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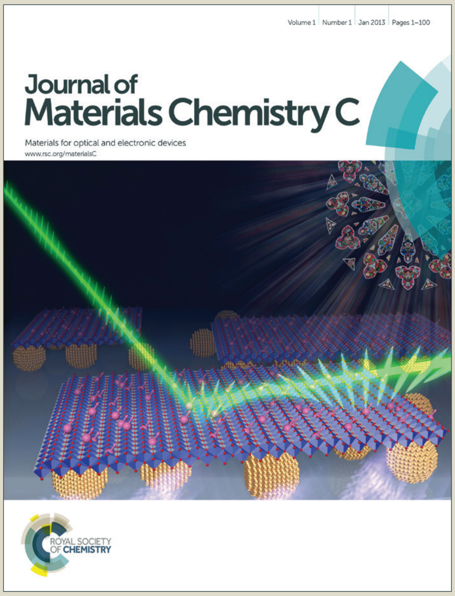
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Facile synthesis of luminescent silver nanoparticles and fluorescent interactions with blue-emitting polyarylene ether nitrile

Kun Jia,*[a,c] Pan Wang, [a,c] Liting Yuan, [a] Xuefei Zhou, [a] Wenjin Chen [b] and Xiaobo Liu*[a]

In this work, the fluorescent silver nanoparticles were synthesized in organic phase *via* a facile one-step reaction. Their fluorescent emission is dependent on the excitation wavelength and can be effectively enhanced by a blue emitting intrinsic fluorescent polymer named polyarylene ether nitrile (PEN) *via* resonant energy transfer process, which is confirmed by the time-correlated photoluminescent decay measurement and stead-state fluorescent spectroscopy. Specifically, luminescent Ag nanoparticles were synthesized by reducing silver nitrate ($AgNO_3$) with polyvinylpyrrolidone (PVP) in *N, N*-dimethylformamide (DMF) solvent under nitrogen atmosphere. It was found that obvious surface plasmon resonance combined with weak fluorescence under UV irradiation was observed from as-synthesized Ag nanoparticles stock solution. The larger sized silver nanoparticles (Ag NPs, 20 ± 4 nm) was responsible for the plasmonic extinction peak at 415 nm, while the weak fluorescence emission around 550 nm was attributed to the presence of ultra-small silver nanostructures. Furthermore, the dramatically enhanced fluorescence was observed from smaller Ag nanoparticles (6 ± 2 nm) in supernatant by removing the excess large sized Ag nanoparticles *via* high speed centrifugation. More interestingly, the purified smaller Ag nanoparticles showed excitation wavelength dependent fluorescent emission profile, and their fluorescence under appropriate excitation can be further enhanced *via* the resonant energy transfer process from energy donor of a blue emitting aromatic polymer that has good spectra overlap with luminescent silver nanoparticles.

Introduction

Noble metal (gold, silver) nanostructures have attracted increasing research interests during recent years and been intensively used in nanomedicine areas,[1-5] mainly due to their rich optical properties, such as localized surface plasmon resonance (LSPR),[6, 7] molecular-like luminescence in the ultra-small size range (less than 2 nm),[8] plasmon modulated or enhanced fluorescence,[9] surface enhanced Raman scattering spectroscopy,[10] and metal enhanced infrared spectroscopy,[11] etc. Among these interesting topics, the plasmonic controlled fluorescence is of particular importance since the fluorescent spectroscopy is widely used in a large amount of scenarios ranging from biomedical research to optoelectronic devices. It has been reported that the fluorescent emission can be enhanced, quenched or spectrally shaped by controlling the near field interaction of fluorophore and metal nanostructures.[12] Generally, the fluorescence emission would be rapidly quenched when the dye molecules directly contact with plasmonic nanostructures due to the non-radiative energy transfer process. However, in the so-called plasmon enhanced fluorescence (PEF), the fluorescent emission of dye molecules can be obviously enhanced when the distance between plasmonic nanostructures and fluorophore is controlled in around 5-10 nm range and the plasmon extinction wavelength is tuned between excitation and emission wavelength of dye molecules.[13] The basic principle for the plasmon enhanced fluorescence (PEF) is attributed to the near field enhancement feature of plasmonic nanostructures, which can be explored to modulate the excitation, relaxation, absorption and re-radiation process of fluorophore near plasmonic nanostructures through fluorescent resonance energy transfer (FRET) process or

Purcell effect.[14] In the majority of reported PEF or fluorescent quenching studies, the fluorescent emission spectra of dye molecules normally remain unchanged. Interestingly, some recently published work demonstrated that the fluorescent emission spectra of dye molecules can be obviously shaped in the presence of plasmonic nanostructures, the reasons for these plasmon induced colouring of fluorescence were assumed as plasmon-enhanced transition rate between different vibrational energy levels of fluorophores,[15, 16] wavelength dependence of metal enhanced fluorescence,[17, 18] modified excited-state decay rate of fluorophore near metal nanostructures,[19] etc.

