Research article

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Plasmon-controlled, ultra-bright, excitation-polarization-independent photoluminescence from individual Ag nanoplates

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Abstract: Fluorescent metallic nanoparticles with high quantum yield are highly desirable for optical imaging in the fields of biology and materials science. We investigate the photoluminescence (PL) properties of Ag nanoplates, particularly triangular ones, systematically at the single-particle level under different excitation conditions. We find that their emission is controlled by surface plasmon resonances (SPRs). Because of their high geometric symmetry, the shape and intensity of the PL spectrum from Ag triangular nanoplates are independent of the excitation polarization. Under excitation wavelengths of 473, 532 and 633 nm, the PL quantum yield (QY) of Ag triangular nanoplates is found to be twice that of Au nanorods at similar SPR wavelengths. It can be attributed to the stronger and broader SPR response, which can make the PL more intense not only in the spatial domain but also over a larger range in the frequency domain. Our investigations will extend the application of Ag nanoplates in imaging, labeling, and emitting, especially at the single-molecule level, due to their ultra-bright, stable, and polarization-independent PL. This method to enhance the PL signal, in both the spatial and frequency domains, can be easily expanded to other systems.

Keywords: Ag nanoplates; surface plasmon resonance; photoluminescence; quantum yield.

1 Introduction

Owing to their unique properties induced by the excitation of localized surface plasmon resonances (SPRs) [1, 2], noble metal nanoparticles (NPs) have attracted much attention in the fields of sensing [3], photovoltaics [4], catalysis [5], and surface-enhanced Raman spectroscopy (SERS) [6], to name but a few. Besides their outstanding absorption and scattering properties, their photoluminescence (PL) is another important characteristic [7]. For example, Au NPs including nanorods [8], nanobipyramids [9] and nanostars [10] possessing strong, non-blinking, and non-bleaching PL are good candidates as fluorophores for biological labeling and light-emitting sources in nanoscale optoelectronic applications. Compared to Au with high intrinsic loss in the visible and near-infrared spectral ranges, Ag has a relatively low imaginary dielectric constant, which means a lower loss [11, 12].

For the PL properties of Ag NPs, most of the research has been concentrated on Ag nanoclusters (NCs; few-atom quantum dots) [13] but also on Ag nanowires to a lesser extent [14–16]. The PL from Ag NCs arises from the discrete electronic transitions due to quantum confinement effects or other mechanisms [17–20]. The PL from Ag NCs is comparable to or even better than that from semiconductor quantum dots and thus can be applied for in vivo imaging in biology due to their low toxicity [21]. Without stabilization, however, Ag NCs would interact with each other and aggregate irreversibly to reduce their surface energy [22]. Further, the PL from individual NPs suffers from fluorescence intermittency [23]. Therefore, Ag NCs need a scaffold to support, encapsulate, and stabilize during applications [24]. For the larger Ag NPs, beyond the quantum size effect, the emission has been proposed to arise from the sub-nanodomains within NPs, which actually originate from NCs as well [25]. The detailed PL mechanism in Ag NPs still remains an open question.

Ag nanoplates possess an extremely high anisotropy because their lateral dimensions are much larger than their heights and have attracted broad interests in

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SPR-related applications [26]. Among them, triangular Ag nanoplates are particularly interesting since they can generate more hot spots and thus huge electric field enhancement around the tips and edges due to their special symmetric characteristics [27]. Furthermore, their unique optical properties can be tuned easily by controlling the aspect ratio. Their far-field scattering can be favored by the sharp edges. Therefore, they have been extensively applied in SERS [28], PL enhancement [29], catalysis [30], biosensing [31], and so forth. However, to the best of our knowledge, there is very little research on their PL properties, let alone the individual ones.

