Plasmon-enhanced yellow light emission in hybrid nanostructures formed by fluorescent molecules and polymer

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Abstract
Two types of hybrid nanostructures were fabricated for surface plasmon-enhanced yellow light emission. One is Ag triangular nanoplates (TNPs) and Rhodamine B (RhB) co-doped poly(methyl methacrylate) (PMMA) structure and the other one is Ag TNPs attached on the surface of RhB-doped PMMA structure. The light emission dependence was investigated as a function of concentration and size of the Ag TNPs. Compared to that of without Ag TNPs, a 13.8-fold enhancement on yellow light emission was obtained by attaching 0.015-nM Ag TNPs on the RhB-doped PMMA layer, while a maximum of 24-fold emission enhancement was obtained by doping 0.015-nM Ag TNPs into the RhB-doped PMMA layer. The hybrid nanostructures would be potentially used as a component of light-emitting devices or solar energy conversion units.

1. Introduction
Polymer nanostructures doped with fluorescent materials can emit light and have led an increased interest in composite hybrid nanostructures with light harvesting capabilities. However, how to improve light emission efficiency of fluorescent molecules in polymer is a critical issue for the applications of light-emitting or conversion of solar radiation. Fortunately, the spontaneous emission of fluorescent molecules could be promoted by surface plasmon effect of noble metal nanoparticles [1,2]. So far, the enhanced light emission of fluorescent molecules by surface plasmon has been used for biological imaging and organic light-emitting devices [3-5]. Early works in the metal-enhanced light emission of fluorescent molecules focused on symmetrical noble metal nanoparticle [6,7]. Anisotropic noble metal nanoparticles, such as nanorods and triangular nanoparticles (TNPs), are more appealing for their novel structure dependent optical features due to the decreased symmetry [8,9]. Among anisotropic noble metal nanoparticles, Ag TNPs are particularly attractive candidates as scattering centers for enhancing spontaneous emission. Furthermore, their surface plasmon peak can be tuned across the entire visible region and even near-IR by controlling the size of Ag TNPs [10,11]. Thus, a hybrid structure consisted of Ag TNPs and fluorescent molecules doped polymer would efficiently serve as the inexpensive alternatives to multicolor light-emitting application covering the entire visible spectrum or conversion device of solar radiation. In this paper, two types of hybrid nanostructures were fabricated for enhanced yellow light emission through Ag TNPs and polymer co-doped with Rhodamine B (RhB) molecules. The RhB molecules were doped into poly(methyl...
methacrylate) (PMMA) thin layer. The Ag TNPs were doped into the RhB-doped PMMA or attached on the surface of it. The hybrid nanostructures were irradiated by a 510 nm light and emitted yellow light at the wavelength range of 580–600 nm. The yellow light emission dependence of RhB molecules in PMMA were systematically studied as functions of Ag TNPs concentration and size.

2. Experiment

2.1. Synthesis of Ag TNPs

The Ag TNPs were synthesized through a thermal synthesis method reported by Métraux and Mirkin [12] with minor modification. In synthesis, 25 mL aqueous solution of AgNO₃ (0.1 mM), 40 μL hydrogen peroxide (30 wt%), 1 mL aqueous solution of poly(vinylpyrolidone) (weight-average molecular weight MW=30,000 g/mol, 3.5 mM), and 1 mL aqueous solution of trisodium citrate (30 mM) were mixed and stirred at room temperature. At the same time, 100 μL sodium borohydride (100 mM) was injected dropwise into this mixture and stirred. By observing the color of the solution, we have got to know that the color of the solution gradually changed to blue. This indicates the formation of Ag TNPs.

