching time of SiNWs is 40 min.)

indicating that the amount of Ag particles may be related to the PL intensity. To confirm, we try another method to remove the silver particles by HNO₃ and the outcome is almost the same as shown in (d). In fact, it has been demonstrated in our previous work that the PL efficiency of the MEH-PPV coupled silver nanostructures may originate from the energy transfer effect in the surface plasmon resonance coupling [7]. The plasmon resonance energy transfer process can occur through the dipole–dipole interaction between the resonating plasmon dipole in Ag caps and the MEH-PPV dipole. The resulting resonance can lead to energy transfer from the Si-Ag “wire-cap” nanostructures to the light-emitting MEH-PPV by irradiating with the 500 nm line of Xe which creates more excitons in the light-emitting MEH-PPV. For confirmation, we obtain the PL excitation (PLE) spectra from our sample and the results are shown in Fig. 3. The samples are cleaned to remove silver particles on the surface. The spectra of the sample without silver particles deviate from the original one (a) by about 16 nm. At the same time, we also acquire the PLE spectra of our sample after ultrasonic treatment for 3 min to partly remove the silver particles on it (b). The peak of the PLE spectra moves from 526 nm to 510 nm as the amount of Ag particles is reduced until they are totally gone (c), indicating that nano-scale Ag particles indeed lead to surface-plasmon resonance with a wavelength shift of about 16 nm, confirming that the PL enhancement observed in this study is surely due to the effect of surface plasmons.

Another more important factor responsible for the enhanced PL is the “hot spots” where the local electric field is drastically enhanced resulting from excitation of localized surface plasmons between the Ag nanocaps in the background of the light-emitting MEH-PPV. Theoretically, the contribution by the enhanced electric field is proportional to $|E_{loc}|^4/E_0^4$, and hence, the PL signal is boosted greatly. An example of using nanowires to engineer “hot spots” can be found in the paper by Mohanty et al. [14] for surface-enhanced Raman scattering. By trapping and automatically positioning the analyte molecules pre-adsorbed on the tips of the nanowires in the junctions between neighboring tips, the Raman signal is enhanced significantly. Similar work reporting that the Raman signal is significantly enhanced only when the laser is focused on the cross junction of crossed or parallel nanowire pairs also provides unequivocal proof about the importance of the “hot spots” in this system [14,15]. To study this effect in metal-enhanced fluorescence, a series of Si-Ag “wire-cap” nanostructures coupled with MEH-PPV are fabricated. By increasing the etching time, the tips of the nanowires bend towards each other while moving the Ag caps closer or further together (see Fig. 1(d)–(f)). Since the spacing of the Ag caps can be tailored by adjusting the

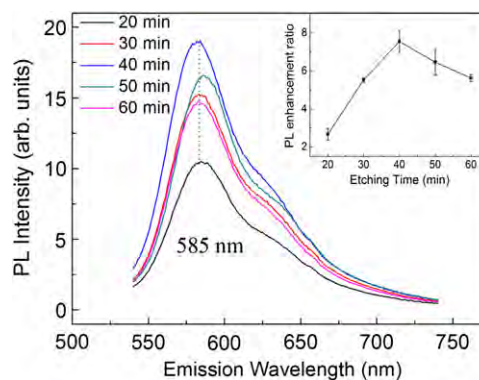


Fig. 4. PL spectra of MEH-PPV coupled Si-Ag “wire-cap” nanostructures formed under different etching time: 20, 30, 40, 50, and 60 min. The dependence of the PL enhancement ratio of MEH-PPV coupled Si-Ag “wire-cap” nanostructures to MEH-PPV coupled corresponding SiNWs without Ag caps is shown in the inset.

etching time, the local EM field enhancement can be modulated to achieve the strongest coupling between adjacent caps.

Fig. 4 displays the PL spectra of MEH-PPV coupled Si-Ag “wire-cap” nanostructures formed using different etching time and excited by the 500 nm line of a Xe lamp. The relationship between the PL enhancement ratio of the MEH-PPV coupled Si-Ag “wire-cap” nanostructures to MEH-PPV coupled corresponding SiNWs without Ag caps and etching time is shown in the inset. The PL intensity increases sharply and then decreases gently with increasing etching time. The maximum PL enhancement ratio (~ 7 times) is observed from the 40 min etched sample in Fig. 1(e). The strong enhancement can be attributed to the fact that the Si-Ag “wire-cap” nanostructures are assembled with the favorable gap configuration of Ag caps. It can be further concluded that a larger spacing of the Ag caps from 20 and 30 min etched samples and mass cap aggregation from 50 and 60 min etched samples may reduce the PL enhancement effect significantly.

4. Conclusion

We experimentally modulated Si-Ag “wire-cap” nanostructures for metal-enhanced fluorescence. The gaps between the individual Ag caps are altered by the length of the SiNWs and can be controlled by the etching time. The enhanced PL from the MEH-PPV coupled Si-Ag “wire-cap” nanostructures derives from the excitation of localized surface plasmons between the Ag nanocaps in the background of the light-emitting MEH-PPV and also the energy transfer effect in the surface plasmon resonant coupling between the MEH-PPV and Ag caps. Our technique has potential applications to biochemical sensors and light emitters.

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