In this article, we study the PL properties of individual Ag nanoplates, especially those with triangular shape, under different excitation conditions. We correlate the scattering and PL spectrum of single nanoplates and find that the PL is plasmon-controlled. The PL spectrum from single Ag nanoplates under different excitation polarizations remains constant and shows similar line shape and line width. By combining in situ atomic force microscopy (AFM) and scattering measurements on the same optical microscope, the quantum yield (QY) of single Ag triangular nanoplates (TNPs) is found to be twice that of Au nanorods (Au NRs), which are the most well studied PL emitters in metallic NPs [9, 32]. Based on the calculated field intensity over the volume surrounding individual Ag TNPs and Au NRs within the whole SPR spectrum range, the high QY of Ag TNPs can be attributed to their stronger and wider SPR response compared to Au NRs. The ultra-bright, stable, and excitation-polarization-independent PL from Ag nanoplates means that they are promising candidates for applications in labeling, imaging, and emitting at the single-nanoparticle level, at which their special properties will greatly relax the constraints for wavelength and excitation-polarization alignments. Our investigations will also be helpful to understand the PL and PL enhancement mechanisms of Ag NPs and other noble metal NPs more comprehensively.

2 Experimental section

The Ag nanoplates were synthesized according to the methods described in the literature [33]. Briefly, two steps were involved: one for Ag seed nanospheres, and the other for nanoplates. First, AgNO_3 (10 mM, 1.5 ml), sodium citrate (30 mM, 5 ml), and polyvinylpyrrolidone (PVP) (0.1 g) were added into 145 ml water (18 M Ω) with vigorous stirring for 10 min. This was followed by the addition of a freshly prepared NaBH_4 solution (20 mM, 0.75 ml). After the reaction

had proceeded for another 30 min, the color of the solution changed to stable deep yellow. The size of the prepared Ag nanospheres was about 5 nm. Next, Ag nanospheres in the solution were irradiated for 40 h by a 70 W halogen lamp to obtain Ag nanoplates. Finally, the synthesized Ag nanoplates were centrifuged to remove excess reagents and redispersed in water for further use. Au NRs were prepared by a wet chemical synthesis method [34].

In order to study the PL from individual Ag nanoplates and Au NRs, an extremely dilute colloidal solution was dispersed by ultrasound for 1 h and dropped onto a glass coverslip, which was then covered by another one. The coverage of the nanoparticles on the coverslip was less than one in $\sim 30 \mu\text{m}^2$ area to avoid the influence from the others. Then, these two coverslips were separated carefully. Finally, a transmission electron microscope (TEM) coordinate copper grid with marked numbers was stuck on one of the coverslips to help find the same NP by both an optical microscope and a scanning electron microscope (SEM). The combination of optical and SEM measurements allowed us to deduce the exact relationship between the shape and optical properties of the NPs. On the other hand, we correlated PL/scattering measurements with an atomic force microscope, which can measure the height of the NPs accurately in situ, to investigate their PL QYs.

We started the characterization from optical measurements since coating a conductive film on the sample for SEM imaging would influence its optical properties. The details for our experiment setup are schematically shown in Figure S1 [35]. In brief, a laser beam of wavelength 473, 532, or 633 nm was focused onto the sample from the glass side using a $100\times$ oil immersion objective (NA 0.6–1.3, tunable). The diameters of the focused spot were 0.8, 1, and 1.1 μm , respectively. Note that the excitation wavelengths 473 and 633 nm were utilized only for PL QY measurements. With a series of long-pass filters to block the scattered excitation light in the detection path, the PL was collected by the same objective with NA=1.3. The dark-field (DF) scattering spectrum was acquired by using a condenser (NA=0.8) and an objective (NA=0.6). An intensified charge-coupled device (CCD) (Zyla Andor) camera was used to record the scattering images. The PL and DF scattering spectra of single NPs were measured using a Shamrock spectrometer (Andor, DU-897E) equipped with a high-sensitivity EMCCD (DU970N-BV, Andor). All optical characterizations were carried out under ambient conditions. The extinction spectra of the NPs in solutions were recorded by an Ocean Optics USB2000+ spectrometer.

The scattering spectra and near-field intensity distributions of the NPs were numerically calculated using the

finite-difference time-domain (FDTD) method (Lumerical Solutions, Inc., Vancouver, Canada). The details of the simulation model and parameters can be found in Supporting Information.

