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NRET from naphthalene labels in multilayer shell wall on melamine formaldehyde microparticles fabricated with layer-by-layer self-assembly to pyrene-labeled polyelectrolyte in solution

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Abstract

Core-shell colloidal particles were prepared with the core of monodisperse melamine formaldehyde particles (MF) with a diameter of 3.5 μm. The shell deposited on the core by the layer-by-layer (LbL) self-assembly was made with a copolymer ANp3 of 2-acrylamido-2-methylpropanesulfonate sodium (AMPS) and 3 mol% naphthalene label monomer and poly(diallyldimethylammonium chloride) (PD). Nonradiative energy transfer (NRET) from the naphthalene labels deposited on the MF particles to pyrene labels at a polyelectrolyte APy3, a copolymer of AMPS and 3 mol% pyrene label monomer, or to an ionic pyrene probe 1-pyrenemethylamine hydrochloride (PyMeA · HCl) in water was observed. The NRET efficiency was expressed as the emission intensity ratio I/I_0 of naphthalene with and without existence of pyrene in the surrounding solution. With increasing pyrene concentration, I/I_0 decreased down to about 0.2 and the mechanism for this NRET from the inner naphthalene label to the pyrene labels in solution is still ambiguous.

Keywords: Polyelectrolyte multilayers; Core-shell colloidal particles; NRET; Layer-by-layer

1. Introduction

The layer-by-layer (LbL) self-assembly technique, which involves the alternate adsorption of oppositely charged polyelectrolytes, is widely used for the formation of polyelectrolyte multilayer films since 1991 [1]. Recently the LbL technique has been applied to fabricate polyelectrolyte multilayers on colloidal particles to build core-shell colloidal particles and hollow capsules by removing the sacrificial template cores [2–4]. This promising technology allows the precisely tailoring over the composition, thickness, structure, and property of the multilayer in nanoscale [5–7]. The functional core-shell particles are being developed for applications ranging from electronics to biomedicine [8–12]. A lot of optional substances can be used in the LbL self-assembly, including inorganic nanoparticles, dyes, DNA, and proteins, thus increase the potential application of the LbL strategy [13–15].

In the nature, sunlight is the harvest of chloroplasts in plants, and is converted into chemical energy through the photosynthetic process [16]. Analogy to chloroplasts

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in the nature has inspired the conception of artificial light-harvesting antenna systems for the usages in solar energy conversion, optoelectronics, photonics, sensor, and other fields of nanotechnology [17,18]. At present, most of the artificial light-harvesting antenna systems are imitated with light-harvesting films or optical active bacteria. For wide applications, much interest is paid to fabricate light-harvesting antenna systems with different structures. Enlightened from the natural cells, it seems to be more efficient that the light is absorbed at the outermost surface of the capsules and transferred to the interior for photosynthesis. Spherical devices with high photosensitive surface area relative to their volume and redox-active cores have advantages for their final application in the light-harvesting antenna system. Recently, Dai et al. first reported a kind of light-harvesting capsules constructed with the LbL self-assembly of polyelectrolytes and dyes and found the energy transfer through the nanoscale wall to the interior of capsules [19,20]. Li et al. have shown the existence of photoinduced vectorial electron transfer from the interior to the surface of capsules fabricated by the LbL of pyrene-labeled polyelectrolyte and proposed a probable electron transfer within the film [21].

In this work, we have prepared a new kind of light-harvesting core-shell colloidal particles using the LbL self-assembly of a naphthalene-labeled polyelectrolyte, and then detected the energy transfer to a pyrene-labeled polyelectrolyte or ionic pyrene probe for the future work in light-harvesting capsules.