2.2. Fabrication of two hybrid structures

Fig. 1a schematically shows the fabrication process of the Ag TNPs and RhB co-doped PMMA. First, the Ag TNPs was added into RhB (C₂₈H₃₁ClN₂O₃, 2.1 mg) doped acetone solution of PMMA (3% PMMA). Second, a clean quartz slide was immersed into the solution. After several seconds, the quartz was taken out. With acetone volatilizing, a layer of Ag TNPs and RhB co-doped PMMA was formed on the surface of the quartz slide. The measured thickness of the layer is 700 nm. Fig. 1b shows the fabrication process of attaching Ag TNPs on the surface of the RhB-doped PMMA. First, a clean quartz slide was immersed into the RhB-doped PMMA solution (3% PMMA). After 10 s, the quartz was taken out from the solution. With acetone volatilizing, a layer of RhB-doped PMMA was obtained on the surface of the quartz slide. Second, the quartz slide with RhB-doped PMMA was immersed in an aqueous solution of Ag TNPs. After 30 s, the quartz slide was taken out and finally, Ag TNPs attached RhB-doped PMMA layer was formed.

3. Results and discussion

The morphology of the Ag TNPs was characterized by transmission electron microscopy (TEM) and as shown in Fig. 2a–c. It shows that the yield of triangular shape is over 95%. The Ag TNPs shown in Fig. 2a have an average edge length of 31 nm. Its maximum absorption wavelength is 553 nm (see Fig. 2d). For simplicity, the sample is denoted as Ag553. The average edge length of the Ag TNPs shown in Fig. 2b is 45 nm. Its corresponding maximum absorption wavelength is 626 nm (denoted as Ag626). From the inset of Fig. 2b, it can be seen that the thickness of Ag TNP is 7 nm. It reveals that the typical aspect ratio of the Ag TNPs exceeds 7. The average edge length of the Ag TNPs shown in Fig. 2c is 55 nm. Its maximum absorption wavelength is 680 nm (denoted as Ag680). It can be seen that the Ag TNPs have round corners and flat surfaces. Fig. 2d shows the normalized optical absorption spectra of the Ag TNPs in the wavelength range of 350–1100 nm. To compare with the absorption spectra of the Ag TNPs, normalized excitation and emission spectra of RhB molecules are also shown in Fig. 2d. To distinguish excitation enhancement and emission enhancement from the RhB molecules, the excitation wavelength of the RhB is chosen to be 510 nm. The optical absorption spectra of the Ag TNPs have two distinct peaks.

![Image](image_url)

Figure 1  Schematic diagrams of fabrication process. (a) Ag TNPs and RhB co-doped PMMA layer. (b) Ag TNPs attached on the surface of RhB-doped PMMA layer.

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One strong and broad surface plasmon resonance peak appears at the wavelength of 553, 626, and 680 nm for Ag553, Ag626, and Ag680, respectively, which can be ascribed to the in-plane dipole plasmon resonance mode. The other weak peak appears at 400, 450, and 465 nm for Ag553, Ag626, and Ag680, respectively, which can be ascribed to the in-plane quadrupole plasmon resonance mode. It can be seen that the surface plasmon absorption peak of Ag553 overlaps with the excitation and emission peaks of the RhB molecules. The surface plasmon absorption peak of the Ag626 and the Ag680 is a little far away from the excitation and emission peaks of the RhB. This implies the surface plasmon resonance of the Ag553 is the optimal option to match the fluorescence emission of the RhB molecules.