Besides playing an important role in modulating the dye fluorescence, noble metal nanostructures can become luminescent *per se* when their size is sharply decreased to subnanometer range and are stabilized with appropriate ligands, which are named as the metal nanoclusters (NCs). As a new type of fluorescent nanomaterials, the gold or silver NCs have exhibited a number of attractive features like brightness, photostability, subnanometer sizes and good biocompatibility.[20] Due to their ultra-small sizes, the metal NCs have discrete energy levels as that of molecular, thus metal NCs can still interact with incident light *via* electronic transitions between discrete energy levels, leading to strong light absorption and emission. Normally, the size of nanoparticles should be less than 2 nm to be luminescent according to the theoretic calculation; however some recent works reported the fluorescence can be detected from much larger silver nanoparticles as well.[21-23] On the other hand, the surface ligands are particularly important for the optical properties of metal NCs, since the metal nanoclusters would rapidly aggregate to lager sized non-fluorescent nanoparticles in the absence of any stabilized ligand. In addition, the fluorescent emission wavelength and quantum yields of metal NCs are strongly dependent on the surface ligands used in the synthesis. For instance, a great amount of different materials, such as DNA oligomers, proteins, peptides, dendrimers and polymers, have been employed as the surface ligands for synthesis of gold or silver nanoclusters with different emission wavelength and quantum yield.[24-28] The ligands effect on the gold NCs fluorescence have already been clarified as charge transfer between ligand and gold core or the direct electron donation from electron-rich group of ligand to gold.[29] However, the understanding of ligands' role on the silver NCs fluorescence is rather limited.

Polymers are considered as the promising scaffold for the silver NCs synthesis mainly due to their easy chemical modification and long term stability of prepared silver nanoclusters. For instance, various acrylates-derived polymers (poly(methacrylic acid), polyglycerol-block-poly(acrylic acid), poly(acrylic acid-*co*-maleic acid)) have been used in the synthesis of fluorescent silver NCs with excellent solution stability over years.[21, 22, 30] Polyvinylpyrrolidone (PVP) is widely used as a good dispersant in the synthesis of plasmonic silver nanoparticles both in aqueous solution and organic solvent.[31, 32] In these studies, the dissolved silver salts were reduced either by a chemical reductant or UV light irradiation to silver atoms, which were subsequently protected by PVP from agglomerating and growing. The good stabilization ability of PVP is resulted from the strong chemical coordination of N/O atoms in PVP to silver ions.[33] Thus, it is expected that the PVP can be employed as a useful ligand to prepare fluorescent silver nanoparticles under appropriate conditions. However, the employment of PVP in the synthesis of fluorescent silver nanoparticles is not reported yet to our best knowledge.

In this work, silver nitrate salts were reduced in the common organic solvent *N, N*-dimethylformamide (DMF) in the presence of PVP, the DMF and PVP were used as the weak reductant and surface ligands for fluorescent silver nanoparticles, respectively. By controlling the experimental conditions (like reaction time or relative concentration ratio of $AgNO_3$: PVP), we were able to obtain the fluorescent silver nanoparticles showing excitation wavelength dependent fluorescent emission. Moreover, the blue intrinsic fluorescent polymer (PEN), previously developed in our lab,[34] is also solubilized in the DMF solvent and shows good spectral overlap with obtained silver nanoparticles, thus the fluorescence of silver nanoparticles can be further enhanced *via* resonant energy transfer process from PEN to Ag NPs.

Experimental

Preparations of fluorescent silver nanoparticles and PEN

The typical synthesis of fluorescent silver nanoparticles is as follows: 2g PVP (K30, molecular weight of 40000) was firstly added into 50 mL DMF in a three necked flask equipped with a mechanical stirrer, condenser and dry nitrogen inlet/outlet. Next, the PVP solution in DMF was refluxed by heating in an oil bath, followed by rapid injection of 250 μL silver nitrate aqueous solution (0.2M). After the reaction was maintained at reflux temperature (156 °C) for different time (10 min, 20 min, 30 min, 40 min, 50 min and 1 h), the solution was cooled rapidly and the smaller luminescent Ag nanoparticles and larger sized Ag nanoparticles can be readily obtained through an ultracentrifugation separation (15000 rpm, 1 h). The intrinsic blue-emitting fluorescent polymer (PEN) was synthesized according to the previously reported protocol and solubilized in DMF for further experiments.[34]

Characterization of fluorescent silver nanoparticles and PEN

The morphology of synthesised Ag nanoparticles was characterized with scanning electron microscope (SEM, JEOL, JSM-6490LV) and transmission electron microscope (TEM, JEOL, JEM-2100F operating at 200.0 kV). The size distribution of obtained silver nanoparticles was analysed by the public domain software of ImageJ developed by National Institutes of Health. The surface plasmon resonance spectra and fluorescent excitation/emission spectra of silver nanoparticles were recorded using a Persee TU 1901 UV-Vis spectrophotometer and a fluorescence spectrophotometer (F-4600, Hitachi), respectively. The time-correlated photoluminescent decay and fluorescent lifetime was determined by using Horiba Jobin Yvon Tempro-01 instrument. The photos of sample vials under UV light and white light illumination were captured using a Nikon D7000 DSLR camera. The molecular weight of synthesized fluorescent PEN was determined with the gel permeation chromatography (GPC, Tosoh, HLC-8320GPC) using polystyrene as standard.