2. Experimental

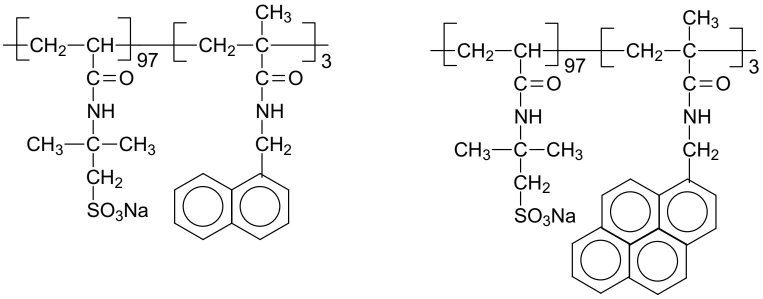
2.1. Materials and fluorophore-labeled polyelectrolytes

Cationic fluorescence probe 1-pyrenemethylamine hydrochloride (PyMeA · HCl, Aldrich), anionic monomer 2-acrylamido-2-methylpropanesulfonic acid (AMPS, Fluka), and cationic polymer poly(diallyldimethylammonium chloride) (PD, Aldrich, M_w 2–3.5 × 10^5) were used as received. Fluorophore label monomers *N*-(1-naphthylmethyl)methacrylamide (NpMAm) and *N*-(1-pyrenylmethyl)methacrylamide (PyMAm) were synthesized in our laboratory following the procedure of Refs. [22] and [23] respectively, and confirmed with ^{1}H NMR spectra [24]. Suspension of monodisperse weakly cross-linked melamine formaldehyde (MF) microparticles with a diameter of 3.5 μm was prepared in our laboratory following Ref. [25]. Highly pure water was obtained by deionization and filtration with a Millipore purification apparatus.

Poly(2-acrylamido-2-methylpropanesulfonic acid) labeled with 3 mol% either naphthalene or pyrene, referred to as ANp3 (with naphthalene residues) or APy3 (with pyrene residues), respectively, were polymerized in dimethylformamide (DMF) solution initiated by 2,2′-azobis(isobutyronitrile) (AIBN) [26]. The total monomer concentration was 0.5 mol/L while AIBN is 0.0025 mol/L. The solution was degassed three times with nitrogen bubbling and sealed in a polymerization bottle, which was maintained at 70 °C for 24 h. The mixture was poured into a large excess of ether to precipitate the copolymer. The copolymer was purified by precipitation from methanol into ether for three times. Finally, the copolymer was dissolved in dilute aqueous NaOH solution of pH 11 and dialyzed against pure water for several days, and then freeze-dried. The purified copolymer was characterized by elemental analysis. Anal. Calcd for ANp3: C: 38.00, H: 5.28, N: 6.12; found: C: 34.58, H: 7.80, N: 6.49. For APy3: C: 38.53, H: 5.26, N: 6.06; found: C: 34.73, H: 8.04, N: 6.72. Fig. 1 is the schematic representation of the fluorophore-labeled polyelectrolytes.

2.2. Fabrication of core-shell colloidal particles

Polyanion ANp3 and polycation PD were assembled alternately on the MF colloidal particles with the layer-by-layer self-assembly in water. The first layer was deposited with addition of 2 mL ANp3 aqueous solution of 2 mg/mL containing 0.5 M NaCl into 2 mL of the



ANp3 **APy3**

Fig. 1. Schematic representation of fluorophore-labeled polyelectrolytes ANp3 and APy3.

MF suspension. The mixture was incubated for 15 min under gently shaking. Excess ANp3 was removed by three repeat cycles of centrifugation (5000 rpm, 5 min)/washing/redispersion. The following PD layer was deposited with 2 mL PD solution of 2 mg/mL containing 0.5 M NaCl using the same procedure. Subsequent alternate ANp3 and PD layers were deposited in the identical way until the desired number of polyelectrolyte layers was achieved. MF-(ANp3/PD)$_4$ANp3 and MF-(ANp3/PD)$_5$ represent the core-shell colloidal particles with 9 and 10 polyelectrolyte layers, respectively, with different surface charges.

2.3. Characterization methods

A scanning electron microscopy (SEM) of Philips XL30 was used to observe the MF particles and core-shell particles. Elementary analysis was conducted using a vario EL (Elementar, German). A bright-line hemacytometer (cell counting chamber) was used to count the amount of particles solution with a microscope.

Fluorescence spectrum was recorded on a Hitachi F-4500 spectrofluorometer. For the energy transfer from naphthalene at the shell of the particles to the pyrene in solution, the solution of pyrene-labeled copolymer APy3 or ionic pyrene probe PyMeA · HCl with different concentrations was added into the suspension containing naphthalene-labeled particles. The naphthalene-labeled particles about 1.2×10^7 were dispersed in 2 mL pure water, added into a 4 cm quartz cell, and agitated for several minutes. Aliquots of the APy3 or PyMeA · HCl solution of high concentration was subsequently added into the cell with a micro-syringe and diluted to desired concentration. The total volume of added APy3 or PyMeA · HCl solution was <100 μL. The excitation wavelength was 290 nm in all of the measurement for energy transfer. Both slits were 2.5 nm and the measurement was at room temperature.