The photoluminescence (PL) measurement was performed for studying the influence of the Ag TNPs on the fluorescence properties of the RhB molecules in PMMA. Compared to the PL intensity of without Ag (black line in Fig. 3a), the PL intensity of the RhB molecules in PMMA with Ag553 increases with increasing Ag553 concentration from 0.006 to 0.015 nM. The PL enhancements are 8.9, 14.9, and 24 for the Ag553 concentrations of 0.006, 0.009, and 0.015 nM, respectively, at the wavelength of 580 nm. It can be seen that the maximum enhancement was obtained for the sample doped with 0.015 nM Ag553. The inset images of Fig. 3a indicate that the yellow light spot of the sample with 0.015 nM Ag553 is brighter than that of without Ag TNPs. Fig. 3b and c shows the concentration influence of Ag626 and Ag680 on the fluorescence properties of the RhB molecules in PMMA. The increased PL intensity is observed with increasing the Ag626 concentration from 0.006 to 0.015 nM (Fig. 3b). Compared to the PL intensity without the Ag626, the PL enhancements are 6.9, 8.0, and 9.5 for the Ag626 concentrations of 0.006, 0.009, and 0.015 nM, respectively, at the wavelength of 580 nm. It can be seen that the PL intensity increases with increasing the Ag680 concentration from 0.006 to 0.015 nM (Fig. 3c). Compared to the PL intensity without the Ag680, the PL enhancements are 4.2, 5.5, and 7.7 for the Ag680 concentrations of 0.006, 0.009, and 0.015 nM, respectively. By comparing the PL enhancements, the maximum PL enhancement was obtained for the sample doped with 0.015 nM Ag553. It implies that the degree of PL enhancement of the RhB molecules is correlated with the spectral overlap between the surface plasmon absorption of Ag TNPs and the emission of the RhB molecules. The fluorescence enhancement of the RhB molecules is mainly attributed to an enhanced incident light absorption of the RhB molecules. This is due to the enhanced excitation rate of the RhB and an emission enhancement, which involves the reduction of fluorescence lifetime and the increased quantum yield of the RhB molecules. When the RhB molecules are adjacent to the Ag TNPs surface, the enhanced local field provided by the surface plasmon can increase a light absorption of the RhB molecules. Furthermore, the Ag TNPs can alter the radiative and the nonradiative decay rates of the nearby RhB molecules, accompanying with the reduction of fluorescence lifetime and the increase of quantum yield.
To study the influence of the Ag concentration on the PL excitation of RhB molecules in PMMA, the PL excitation of without and with Ag553 was investigated at around the RhB molecules’ emission wavelength of 580 nm (Fig. 3d). It can be seen that the excitation of the RhB in PMMA gradually increases with increasing the Ag553 concentration. Compared to the excitation intensity without the Ag553 (black line), there are 6.2, 14, and 15.6 fold enhancements on the PL excitation intensity at the wavelength of 510 nm for Ag553 concentration of 0.006, 0.009, and 0.015 nM, respectively. This confirms that enhanced excitation of the RhB molecules is due to the enhanced local optical field. In order to precisely study the influence of the Ag TNPs on the PL lifetime of the RhB molecules, the PL decay spectra of the RhB molecules in PMMA were measured without and with the Ag553 (excitation with a pulsed laser of 405 nm, 5 MHz, 122 mW; Fig. 3e). The lifetime is obtained by fitting the decay curve to a stretched exponential function convoluted with the instrument response function. A lifetime of 3.42 ns was obtained for the RhB molecules without the Ag TNPs. The lifetimes of the RhB molecules decreased to 3.16, 2.98, and 2.95 ns with the presence of Ag553 at the concentrations of 0.006, 0.009, and 0.015 nM, respectively. Compared to the lifetime of the RhB molecules without the Ag TNPs, the lifetime gradually decreases with increasing the concentration of Ag553. This implies that the intensity of local optical field gradually increases with increasing the concentration of Ag553. Therefore, the decrease of PL lifetime confirms the near-field interaction between the surface plasmon enhanced local optical field by the Ag TNPs and the radiative decay of

Figure 3 PL spectra of Ag TNPs and RhB co-doped PMMA. (a) PL spectra of Ag553 and RhB co-doped PMMA with different Ag553 concentration. The insets are optical images of the emitted yellow light spots from the samples indicated by respective arrows (scale bars: 5 mm). (b) PL spectra of Ag626 and RhB co-doped PMMA with different Ag626 concentration. (c) PL spectra of Ag680 and RhB co-doped PMMA with different Ag680 concentration. (d) PL excitation spectra from Ag553 and RhB co-doped PMMA with different Ag553 concentration. (e) PL decays of Ag553 and RhB co-doped PMMA with different Ag553 concentration. (f) PL decays of Ag TNPs (i.e., Ag553, Ag626, and Ag680) and RhB co-doped PMMA with the Ag TNPs concentration of 0.015 nM.
the RhB molecules. In addition, to study the PL lifetime of the RhB influenced by the Ag TNPs, the PL decay curves of the RhB molecules in PMMA without and with the Ag TNPs (i.e., Ag553, Ag626, and Ag680) at the concentration of 0.015 nM were performed (Fig. 3f). The lifetimes of the RhB molecules are 2.93, 3.09, and 3.18 ns for the presences of Ag553, Ag626, and Ag680, respectively. Compared to the lifetime of the RhB without Ag TNPs, it can be seen that the lifetime with Ag553 is the shortest. This indicates that the radiative decay rate of the RhB molecules is strongly influenced by the surface plasmon of Ag553. In other words, the lifetime is related with the spectral overlap between the surface plasmon absorption of the Ag TNPs and the PL emission of the RhB molecules.