Results and discussion

In the typical synthesis of silver nanoparticles, the silver ions are reduced by the strong chemical reductant (sodium borohydride, sodium hydroxide, etc) or subjected to mild UV photo-reduction in the presence of appropriate stabilizing agent. It is well-known that the luminescent silver nanoclusters will be obtained when the nanoparticle size is approached to the Fermi wavelength of an electron (ca. 0.5 nm for silver and gold), while the larger sized silver nanoparticles (> 2 nm) exhibit typical surface plasmon resonance and are non-fluorescent.[23] However, some recent works have reported the co-existence of surface plasmonic resonance and fluorescence from bigger silver nanoparticles[21, 35] and even as large as 18 nm.[23] Although the different mechanisms were proposed for the observed photoluminescence in these published works, the common argument is that the mild reductant and appropriated surface ligand should be used for the synthesis of fluorescent silver nanoparticles. The standard organic compound of *N, N*-dimethylformamide (DMF) is widely used as a polar solvent in chemistry and it has been reported that DMF can be an active reducing agent for silver ions under appropriated conditions, and the underline chemical reaction was proposed as follow:

$$HCONMe_2 + 2Ag^+ + H_2O \rightarrow 2Ag^0 + Me_2NCOOH + 2H^+$$

where the DMF was oxidized to a carbamic acid and the acid environment with increased conductivity was generated.[36]

In our experiments, the organic solvent of *N, N*-dimethylformamide (DMF) and water soluble polymer of polyvinylpyrrolidone (PVP) were employed as the mild reductant and silver coordination/stabilization agent for the synthesis of fluorescent silver nanoparticles. The UV-Vis spectra of silver nanoparticles synthesized using different experimental parameters were recorded, and it was found that the relative concentration ratio between $AgNO_3$ and PVP and reaction time played an important role in determining the optical properties of obtained silver nanoparticles. Generally, the higher relative concentration ratio of $AgNO_3$: PVP leads to a larger extinction wavelength and broader width of synthesized silver nanoparticles. Specifically, when the relative molar concentration ratio of $[AgNO_3]$: [PVP] increases from 1 to 100, the resonant wavelength was red-shifted from 420 nm to 433 nm and the full width at half maximum (FWHM) of surface resonant peak was increased from 78 nm to 115 nm (Fig. 1a), indicating the larger sized silver nanoparticles and inhomogeneous broadening effects were obtained at higher $AgNO_3$ concentration, which was also confirmed by the SEM imaging of obtained silver nanoparticles (Fig. 1c, d). Interestingly, there was weak fluorescence observed from the smaller silver nanoparticles solution under UV light illumination, while the solution containing large silver nanoparticles was basically non-luminescent (see Fig. 1b).

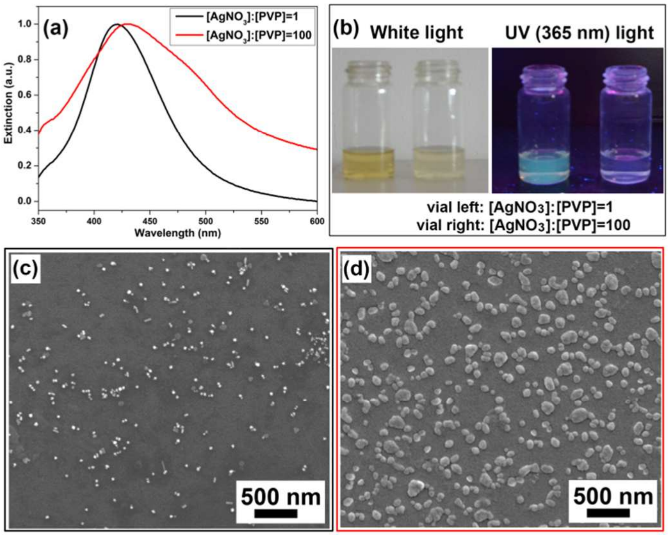

Fig. 1 The normalized UV-Vis spectra of synthesized Ag NPs using different $AgNO_3$/PVP concentration ratio ($[AgNO_3]$:[PVP]) in DMF solution (a), photos of vials containing Ag NPs under white light and UV light illumination (b), SEM images of obtained Ag NPs, the concentration ratio $[AgNO_3/PVP]$ in the synthesis was 1:1 (c) and 100:1 (d), respectively. The reaction time was 30 min under nitrogen protection.