3. Results and discussion

3.1. Fluorescence spectra of fluorophore-labeled polyelectrolytes

Fig. 2 shows the fluorescence excitation and emission spectra of ANp3, APy3, and PyMeA · HCl in dilute aqueous solution. The maximal excitation (c) and emission (f) bands of ANp3 are at 280 nm and 325 nm, respectively. The excitation and emission spectra of APy3 (a and d) are quite similar to the corresponding ones of PyMeA · HCl (b and e) considering all of the character bands. There is no excimer emission for the APy3 and PyMeA · HCl at the test concentrations, which appears as a structureless broad band centered around 480 nm. Due to the overlap of the ANp3 emission with the excitation of APy3 and PyMeA · HCl at 310–350 nm, we can adopt the efficient nonradiative energy transfer (NRET) from naphthalene (donor) to pyrene (acceptor) with selective excitation of naphthalene at wavelength of 290 nm to investigate the energy transfer.

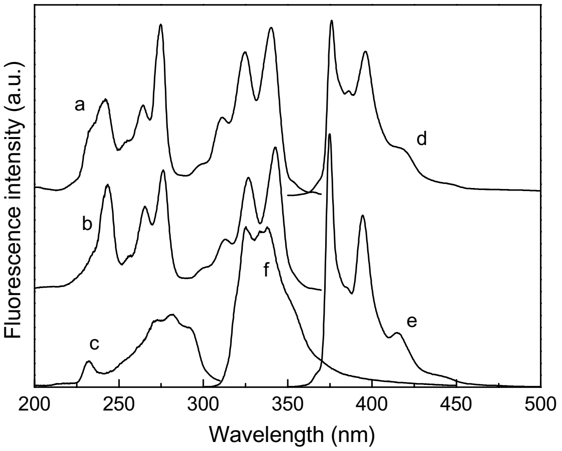


Fig. 2. Fluorescence excitation and emission spectra: (a, b): excitation spectra of APy3 and PyMeA · HCl emitting at 375 nm; (c): excitation spectrum of ANp3 emitting at 336 nm; (d, e): emission spectra of APy3 and PyMeA · HCl excited at 343 nm; (f): emission spectrum of ANp3 excited at 290 nm.

3.2. Naphthalene-labeled core-shell colloidal particles

We have prepared naphthalene-labeled core-shell colloid particles with the LbL self-assembly of polycation PD and naphthalene-labeled polyanion ANp3 on the surface of MF colloid particles and monitored this depositing process with the fluorescence of ANp3 excited at 290 nm. Fig. 3 depicts the fluorescence emission

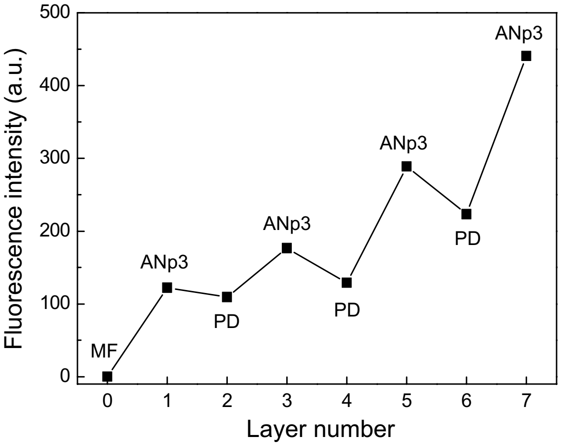


Fig. 3. Fluorescence intensity of ANp3 and PD coated MF particles as a function of deposited layer number.

