

Plasmonic photoluminescence enhancement by silver nanowires

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Abstract

Strong enhancement of photoluminescence is demonstrated for CdS nanocrystals and ruthenium-based dye (N719) due to localized surface plasmon resonance of silver nanowires placed on silver film. Alternative reasons for photoluminescence modulation such as mirror effect and uneven coating by dye or nanocrystals due to geometrical factors are discussed. An artifact such as carbon contamination at the surface of silver nanowires at high laser power is demonstrated and taken into consideration. Silver nanowire on silver film is proved to be an effective system for photoluminescence enhancement by localized surface plasmon resonance.

Keywords: nanowires, plasmon resonance, photoluminescence enhancement, nanocrystals, confocal microscope

(Some figures may appear in colour only in the online journal)

1. Introduction

The collective excitation of the electron gas in the conduction band of metal nanoparticles (NPs)/nanowires (NWs) can result in strong optical response known as localized surface plasmon resonance (LSPR) and representing considerable interest in the field of nanophotonics and plasmonics [1]. Moreover, metal NWs can be used as a plasmonic waveguide to enhance Raman scattering or photoluminescence (PL) signals very locally for a nanoscale object (single molecule, quantum dot, etc), realizing so called 'remote surface enhanced Raman spectroscopy' or PL [2, 3]. There is plethora of publications where LSPR is used for enhancement of a Raman signal [4–6], but considerably fewer works where LSPR is employed to intensify the PL signal [1, 7]. In most works the effect of dramatic increase of optical signal (Raman or luminescence) due to LSPR was demonstrated for organic dyes [4]. At the same time, in relatively few works quantum dots (QDs) or nanocrystals (NCs), (CdSe or CdSeTe), were used to show an LSPR-related enhancement phenomenon [8, 9].

Coupling of LSPRs can create regions of concentrated electric fields, so-called 'hot-spots', in the gaps between metal NPs/NWs, leading to PL enhancement from nearby QDs or dye molecules. There are several systems of metal nanostructures that can be used for LSPR coupling, for example, metal NPs on metal NWs [10] or NPs on metal film [11],

closely packed metal NPs [12], or closely packed metal NWs [13]. Here we used square-patterned silver films on a glass substrate with deposited silver NWs on top of it. The main advantage of our system is the possibility to check and exclude possible non-LSPR-related luminescence enhancement.

There are several possible reasons for non-LSPR-related luminescence enhancement, for example, the mirror effect from a metal substrate, a geometrical effect causing non-uniform coating with dye or QDs, etc. The mirror effect may be responsible for an optical signal up to two times stronger due to sample interaction with incident and reflected laser beams. The geometrical effect may appear when dye or QDs are deposited from solution condensate in proximity to any pronounced features at the substrate surface during drying.

In this study we compare the luminescence enhancement effect on ruthenium-based dye (Ruthenizer 535-bisTBA or N719) and CdS QDs on the same substrates, that allows direct comparison of obtained results. The analysis of possible geometrical effects and their separation from LSPR-related luminescence enhancement is analysed.

2. Experimental setup

Silver NWs (120 nm in diameter), dispersed in ethanol, were purchased from Blue Nano. Ruthenizer 535-bisTBA (N719)

dye was purchased from Solaronix. CdS NCs were synthesized according to the procedure described in [14, 15]. An oleylamine-sulfur solution was prepared by dissolving 0.4 g of sulfur (6 mmol) in 10 mL of oleylamine. Separately, 1 mmol of CdCl₂ was dissolved in 10 mL of oleylamine. The CdCl₂ solution was heated in a three-neck flask in an oil bath to 175 °C for 20–35 min under nitrogen flow and magnetic stirring. Then the oleylamine-sulfur solution was injected under gentle stirring into the hot reaction mixture. The reaction mixture was held at 175 °C and stirred for 3 h, then cooled down naturally to room temperature and mixed with an equal amount of toluene. The NCs were separated from the toluene solution by the addition of ethanol and centrifugation. Produced NCs could be re-dispersed in various organic solvents including hexane, toluene, and chloroform. Average CdS NCs size was ~12 nm.