The reaction time is another important factor to determine the optical properties of silver nanoparticles. As the reaction time increased from 10 min to 40 min, the extinction wavelength of obtained silver nanoparticles red shifted from 409 nm to 424 nm, indicating the size of silver nanoparticles was steadily increased. However the resonant wavelength blue-shifted back to 410 nm after 60 min reaction (Fig. 2), which revealed that the chemical etching of pre-formed larger-sized silver nanoparticles occurred after certain reaction time. Thus, it is expected that the ultra-small silver nanoparticles would be generated after longer reaction time using a small relative concentration ratio of $AgNO_3$: PVP. In addition, the nitrogen atmosphere used in the synthesis also contributes to the decreasing of Ag nanoparticles sizes, as the continuous growing of silver nanoparticles *via* O_2-mediated Ostwald ripening process in the $AgNO_3$/PVP system is highly inhibited.[37]

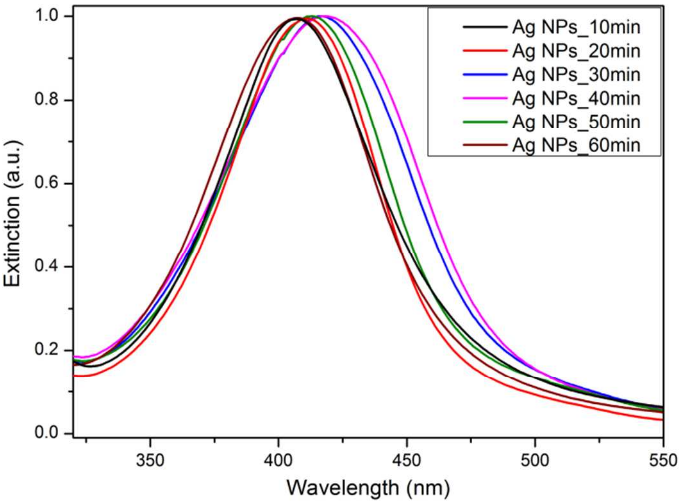

Fig. 2 The normalized UV-Vis spectra of synthesized Ag NPs in DMF solution using equal molar concentration of $AgNO_3$ and PVP under N_2 atmosphere for different reaction time.

Next, the optical properties of silver nanoparticles synthesized after 1 h reaction were systematically studied. The UV-Vis spectra were shown in Fig. 3a, for the as-synthesized silver nanoparticles stock solution, one strong sharp peak and a much weaker peak were recorded at 410 nm and 520 nm, respectively. The former one is attributed to the surface plasmon resonance of silver nanoparticles while the later one is ascribed to the ligand to metal charge transfer (LCMT).[35] When the stock solution was separated to supernatant and precipitate *via* high speed centrifugation, the re-dispersed precipitate solution exhibited one single peak at 410 nm, which was attributed to the extinction peak of larger sized silver nanoparticles with average size of 20 ± 4 nm as confirmed by TEM imaging (Fig. 3b), while the supernatant solution shared similar absorption spectrum like stock solution except that a wider, much weaker and slightly blue shifted peak at 407 nm was recorded, and the shoulder peak at 520 nm still existed. The broader width of absorption spectra from supernatant solution implied the presence of additional optical transition besides plasmons. According to the TEM image shown in Fig. 3c, the average silver nanoparticles size in the supernatant solution was determined to be 6 ± 2 nm. The silver nanoparticles in this size range was expected to be non-fluorescence, however when the stock solution were excited with 365 nm UV light, it was found that a wide fluorescent peak centred at 550 nm was detected and the obvious fluorescence was also visualized on the top layer of as-synthesized Ag nanoparticles stock solution. Furthermore, the fluorescent emission spectrum was split into two peaks with obviously enhanced intensity for the supernatant solution after the ultra-centrifugation, while the re-dispersed precipitate solution was indeed non-fluorescent (Fig. 3d). There was no fluorescence detected from the DMF solvent, PVP solution and silver ions-PVP mixture solution at room temperature in the studied wavelength range (data not shown), further confirming that observed photoluminescence was unambiguously attributed to the ultra-small silver nanostructures presented in supernatant solution.