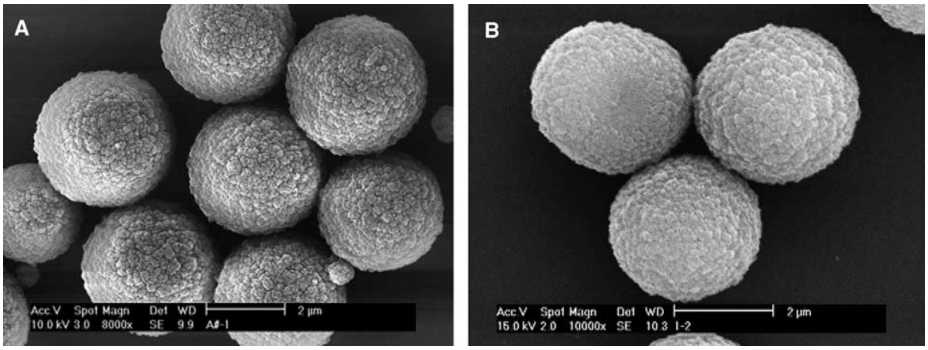


Fig. 4. SEM photographs of bare MF colloidal particles (A) and polyelectrolyte coated MF colloidal particles (B).

intensity of the core-shell colloid particles as a function of polyelectrolyte layer number of PD and ANp3. The fluorescence intensity increases when the outermost layer is ANp3 and decreases a little when the outermost layer is PD. This intensity decrease is caused by the PD coverage, which reduces the exciting efficiency to the ANp3 layer just under it. By any means, the fluorescence emission intensity is increased with the total layer number of ANp3, this confirms that the polyelectrolytes have been successfully deposited on the MF particles alternately and that the naphthalene-labeled polymer ANp3 at the inner layers can be excited.

SEM visualization of the MF colloid particles and the core-shell colloid particles with 10 layers of deposited polyelectrolytes is shown in Fig. 4A and B, respectively. The MF particles in Fig. 4A have a similar diameter of ~3.5 µm with a rough surface, which is benefit to the adsorption and anchoring of deposited polyelectrolytes. The photo of coated MF-$(ANp3/PD)_5$ particles in Fig. 4B shows that the surface becomes somewhat smooth compared with that of the bare MF particles due to the coverage of deposited polyelectrolyte layers.

3.3. NRET from naphthalene-labeled layer on colloid particles to pyrene in solution

Fig. 5 is the emission spectra excited at 290 nm for the naphthalene-labeled ANp3 covered on the MF-$(ANp3/PD)_5$ particles dispersed in water containing APy3 of different concentrations. The emission band centered at 330 nm is attributed to the direct excitation of naphthalene labels (enlarged in the inset) and the emission bands ranging 360–420 nm are the contribution of pyrene monomers excited by the NRET from naphthalene. The broad peak around 480 nm is due to the pyrene excimer formed in the solution for the concentration of pyrene unit is above 1×10^{-4} mol/L, high enough to produce excimer. This observation clearly indicates that the naphthalene emission is gradually quenched while the pyrene emission is enhanced with increasing APy3 concentration in the bulk suspension, which reveals the occurrence of the NRET from naphthalene-labeled layers on the MF particles to the pyrene label in the surrounding solution. However, we cannot use the intensity ratio I_{Py}/I_{Np} of pyrene to naphthalene to evaluate the NRET efficiency in this work as used in normal cases. Because the pyrene label concentration is varied independently with the naphthalene label concentration and a part of increase in the pyrene emission intensity is induced by its amount increase in the solution. Therefore, we have to use the intensity ratio I/I_0 of naphthalene emission with pyrene in the bulk solution I to that without pyrene I_0 to express the NRET efficiency in this work.

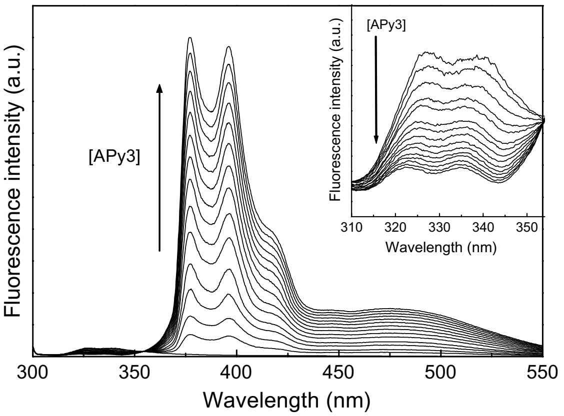


Fig. 5. Fluorescence emission spectra of MF-$(ANp3/PD)_5$ colloidal particles in water containing APy3 of concentration from 0 to 0.325 g/L. The insert shows the fluorescence emission spectra of naphthalene from 300 nm to 350 nm.