Square-patterned silver films were fabricated by vacuum thermal evaporation of metallic silver on glass substrates through a transmission electron microscopy grid used as the shadow mask. In some cases sapphire wafer (Roditi International) was used instead of a glass substrate. Next, they were coated with silver NWs and then with a thin layer of CdS NCs or Ruthenizer 535-bisTBA (N719) commercial dye. All materials were drop deposited from corresponding solutions and dried. Scanning electron microscopy (SEM) images of Ag NWs were obtained by FIB-SEM microscope FEI Helios Nanolab. Silver film thickness measured by CP-II (Veeco) atomic force microscope was ~50 nm thick.

Confocal spectromicroscopy and PL spectroscopy were performed using a confocal microscope with spectrometer Nanofinder-S (SOLAR TII) [16]. All experiments were performed in back-scattering geometry at room temperature (20 °C) through a Nikon CF Plan Apo 100 × (NA = 0.95) optical objective. A diode pumped solid-state (DPSS) Nd:YAG laser (532 nm, max cw power $P_{ex} = 150$ mW) was used as the excitation source, and the spectra were dispersed by 150 grooves/mm diffraction grating mounted in the 520 mm focal length monochromator. The elastic laser light component was eliminated by the edge filter (Semrock LP03-532RE). A Peltier-cooled back-thinned CCD camera (ProScan HS-101 H) was used for detection of PL spectra, whereas the Hamamatsu R928 photomultiplier tube was employed in confocal-spectral imaging experiments. The laser power at the sample was controlled by a variable neutral filter with the optical density OD = 0–3.

3. Results and discussion

Confocal optical image of the square-patterned silver film coated by silver NWs at low magnification is shown in figure 1(a). More detailed information was obtained by SEM: NWs demonstrate the smooth surface and faceted morphology typical for chemically synthesized silver NWs, as can be seen in figures 1(b) and (c). The length of NWs was several tens of microns, and the diameter was in the range of 100–200 nm.

The PL spectra of CdS NCs at four different sample points, excited with strongly reduced laser light power using the neutral filter with OD = 3, are shown in figure 2(c). A red emission band due to CdS NCs is observed at about 720 nm on pure glass and on Ag NW/glass, while the band maximum shifts to a longer wavelength of 750 nm on Ag NW/Ag film. This effect can be explained by a plasmon-modulated luminescence shift induced by metal nanostructures [17]. A similar PL band was detected in CdS NWs and interpreted as the emission due to surface states [18]. The largest PL enhancement of about 3–5 times occurs at the hot spots, where near-field coupling between silver NWs and an underlying silver film occurs (figure 1(b)). It is important to note that an increase of the PL intensity was detected also in places where the hot spots are formed by two crossed NWs on pure glass (see inserts in figures 2(a) and (b)). At the NWs' cross point, there is an empty space beneath the upper NW (figure 1(c)), which can be filled by NCs and be a reason for a PL increase due to a geometrical factor (uneven NC coating). However, a similar effect should occur also in the region where NW is suspended at the patterned film border (figure 2(b) for CdS and figure 3(b) for N719 dye). However, no PL increase was found in the place of the NW crossing the patterned film border. Therefore, we can conclude that an increase of PL intensity at the cross point of two NWs is completely related to the LSPR enhancement effect.

Similar measurements were performed using ruthenium-based dye (N719) deposited on a NWs/film substrate. A broad red PL band with the maximum at about 670–750 nm was recorded and attributed to the dye luminescence (figure 3(c)). Note that our PL spectrum agrees well with that measured in [19], and the effect of the band maximum shift has been observed previously in [20]. A part of the NW (figure 3(a)) is located on silver film, while the remaining part is on a pure glass substrate. As one can see, the strongest emission intensity originates from the NW part lying on silver film (figure 3(b)) and is related to the LSPR coupling effect. The LSPR-related PL enhancement factor on AgNW/Ag film for N719 dyes is about 10^2 – 10^3 (figure 3(c)), which is significantly higher in comparison to the enhancement for CdS NCs. The emission from the remaining NW part on the glass substrate is much weaker, but stronger than that of the ruthenium dye on both plane glass and silver film surfaces. The mirror effect (enhancement of luminescence on silver film) is below the detection limit at the given exciting laser power. Some emission enhancement is present along the border of the silver film and along the NW on glass. Unfortunately, the geometrical effect causing dye molecule condensation along the NW and along the border cannot be distinguished from LSPR effect and diffraction on the half plane, causing a well-known redistribution of the electric field [21, 22].