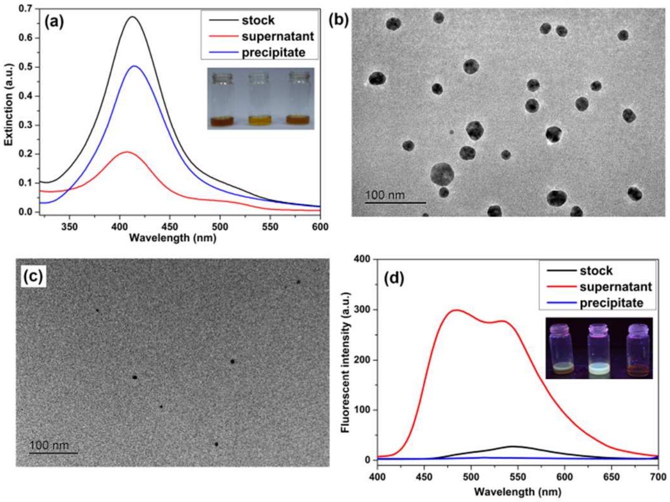

Fig. 3 The UV-Vis spectra (a) and fluorescent emission spectra (d) of as synthesized Ag NPs stock solution, the corresponding supernatant solution containing smaller Ag nanoparticles and re-dispersed precipitate solution with larger-sized Ag nanoparticles separated by high speed centrifugation, all the samples were dispersed in DMF solvent for UV-Vis measurement and the inset showed the vials containing stock (left), small Ag nanoparticles (middle) and big Ag nanoparticles (right) under white light (a) and 365 nm UV light (d), and the high resolution TEM imaging of obtained big Ag nanoparticles (b) and small fluorescent Ag nanoparticles (c).

It is well-known that the silver nanoparticles with size larger than 2 nm exhibit typical localized surface plasmon resonance and normally are non-luminescent, thus the strong fluorescence recoded from the 6 ± 2 nm silver nanoparticles in this work is quite unusual. The high resolution TEM (HRTEM) imaging and selected area electron diffraction (SAED) technique were explored to further probe the fine structures of obtained luminescent silver nanoparticles. As shown in Fig. 4, the luminescent 6 nm silver NPs display typical polycrystalline structures (see the SAED image in inset) and contain several ultra-small domains with size in the 1~2 nm range (Fig. 4a). On the contrary, the average domain sizes of non-luminescent large silver NPs are basically larger than 5 nm (Fig. 4b). Therefore, these ultra-small sized (1~2 nm) domains of polycrystalline 6 nm small silver NPs likely result in discrete energy states that lead to the strong luminescence. The similar results were reported by Zheng et al. as well.[23]

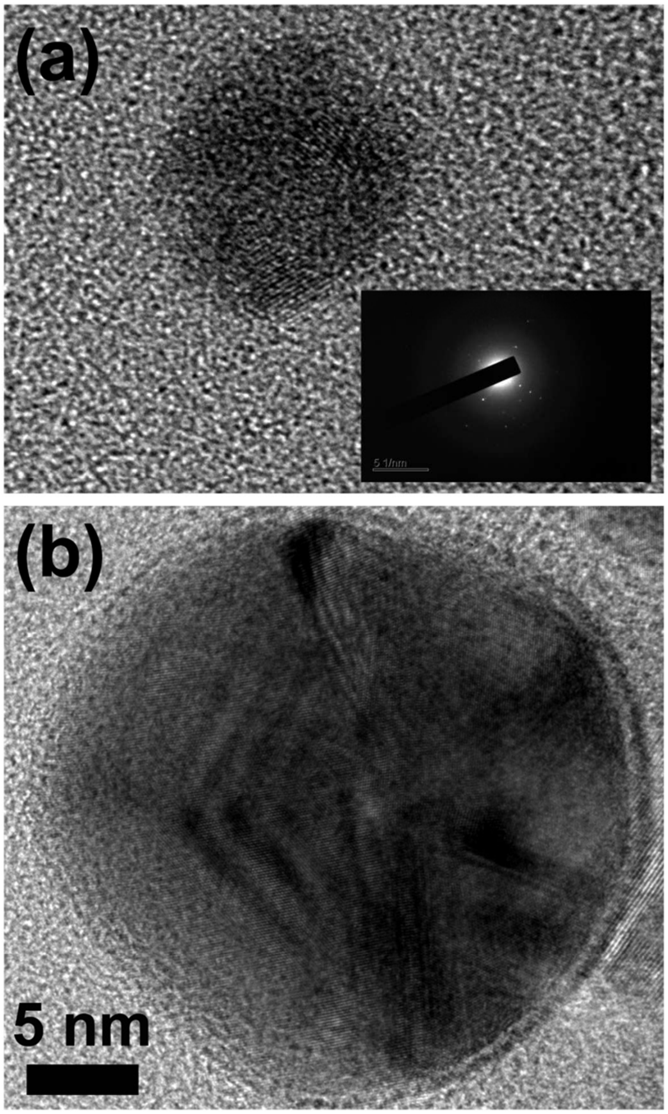

Fig. 4 The HRTEM images of synthesized luminescent small silver nanoparticles (a) and non-luminescent large silver nanoparticles (b), the SEAD image of luminescent silver nanoparticles was shown in inset as well.