Fig. 6 shows that this I/I_0 ratio decreases with increasing APy3 concentration in the bulk suspension as expected according to the NRET principle. The outermost surface is either negatively charged as MF-$(ANp3/PD)_4ANp3$ or positively charged as MF-

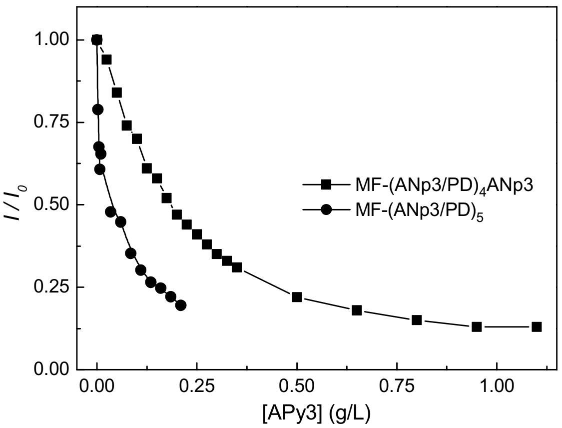


Fig. 6. Emission intensity ratio I/I_0 as a function of APy3 concentration, where I and I_0 are the emission intensity of naphthalene with and without pyrene in the solution.

(ANp3/PD)$_5$. The NRET efficiency depends on the polarity of the surface charge due to the negative charge of APy3, which enhances the NRET from the MF-(ANp3/PD)$_5$ particles and depresses the NRET from the MF-(ANp3/PD)$_4$ANp3 particles owing to the electrostatic interaction. For examples, in the case of MF-(ANp3/PD)$_4$ANp3 the APy3 concentration required for reducing I/I_0 to 0.2 is about 0.5 g/L (corresponding to 7.2×10^{-5} mol pyrene unit/L), while in the case of the MF-(ANp3/PD)$_5$ only 0.2 g/L of APy3 (corresponding to 2.9×10^{-5} mol pyrene unit/L) is enough to achieve the same I/I_0 level.

According to the results in Figs. 5 and 6, we understand that the NRET from the inner naphthalene labels to the pyrene labels in solution does occur. Because the APy3 is a polymer (M_w 45,000 by GPC) its penetration into the deposited polyelectrolyte layers on the MF particles should be difficult. The averaged layer thickness of polyelectrolyte deposited multilayer is in the order of magnitude of 2 nm [27], it is improbable for the energy of excited naphthalene labels at the inner layers on the MF particles transfers directly to the pyrene labels dispersed in the bulk solution because the Förster distance for the NRET from naphthalene to pyrene is ~2.9 nm [24]. Therefore, the NRET from naphthalene to pyrene probably occurs at the surface of the polyelectrolyte deposited particles in the APy3 solution. The problem is the mechanism for this energy transfer from the excited inner ANp3 layers to the outermost layer and pyrene labels in the bulk solution.

Owing to the lack of experimental evidence, we follow the mechanism of electron hopping within the film due to relative long lifetime of the fluorophore anions in the polar multilayer wall and short range interactions of the fluorophores within 3 nm proposed by Li and Möhwald for the photoinduced vectorial charge transfer across the multilayer films [28]. This process is schematically illustrated in Fig. 7 as the electron transfer within the film and finally to the pyrene labels at the surface of polyelectrolyte coated particles. There remain many unsolved questions for this mechanism, such as large hopping distance, short lifetime of excited naphthalene.