3 Results and discussion

Figure 1A shows a typical TEM image showing the morphology of the synthesized Ag NPs. Almost all the NPs are nanoplates, as they are semi-transparent under electron illumination. From the high-resolution TEM images of three typical Ag nanoplates (Figure S2), their monocrystalline characteristics and detailed lattice structures can be distinguished readily. They are bounded by the most stable crystal facets [36], and no Ag islands are observed. Figure 1B shows the normalized extinction spectrum of the corresponding Ag NPs in solution, which exhibits two distinct peaks. The peak around 490 nm can be attributed

to the dipole modes of the isotropic nanospheres as well as the in-plane quadrupole modes of the nanoplates [26]. The peak at the longer wavelength (690 nm) is dominant and corresponds to the in-plane dipole modes [26]. Figure 1A, B shows that the size distribution of Ag NPs is quite broad, which emphasizes the significance of conducting measurements on individual NPs. The height of the nanoplates is measured to be 16 nm by AFM (Figure S3), which is similar to that reported in the literature [33]. We utilize this height in all the following simulations since it is quite stable by the fabrication method used here.

Based on the TEM results shown in Figure 1A, we use two models, namely tip-truncated triangular and circular NPs, to carry out our simulations. The triangular shape is defined by the radius r of the truncating circle and the distance L between the centers of the truncating circles, as shown in Figure 1C. Note that the hexagonal nanoplate is approximated as a severely truncated triangular one (i.e. with large r) for simplicity. Figure 1D plots the DF scattering spectra from two typical shapes (with similar

Figure 1: Characterization of Ag nanoplates.

(A) A typical TEM image of the synthesized Ag nanoplates. Triangular, hexagonal, and circular shapes can be observed. (B) The black solid line represents the extinction spectrum of Ag nanoparticles in water (refractive index = 1.33) while the red one shows the simulation result from a triangular nanoplate (TNP) with $L = 62$ nm and $r = 16$ nm. (C) The schematic of the two models (triangular and circular) applied in the simulations. (D) Dark-field scattering spectra for one circular Ag NP and two Ag TNPs. The middle TNP is severely truncated. All scale bars in the inset SEM images are 100 nm in this paper. As can be seen, the resonant peak is blue-shifted from 692 to 652 or 606 nm, respectively, when the shape varies from a triangle ($L = 85$ nm, $r = 9$ nm) to a severely truncated triangle ($L = 55$ nm, $r = 23$ nm) or a circle ($R = 47$ nm).

sizes). The experimental results (scattered lines) and the simulation results (solid lines) match very well. As can be observed, when the shape varies from the tip-truncated triangular nanoplate to circular, the resonant peak is blue-shifted from 690 to 587 nm, indicating that the effective size is smaller for nanoplates with a smaller radius r at a similar resonant wavelength [33].

Figure 2A shows the PL and corresponding DF scattering spectra from two typical individual Ag TNPs. Obviously, the spectral shape of the PL follows closely that of scattering and can be perfectly fitted by Lorentz functions (red solid lines), suggesting that the PL is from single Ag TNP [37]. It can be confirmed by combining with the in situ AFM measurement. Since the scattering of the Ag TNP is controlled by its SPR, the consistency between the PL and DF scattering spectra reveals that the PL from the Ag TNP is also controlled by SPR. Furthermore, when the power density of excitation is less than 10^5 W/cm^2 , the PL from individual Ag TNPs does not

exhibit any blinking behavior as is often observed in a single Ag NC [23].

When water ($n=1.33$) or oil ($n=1.518$) was dropped on top of the Ag nanoplates to modify the embedding medium, an obvious red shift of the PL peak could be observed, as shown in Figure 2B, C. After covering the NP, especially by oil, it is very difficult to observe its morphology by SEM. We thus utilize both triangular and circular models to perform simulations. Figure S4A, B shows that the red shift of the scattering spectrum is almost the same for the two types of Ag nanoplates when the embedding medium is changed from air to oil or water. However, the bandwidth for the circular nanoplate is obviously broader than that for the triangular ones. We summarize the full width at half-maximum (FWHM) of the scattering spectra in Table S1. Considering that the width obtained from the simulation is smaller than that from the experiment [38], the measured nanoplate in water is most likely triangular, while in oil it is triangular or severely truncated triangular.