The fluorescent properties of obtained luminescent silver nanoparticles were thus studied in detail to clarify the origin of fluorescence. It is worth noting that the obtained small silver nanoparticles in the supernatant exhibit excitation wavelength dependent fluorescent emission. As shown in Fig. 5a, the excitation spectra showed a plateau below 365 nm and a sharp peak centred at 450 nm. Interestingly, the excitation minimum was detected at 410 nm, which was exactly at the same position as the surface plasmon resonance recorded from UV-Vis spectroscopy (see Fig. 3a), indicating that the observed fluorescence was mainly derived from the single-electron excitations between discrete energy levels rather than the surface plasmon resonance.[23] Therefore, we choose three different excitation wavelengths (365 nm, 410 nm and 450 nm) for the fluorescent emission measurement. It was found that there were two strong fluorescent emission peaks and one fluorescent peak of decreased intensity recorded when the small silver nanoparticles solution was excited at 365 nm and 450 nm, respectively. While only the weak fluorescent emission was observed when using an excitation wavelength of 410 nm. The excitation wavelength dependent fluorescent emission from silver nanoparticles implied that the strong coupling existed between plasmon resonance and ultra-small-sized emitters (nanoclusters).[35] Although the exact mechanism for the silver nanoparticles fluorescence remains unclear at present, the polycrystalline structures of silver nanoparticles with numerous ultra-small domains or the particles-supported ultra-small silver nanoclusters would be the possible reasons for the observed luminescence. Moreover, the two fluorescent peaks (located at 485 nm and 535 nm) upon 365 nm excitation would be attributed to the presence of silver nanoclusters with different association atom numbers, which was previously reported by Shang et al. as well.[30]

The synthesized fluorescent silver nanoparticles were dispersed in the common organic solvent of DMF in this work, the solution exhibited good stability as their fluorescent emission was unchanged for at least one month even stored in ambient natural light environment, which served as a good candidate for the study of fluorescent interaction with luminescent polymer that were normally solubilized in organic solvent (e.g. DMF). In our previous work,[38] the fluorescent emission of an intrinsic fluorescent polymer named polyarylene ether nitrile has been modulated by using water soluble gold nanoclusters *via* fluorescent resonance energy transfer (FRET) process, proving that the strong fluorescent interaction existed between PEN and fluorescent metal nanoclusters. In addition, other groups also reported the tailoring of fluorescent emission of conjugated polymers by exploring the plasmon mediated energy transfer between polymers and silver nanoparticles.[39, 40]

Based on these results, we expected that the fluorescent emission of obtained silver nanoparticles could be further modulated by controlling their optical interaction with fluorescent polymer in the solution phase. The fluorescent excitation and emission spectra of PEN polymer (backbone structures were shown in inset, weight average molecule weight of 28337, polydispersity index of 2.38) were displayed in Fig. 5b, a broad excitation peak and a sharp emission peak were observed and the maximum extinction wavelength and emission wavelength was recorded at 365 nm and 432 nm, respectively. It is believed that the effective FRET process will be established between PEN and silver nanoparticles due to their good spectra overlap, thus it is possible to tune the fluorescent emission of silver nanoparticles by providing additional excitation energy from fluorescent PEN. Moreover, two different solvents of water and DMF were involved in our previous work, thus the complex solvents effects and dynamic interaction kinetics brought additional variations to the fluorescent spectroscopy measurement, which would hinder the precise tuning of fluorescent emission spectra. However, in the present work, the unified solvent of DMF was used for the synthesis of luminescent Ag nanoparticles and fluorescent PEN, thus the fluorescent interactions of Ag NPs/PEN system were mainly determined by their optical spectra overlap, surface chemical structures (to control distance), and relative orientation. The influences of donor-acceptor surface chemical structures and relative orientation of transition dipoles towards fluorescent emission are beyond the scope of present work, and these experiments are currently in progress.