We further investigated the enhanced emission of the RhB by calculating the radiative decay rate and the quantum yield of the RhB without and with Ag553. The radiative decay rate of the RhB molecules ($\gamma_r$) is 0.198 ns$^{-1}$ without the Ag553. With the presence of Ag553, a radiative decay rate enhancement factor ($\Gamma$) is used to characterize the enhancement of radiative decay rate of the RhB. The calculated $\Gamma$ are 1.38, 1.42, and 1.52 for the presences of 0.006, 0.009, and 0.015 nM Ag553, respectively. The increased radiative decay rates, which were calculated according the formula $\gamma_r=\Gamma \cdot \gamma_r^{0}$, are 0.273, 0.281, and 0.30 ns$^{-1}$ for the presence of 0.006, 0.009, and 0.015 nM Ag553, respectively. It indicates that the radiative decay rate increases with increasing the Ag553 concentration. According to the formula $q = \gamma_r / (\gamma_r + k_{nr})$, where $\gamma_r$, $\gamma_n$, and $k_{nr}$ are the radiative decay rate, total decay rate, and nonradiative decay rate, respectively [1,13], we calculated that the quantum yield ($q$) of the RhB without Ag553 is 68%. With 0.006, 0.009, and 0.015 nM Ag553, the calculated $q$ are 86%, 86.5%, and 88%, respectively. By comparing the quantum yield of RhB without the Ag553, 26.5%, 27.2%, and 29.4% increments in $q$ were obtained for 0.006, 0.009, and 0.015 nM Ag553, respectively. The results of the radiative decay rate and the quantum yield confirm that the emission of the RhB molecules in PMMA is promoted by the presence of Ag553.

The fluorescence emission of the RhB molecules was also investigated by attaching Ag TNPs (i.e., Ag553, Ag626, and Ag680) on the surface of the RhB-doped PMMA layer and shown in Fig. 4a and b. It can be seen that the PL intensity increases with increasing the Ag553 concentration from 0.006 to 0.015 nM (Fig. 4a). Compared to the PL intensity without the Ag553, the PL enhancements are 1.5, 2.2, and 13.8 with the Ag553 at the concentrations of 0.006, 0.009, and 0.015 nM, respectively. It shows a lower fluorescence enhancement (13.8-fold) of the Ag553-attached structure.

Figure 4 PL spectra of attaching Ag TNPs on the surface of the RhB-doped PMMA. (a) PL spectra of attaching Ag553 on the surface of the RhB-doped PMMA with different Ag553 concentration. The insets are optical images of the emitted yellow light spots from the samples indicated by respective arrows (scale bars: 5 mm). (b) PL spectra of attaching the Ag TNPs (i.e., Ag553, Ag626, and Ag680) on the surface of the RhB-doped PMMA with the Ag TNPs concentration of 0.015 nM. (c) PL excitation spectra of attaching the Ag TNPs (i.e., Ag553, Ag626, and Ag680) on the surface of the RhB-doped PMMA. (d) PL decay spectra of attaching the Ag TNPs (i.e., Ag553, Ag626, and Ag680) on the surface of the RhB-doped PMMA.