Figure 2: DF scattering and PL spectra of Ag TNPs.

(A) Two typical DF scattering spectra (green scattered lines) and corresponding PL spectra (blue dashed lines) of two individual Ag TNPs with different sizes. The PL can be perfectly fitted by Lorentz functions (red solid lines). (B, C) The PL spectrum of an individual Ag nanoplate that was immobilized on a glass coverslip surrounded by air (black line) and water/oil (red line).

The consistency between experiments and simulations confirms that the PL from Ag nanoplates is controlled by SPR.

Figure 3 demonstrates the influence of the excitation polarization on the PL and DF scattering spectrum. The PL and DF scattering spectra for a monitored Ag TNP show agreement in Figure 3A. The excitation power was kept low enough to avoid photothermally induced reshaping of the monitored Ag TNP, which was confirmed by the same DF scattering spectrum after the PL measurements. Figure 3B, C displays a series of PL/scattering spectra and Figure 3D, E summarizes the polar plot for the PL/scattering intensity integrated in the SPR spectrum range as a function of the excitation polarization. Obviously, the PL/scattering remains almost constant under different polarizations in terms of both spectral shape and intensity. The isotropic polarization feature is totally different from that of the Au nanorod, whose PL/scattering is the strongest/weakest when the excitation polarization is along its longitudinal/transverse axis, as shown in Figure S5 and emphasized earlier [39].

According to Fermi's golden rule, the spontaneous emission lifetime for a radiating dipole is dependent on

its surrounding density of states (DOS) [40, 41]. Controlling the field intensity can modulate DOS and the radiative recombination rate between excited electrons and holes, whereby the emission QY can be altered. It has been noticed that when the geometric symmetry of the NP is higher than 3-fold, the scattering spectrum is not dependent on the excitation polarization [36]. Under different polarization excitations, we calculated the near-field intensity distributions and integrated them over the volume (with a thickness of 20 nm from the surface, refer to Figure S6A) around a Ag TNP. They displayed polarization-independent characteristic. The results at the resonant wavelength are plotted in Figure 3D and indicate that the experiment and simulation results are consistent.

We emphasize here on the selection of the dielectric constant of Ag and Au. Normally, they are taken from either Palik or Johnson and Christy [42]. We tried both of them in our simulations and found that the values from Palik gave much better agreement with the experimental data (especially the FWHM) for our chemically synthesized Ag nanoplates at least over the wavelength range 630–720 nm. But the simulation results for Au NRs are

Figure 3: PL and scattering intensity under different excitation polarizations.

(A) PL and dark-field scattering spectra for a single Ag TNP, with the SEM image shown in the inset. (B)/(C) PL/scattering spectra under different excitation polarizations. (D)/(E) Polar plot of the measured PL/scattering intensity integrated under the whole spectrum (550–850 nm) versus the excitation polarization direction varied from 0° to 180° in steps of 10°. (F) Corresponding field intensity $|E|^2$ integrated over the volume surrounding the TNP (with a thickness of 20 nm as shown in 6A).

quite consistent for both of them. We thus use the dielectric constants from Palik in all our calculations.

In order to further reveal the origin of the PL from Ag nanoplates, we investigated the relationship between the integrated PL intensity from a single NP and the excitation power. As shown in Figure 4A, when the excitation power is low (<1.6 mW), the relationship is linear, suggesting that the PL from the monitored Ag TNP is due to one-photon excitation. The similar scattering spectra before and after the PL measurements illustrate that the shape of the Ag TNP remained constant in this power range, as shown in Figure 4B.