The enhancement of red PL from N719 occurs also at the intersection points (hot spots) of two NWs (figure 4(a)). However, one should point out another important phenomenon, which may influence the interpretation and is related to carbon contamination [23] at the surface of silver NWs under exposure to high intensity laser light. In this case the laser

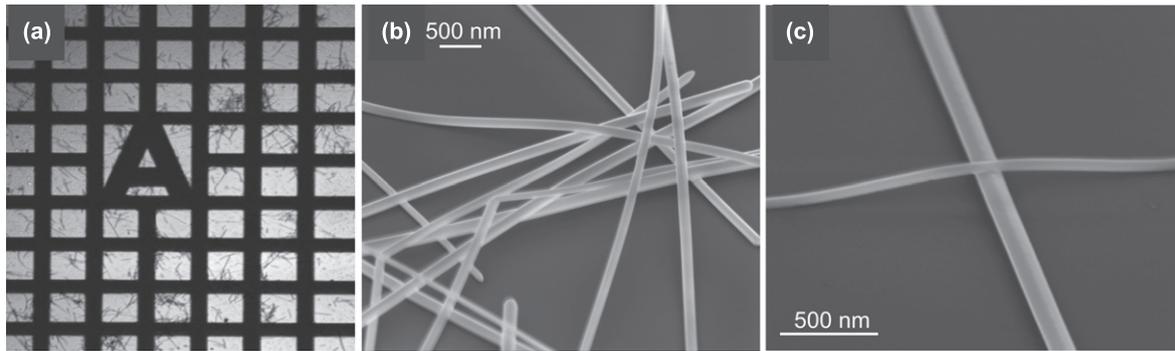


Figure 1. (a) Confocal image (size $559 \times 666 \mu\text{m}$) of square-patterned silver film covered by silver nanowires. (b)–(c) SEM images of silver nanowires on silicon wafer. Both images were taken at 52° sample tilt and acceleration voltage of 10 kV.

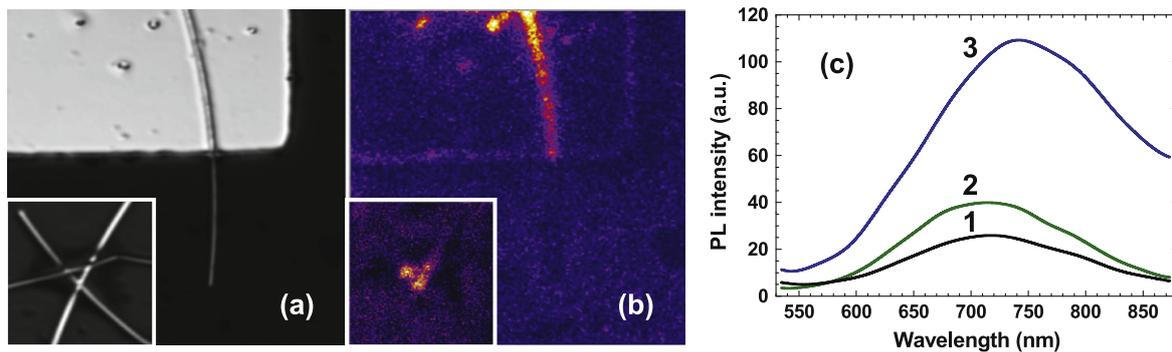


Figure 2. Confocal (a) and spectral (b) images (size $24 \times 29 \mu\text{m}$, insert image size $8 \times 10 \mu\text{m}$) of silver nanowires (NWs) placed above the patterned silver film on a glass substrate and uniformly covered with CdS nanocrystals (NCs). Spectral image was acquired at 750 nm. (c) Room temperature photoluminescence spectra of CdS nanocrystals excited by a 532 nm laser at four different sample points: (1) CdS NCs/Ag NWs/glass; (2) CdS NCs/glass; and (3) CdS NCs/Ag NWs/Ag film/glass.