Fig. 8 shows the relative fluorescence intensity I/I_0 of naphthalene after the addition of different concentrations of small molecular pyrene probe (PyMeA · HCl) to the solution containing either negatively charged MF-(ANp3/PD)$_4$ANp3 or positively charged MF-(ANp3/PD)$_5$. I/I_0 is also decreased gradually with increasing concentration of (PyMeA · HCl), similar to that observed from Fig. 6. For reaching the end-point of steep quench at the I/I_0 vs. [PyMeA · HCl] curve, the necessary concentration of PyMeA · HCl is about 0.02 and 0.0275 mg/L for MF-(ANp3/PD)$_4$ANp3 and MF-(ANp3/PD)$_5$, respectively (corresponding to

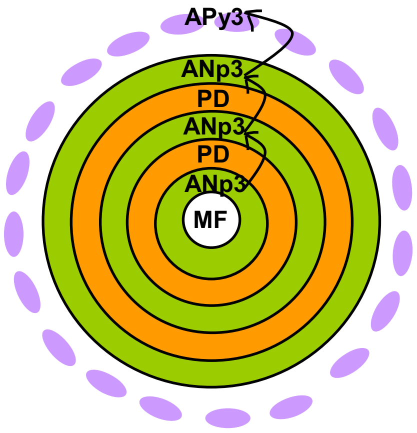


Fig. 7. Schematic representation for energy transfer between fluorophores in the multilayer shell wall with naphthalene labels on MF particles to the pyrene on their surface.

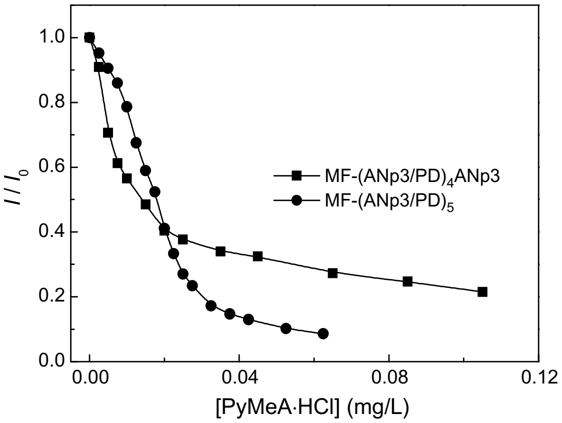


Fig. 8. I/I_0 as a function of PyMeA · HCl concentration.

7.6×10^{-5} and 1×10^{-4} mmol pyrene unit/L, respectively). In the case of quenching with APy3, the concentration at which I/I_0 is reduced to 0.2 is 0.2 and 0.5 g/L for the core-shell particles MF-(ANp3/PD)$_5$ and MF-(ANp3/PD)$_4$ANp3, respectively, corresponding to 5.7 and 14.4 mg/L of pyrene. In contrast, the PyMeA · HCl concentrations, at which I/I_0 becomes 0.2, response to 0.02 and 0.015 mg/L of pyrene, respectively, much lower than those for APy3. This high quenching efficiency of PyMeA · HCl is due to its interpenetration into the inner naphthalene-labeled layers in the shell wall. When the outmost layer is negative, the PyMeA · HCl with positive charged is easy to contact, so that the I/I_0 for the MF-(ANp3/PD)$_4$ANp3 decreases faster at lower PyMeA · HCl concentration than that for the MF-(ANp3/PD)$_5$. When the concentration of PyMeA · HCl is high, enough pyrene probes penetrate the inner layers, the effect of surface polarity on the NRET will be weakened. Neither the pyrene probe (Fig. 8) nor the pyrene-labeled polyelectrolyte APy3 (Fig. 6) can completely quench the naphthalene emission from the shell wall. Li and Möhwald reported that when the pyrene labels in the multilayer wall were reduced below ~2 mol% the fluorescence intensity decayed only to about half the initial intensity. The naphthalene label density of 3 mol% in the present work is similar to their value of 3.2 mol%, where the pyrene label emission can decay to zero with increasing the polyviologen concentration of the bulk suspension. Therefore, the mechanism for this NRET is still an open question.

4. Conclusion

In this work we have prepared naphthalene-labeled core-shell colloidal particles MF-(ANp3/PD)$_4$ANp3 and MF-(ANp3/PD)$_5$ by the LbL self-assembly. The NRET from the naphthalene-labeled particles to the pyrene-labeled polyelectrolyte APy3 or pyrene probe PyMeA · HCl has been observed to increase with the pyrene concentration and the NRET efficiency to PyMeA · HCl is higher than to APy3 for small molecules can penetrate into the multilayer shell wall. However, the mechanism for this NRET is still ambiguous though the electron hopping within the wall has been proposed.

Acknowledgments

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