As Au NR is the most widely studied metallic PL label applied in biology and chemistry [43], we selected it as a reference to evaluate the PL QY of Ag TNPs. The Au NRs used in the measurements are shown in Figure S7. The PL QY of both types of NPs can be obtained from the measured PL spectrum and the estimated effective volume [10]. Specifically, it can be calculated according to the following equation:

$$\Phi = \frac{N_{\text{em}}}{N_{\text{abs}}} = \frac{N_{\text{signal}} / \text{Det.Eff.}}{\sigma_{\text{abs}} I / h\nu}$$

where N_{em} and N_{abs} are, respectively, the number of the emitted and absorbed photons excited by linearly polarized light (along their long axes for Au NRs). N_{signal} is the background-corrected signal intensity, and I is the incident laser intensity. The detection efficiency (Det.Eff.) is estimated to be 0.5% in our measurement. The absorption cross-section σ_{abs} is related to the size of the nanoparticles, which is acquired by the method described in Supporting Information. The PL QYs of a series Ag TNPs and Au NRs with different sizes and resonant wavelengths are

displayed in Figure 5A–C. It is important to note that the effective sizes of the NPs are normalized, i.e. we can consider the effective size of a Ag TNP and a Au NR at a similar resonant wavelength to be close to each other. The excitation power was tuned to be as low as 0.3 mW to ensure that these NPs were not melted by the excitation laser.

Although there is some scatter in the data, three trends are apparent upon close inspection. First, the PL QY of Ag TNPs is almost twice that of the Au NRs at similar resonance wavelength under 473, 532, and 633 nm excitation. As mentioned above, PL QY is dependent on the DOS and field intensity. Based on the measured geometric parameters and resonant wavelengths, we calculated the field enhancement ($|E|/|E_0|^2$) at the peak of the resonance wavelengths for both types of NPs and found that it was higher for Ag TNPs, as shown in Figure 5D. This can be ascribed to the sharper edges of Ag TNPs [9, 44] and means that the signal is enhanced in the spatial domain. However, the difference is not as significant as that of the PL QY measured in the experiments. For example, at 630 nm, the field enhancement for a Au NR is 1.6 while that for a Ag TNP is only 2.4. This inconsistency is not related to the thickness around the NPs since the values for 20 and 30 nm are quite consistent, as illustrated in Figure S8D, E. We picked three typical Ag TNPs and Au NRs (marked by dark dashed circles and “1”, “2”, and “3” in Figure 5B) at similar resonant wavelengths to calculate the field enhancement; the results are shown in Figure S8A–C. As can be seen, the SPR response for Ag TNPs is broader than that of Au NRs for three groups of data, both at the long resonant wavelength and the short one, indicating that the signal can be enhanced in the frequency domain. The FWHM of the SPR response shown in Figure 5E confirms this trend. Figure 5F combines the data

Figure 4: The property of one-photon PL from a single Ag TNP.

(A) Relationship between the PL intensity integrated under the whole spectrum from a single Ag TNP (as shown in the inset SEM image) and the excitation power (532 nm, CW laser). When the excitation power is below 1.6 mW, the relationship is linear, revealing that the PL from the Ag TNP is due to one-photon excitation. (B) The scattering spectra for the tracked Ag TNP before and after the PL measurement.

Figure 5: PL QY and simulated field enhancement of Ag TNPs and Au NRs.

(A–C) PL QY of a series of Ag TNPs and Au NRs at different resonant wavelengths under excitations at 473, 532, and 633 nm, respectively. The PL spectra of Au NRs were taken with the excitation polarization direction aligned with its longitudinal mode. Corresponding to the NPs in (B), the simulated field enhancement integrated in the volume surrounding the NPs with a thickness of 20 nm from the surface at the peak of the resonant wavelengths, the FWHM of the SPR response are shown in (D) and (E), respectively. Note that the simulation results are normalized to the maximum for comparison. (F) The field enhancement integrated in the same volume as in (D) but under the whole SPR response (550–850 nm) as a function of the resonant wavelength.

shown in Figure 5D, E by integrating the field intensity surrounding the volume of the NP over the wavelength range available in the experiments. In this case, the field enhancement for Ag NPs is nearly twice that of the Au NRs, which is consistent with the experimental results. Therefore, the higher PL QY of Ag nanoplates should be caused by both the stronger field intensity and the broader SPR response compared to those of Au NRs.