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at the concentration of 0.015 nM compared to the 24-fold enhancement of the Ag553 doped one. For the Ag TNPs attached structure, the enhanced fluorescence emission is correlated with surface plasmon generated at the surface of Ag TNPs. The surface plasmon decays exponentially with distance from the Ag TNPs surface. When the Ag TNPs are attached on the surface of PMMA, a surface plasmon penetration depth (Z) in the PMMA layer can be expressed as: $Z = (\lambda^2 / 4 \pi n)^{1/2} / (e_2 - e_1)^{1/2}$, where $e_1$ and $e_2$ are the real parts dielectric constant of the Ag TNPs and PMMA, respectively, $\lambda$ is the wavelength of the excitation light [14]. For the Ag TNPs attached structure, the calculated surface plasmon penetration depth is $Z = 400$ nm at the wavelength of 510 nm. This indicates that the surface plasmon of the Ag TNPs can only influences the emission of the RhB molecules in the range of a surface plasmon penetration depth.

To compare with the fluorescence properties of the RhB and Ag TNPs co-doped PMMA, the PL measurement of the RhB molecules in PMMA attached with Ag553, Ag626, and Ag680 at the same concentration of 0.015 nM were performed as shown in Fig. 4b. It can be seen that the PL intensity of the RhB molecules in PMMA attached with Ag553 is maximum. This implies that the degree of PL enhancement of the RhB molecules is closely correlated with the spectral overlap between the surface plasmon absorption of the Ag TNPs and the emission of the RhB molecules for the Ag attached structure. As the surface plasmon absorption peak of Ag TNPs overlaps with the emission peak of the RhB, the interaction between the surface plasmon of the Ag TNPs and the emission of the RhB become strong. To investigate the influence of the Ag TNPs size on the excitation of the RhB molecules in PMMA with attached the Ag TNPs on the surface of the RhB-doped PMMA, the PL excitation of the RhB-doped PMMA without and with attaching Ag TNPs (i.e., Ag553, Ag626, and Ag680) was performed, as shown in Fig. 4c. It can be seen that the PL excitation of the RhB in PMMA is enhanced by the attached Ag553, Ag626, and Ag680 TNPs. The maximal excitation of the RhB in PMMA is obtained from the Ag553-attached one. The PL decays of the RhB in PMMA attached with Ag TNPs were measured, as shown in Fig. 4d. From the PL decay curves, it can be seen that, compared to the lifetime without Ag TNPs, the lifetime of the RhB decrease due to the presence of Ag553, Ag626, and Ag680. Decreases of 0.61, 0.53, and 0.51 ns in lifetime are obtained for the Ag553, Ag626, and Ag680, respectively, at the concentration of 0.015 nM. The PL lifetime reduction reveals that the lifetime of the RhB attached with Ag553 is shorter. This is because the spectral overlap between the surface plasmon absorption of the Ag TNPs and the PL emission of the RhB molecules is maximal. Therefore, the radiative decay rate of the RhB molecules is strongly influenced by the surface plasmon of Ag553.

By comparing the PL spectra of the two structures (i.e., Ag TNPs and RhB co-doped PMMA structure and Ag TNPs attached on the surface of RhB-doped PMMA structure), it can be seen that the yellow light emission was highly increased in the Ag TNPs doped structure than that of the Ag TNPs attached structure. The reason is the surface plasmon for the Ag TNPs attached structure only influences the RhB molecules in a surface plasmon penetration depth adjacent to the interface of the Ag TNPs and PMMA layer, while the surface plasmon for the Ag TNPs doped structure influences the whole RhB molecules in PMMA around the Ag TNPs.

4. Conclusions

Ag TNPs and RhB co-doped PMMA structure and Ag TNPs attached on the surface of RhB-doped PMMA structure were fabricated for surface plasmon-enhanced yellow light emission. Experiments show that an enhanced yellow emission in these polymer nanostructures can be achieved. For example, at the same concentration of Ag TNPs (0.015 nM), the Ag TNPs doped structure is more efficient in improving the emission. A 13.8-fold yellow light emission enhancement was obtained from the nanostructure of attaching 0.015-nM Ag TNPs on the RhB-doped PMMA layer. A maximum of 24-fold yellow light emission enhancement was obtained from the nanostructure of doping 0.015-nM Ag TNPs into the RhB-doped PMMA layer. We believe that the hybrid nanostructures are potentially useful as a component of light-emitting devices or solar energy conversion units.

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References


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