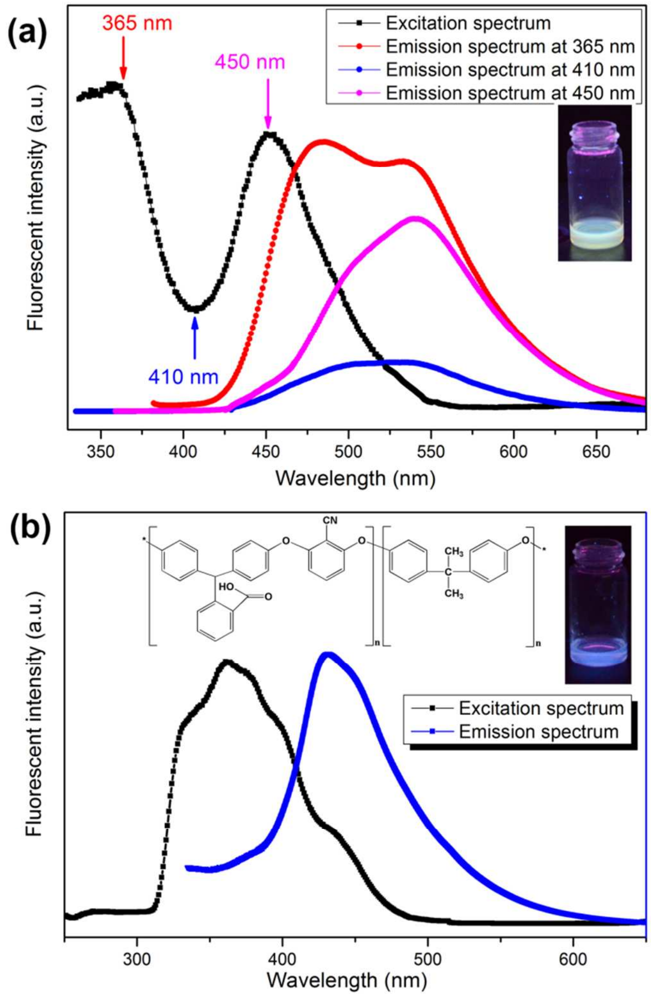

Fig. 5 The fluorescent excitation and emission spectra of Ag nanoparticles (a) and polyarylene ether nitrile (b) in DMF solution. The excitation spectra of Ag nanoparticles and PEN were recorded at emission wavelength of 540 nm and 430 nm, respectively. The vials containing Ag nanoparticles and PEN under a 365 nm UV light illumination was shown in corresponding inset.

As discussed previously, the emission spectrum of obtained silver nanoparticles was dependent on the excitation wavelength (see Fig. 5a), thus the fluorescent emission spectra upon three representative excitation wavelengths at 365 nm, 410 nm and 450 nm were modulated *via* the FRET process from fluorescent PEN polymer. When the PEN/silver nanoparticles mixture solutions were excited at 365 nm, both the PEN and silver nanoparticles were fluorescent, thus the fluorescent emission intensity of silver nanoparticles can be effectively enhanced due to the resonant energy transfer from PEN to silver nanoparticles, especially for the first peak located around 485 nm. Indeed, as the loading PEN content (volume ratio) increased from 5 % to 33 %, a 82% increasing of fluorescent intensity (integrated area under the fluorescent emission spectra from 400 nm to 650 nm) was observed, moreover the fluorescent emission spectra of silver nanoparticles were dramatically reshaped, as the first luminescent peak became the dominate one at higher PEN content (Fig. 6a). When the PEN/Ag nanoparticles solution was excited at 410 nm, the silver nanoparticles solution was almost non-luminescent due to the presence of excitation minimum while PEN was still luminescent, thus it was expected that the silver nanoparticles could be "lighten up" thanks to the resonant energy transfer from PEN donor. As shown in Fig. 6b, the weak fluorescence of silver nanoparticles upon 410 nm excitation was indeed obviously enhanced in the presence of blue-emitting fluorescent PEN, the fluorescent intensity was increased by 75% as the loading content of PEN increased to 33% and the fluorescent emission wavelength was obviously blue shifted from 535 nm to 504 nm. Lastly, when the PEN/Ag nanoparticles solution was excited at 450 nm, only the silver nanoparticles solution was luminescent, and their fluorescent emission was only slightly increased in the presence of fluorescent PEN as shown in Fig. 6c (only 10% increasing of fluorescent intensity after adding 30% PEN). Based on these results, the fluorescent emission profile of obtained silver nanoparticles could be readily modulated *via* the fluorescent interactions with the intrinsic blue emitting fluorescent polymer. More interestingly, the fluorescent emission of silver nanoparticles can be excited in a much wider range of wavelength in the presence of PEN fluorescent polymer, since the minimum in the excitation spectrum (around 410 nm) of as-synthesized silver nanoparticles is well compensated by the fluorescent emission and subsequent energy transfer of PEN polymer. The fluorescent intensity (integrated value under the fluorescent emission curve) and emission wavelength for the PEN/Ag nanoparticles under different excitation wavelengths were summarized in Table 1.

Table 1 The fluorescent emission wavelength and intensity of Ag NPs/PEN complex solution

Excitation wavelength	Fluorescent emission	Ag NPs	Ag NPs+5% PEN	Ag NPs+20% PEN	Ag NPs+33% PEN
365 nm	wavelength (nm) [a]	485	485	483	481
	intensity [b]	40017	43506	57919	72808
410 nm	wavelength (nm)	535	524	516	504
	intensity	6824	7345	9442	11828
450 nm	wavelength (nm)	539	540	541	539
	intensity	17257	18196	19270	19857

a. Only the wavelength for the peak with maximum intensity was listed.

b. The intensity was the integrated value of fluorescent emission.