It is worth noting that the excitation light here is linearly polarized. Under this condition, only two hot spots in the Ag TNPs can be excited for its dipole mode characteristic (refer to Figure S6B). If the polarization is changed to circular, although the strongest field intensity at the tips of the Ag nanoplate is reduced, the total intensity can be maintained because three hot spots, corresponding to its 3-fold symmetry property as shown in Figure S6C, can be excited. For the Au NR, the total field intensity is reduced. This point can be observed in Figure S8F, in which the peak intensity of the Ag TNP is more than double that of the Au NR. In the experiments, with the same excitation power, we did observe that the PL intensity remained

similar for the Ag nanoplates when the polarization was changed from linear to circular while that of the Au NRs became much weaker. Unfortunately, we did not obtain enough data with good signal-to-noise ratio, as the PL of our Au NRs was too weak under circular polarization excitation.

The second trend we can observe from Figure 5A–C is that the PL QY increases with the red shift of the resonant wavelength for both types of NPs. For Au NRs, it may be correlated with the decreased damping of the plasmon by the creation of interband excitations [45]. As the SPR moves away from the interband transitions with the red shift, fewer channels are available for dissipation, which raises the efficiency of radiative emission and PL QY. However, this deduction is not applicable for Ag TNPs, as even the shortest wavelength 473 nm (2.62 eV) cannot excite their interband transitions (3.9 eV). We have not found any reasonable explanation yet and are still working on this at the moment.

Third, the PL QY from both types of NPs increases with the excitation wavelength, although slightly but clearly.

This trend can be attributed to the fact that a smaller gap between the excitation and SPR radiative mode results in more efficient coupling, whereby the radiative rate and the absorption are enhanced [46].

Finally, we discuss the mechanism of PL from Ag TNPs. Our experimental results have shown that the spectral shape of PL follows closely that of scattering. As the interband transition of Ag cannot be excited efficiently in our experiments, PL should be the response of the carriers in the conduction band. There are normally two models to explain the interaction of photons and electrons in the conduction band. The first one suggests that the PL should actually be the plasmon-enhanced electronic Raman scattering, which is wavelength-independent [12]. However, the PL QY of Ag TNPs increases with the excitation wavelength, as mentioned above. Thus this model is not likely applicable. The second model proposes that intraband transition of the electrons within the conduction band may happen and the radiative recombination of electrons and holes generates PL. The PL signal may be enhanced by the incoming and outgoing electric field via coupling to the SPR (lightning-rod effect) [47]. Or the energy from the recombination of electron-hole pairs is transferred to a plasmon excitation, which then emits a photon. Through both these processes, the PL can be considered as plasmon-controlled.

4 Conclusion

Based on single-particle measurements, we have correlated the PL properties of individual Ag NPs with their scattering properties under different excitation conditions and in different media. The results reveal that they are controlled by SPR. With the change of the excitation polarization, the PL spectrum remains constant, which originates from the high degree (≥ 3 -fold) of the geometric symmetry of the NPs. By adjusting the irradiation power carefully, the relationship between the intensity and the excitation power confirms that the PL under CW excitation at 532 nm is due to a one-photon process. More importantly, under 473, 532, and 633 nm linearly polarized excitations, we found that the PL QY of Ag TNPs was about twice as high as that of Au NRs with same effective sizes at similar SPR wavelengths. The higher PL QY can be attributed to stronger field intensity enhancement as well as broader SPR response. It can be further boosted under circular polarization excitation. Higher PL QY means that the PL from Ag TNPs is brighter without increasing their effective sizes, indicating that they can be utilized as labels without

disturbing the system seriously. Furthermore, their PL is non-blinking and excitation-polarization-independent, meaning that their excitation is very easy to be accessed. Therefore, the Ag NPs, particularly the triangular ones, can find wide applications in imaging, labeling, and light emission at the single-nanoparticle level. On the other hand, the PL enhancement mechanism in our research offers a method to boost various signals, not only in the spatial domain but also in the frequency domain.

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