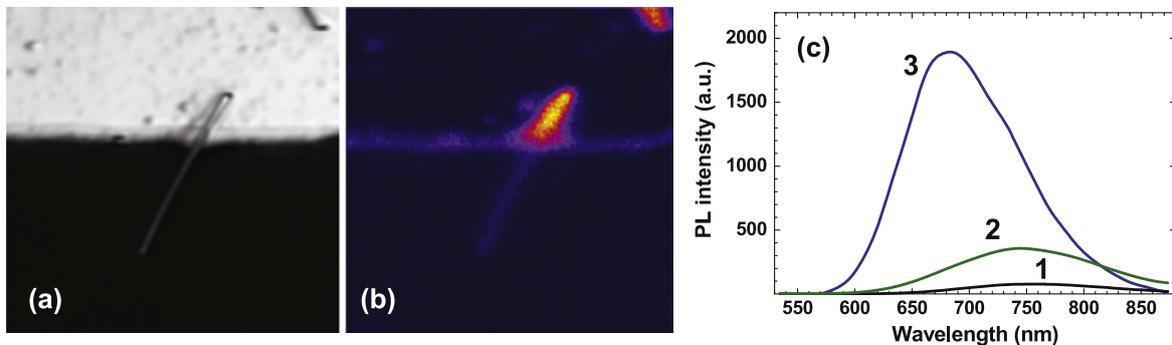


Figure 3. Confocal (a) and spectral (b) images (size $8 \times 10 \mu\text{m}$) of silver nanowire placed above the silver film on a glass substrate and uniformly covered with ruthenium-based dye (N719). Spectral image was acquired at 730 nm. (c) Room temperature photoluminescence spectrum of N719 excited by a 532 nm laser at three different sample points: (1) N719/glass; (2) N719/Ag film/glass; and (3) N719/Ag NWs/Ag film/glass.

light power was reduced by the neutral filter with $\text{OD} = 1.5$, and the Raman spectrum measured at the location of the silver NW is shown in figure 4(c). The presence of graphite-like carbon can be identified by characteristic D (1350 cm^{-1}) and G (1590 cm^{-1}) bands [24]. The Raman signal due to carbon contamination is well detected at sufficient laser power, especially at the NW ends and at the NW intersection points (figure 4(b)). The appearance of the Raman signal from carbon may be caused by photocatalytic activity of silver NWs and plasmon-related thermal heating of NWs [25, 26].

Therefore, it is important to control the intensity of laser light during LSPR enhancement measurements of the Raman or PL signal to avoid carbon contamination, which can distort the results and cause misinterpretation of obtained data.

4. Conclusions

The phenomenon of PL enhancement due to LSPR in silver NWs has been studied on samples of CdS NCs and

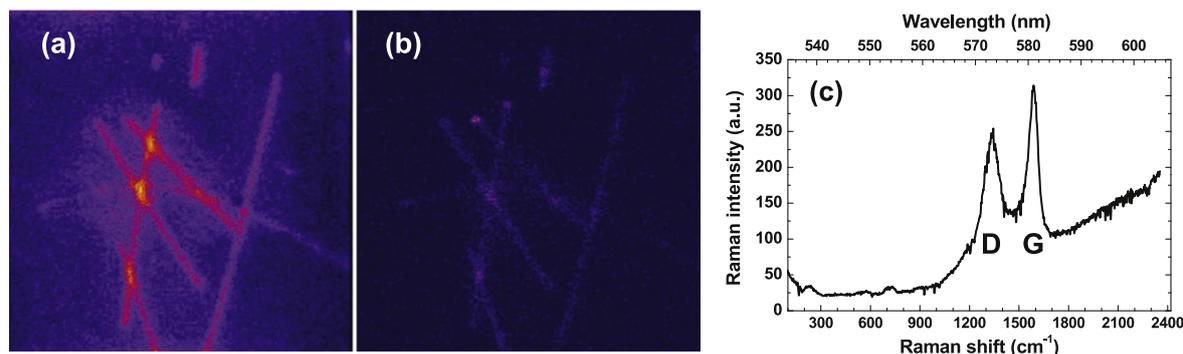


Figure 4. (a) Spectral image of photoluminescence from ruthenium-based dye (N719), taken at 790 nm. (b) Spectral image of the Raman signal from carbon, taken at 570–580 nm. Size of both images is $39 \times 38 \mu\text{m}$. (c) Raman spectrum of carbon contamination recorded on silver nanowire.

ruthenium-based dye (N719). PL enhancement for N719 dyes was much more significant in comparison to CdS NCs. The largest enhancement was detected (i) in the case when an NW is placed above the silver film or (ii) at the intersection point of two NWs, where the hot spots are created. The carbon contamination effect [23] at the surface of silver NWs occurs at high laser light intensities and may result in some artifacts; therefore, one should be aware of it during measurements of PL enhanced by LSPR. Silver NW on silver film is proved to be an effective system for LSPR-related PL enhancement.

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