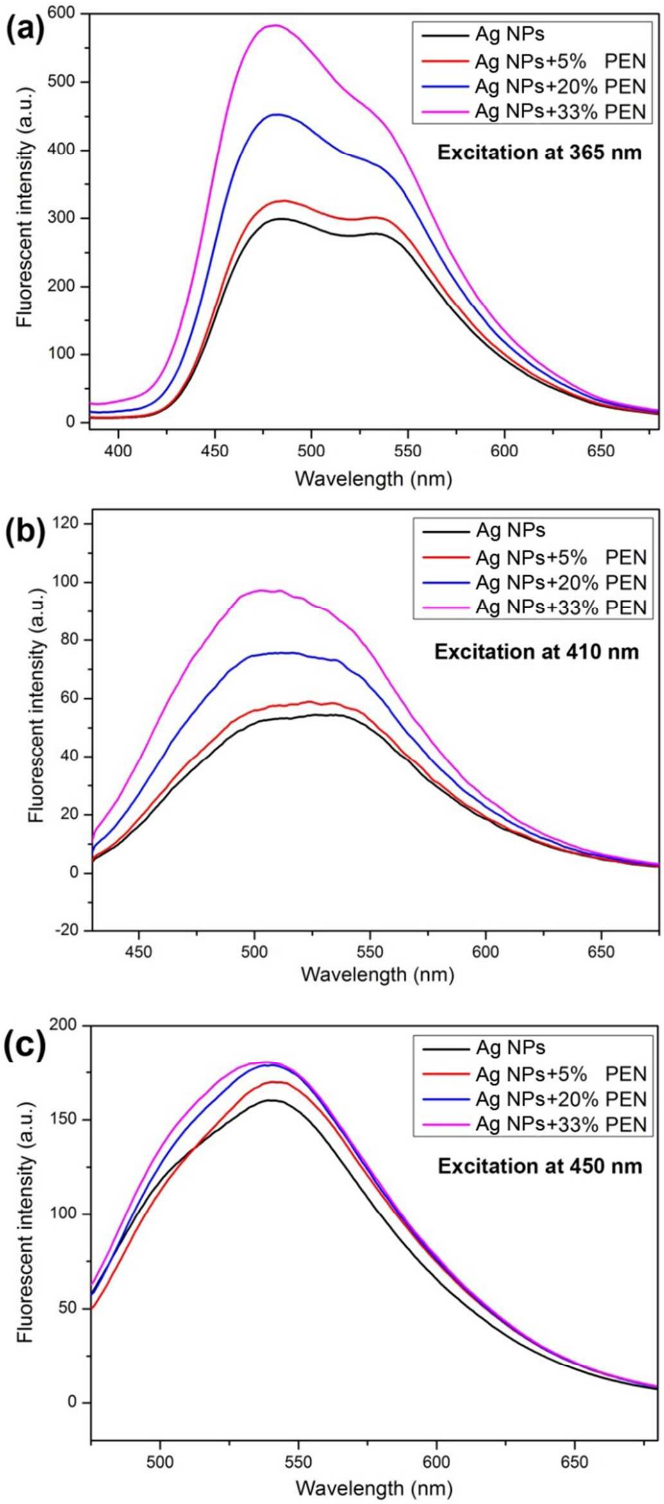

Fig. 6 The fluorescent emission spectra of luminescent Ag NPs solution in the presence of different contents (relative volume ratio) of PEN. The excitation wavelength in the photoluminescent measurement was 365 nm (a), 410 nm (b) and 450 nm (c), respectively.

On the other hand, the fluorescent emission of PEN in DMF solution can be effectively modulated in the presence of luminescent silver nanoparticles via the fluorescent resonant energy transfer process as well. As a proof, the lifetime of PEN and silver NPs were firstly determined by the time-resolved fluorescent technique of time correlated single photon counting (TCSPC) using a Horiba Jobin Yvon Tempro-01 instrument. As shown in Fig. 7, the time-resolved photoluminescent decay of PEN and PEN/luminescent Ag NPs were measured in DMF solvent (excitation at 365 nm, emission at 435 nm) and well fitted by triple-exponential to show the average lifetimes of 3.25 ns and 1.92 ns, respectively. The significant decreasing of lifetime indicated the faster photoluminescent decay of PEN donor in the presence of luminescent silver NPs as the energy acceptor, confirming the effective energy transfer process between PEN and silver NPs.

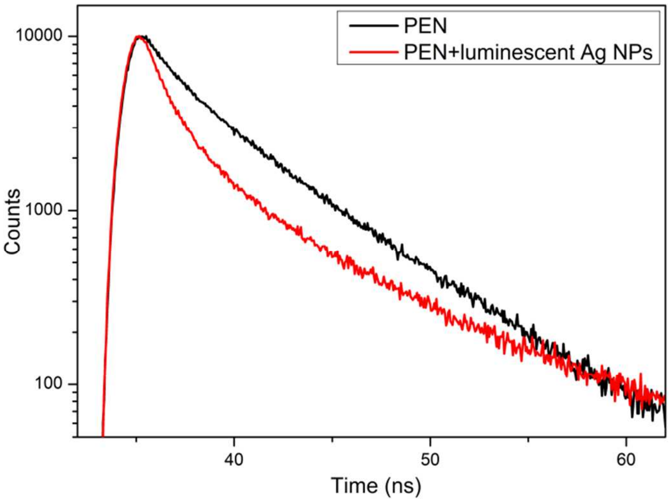

Fig. 7 The time-resolved photoluminescent decay of PEN and PEN/luminescent silver nanoparticles (the relative volume ratio of luminescent Ag NPs was 33%) in DMF solution. The excitation and emission wavelength was 365 nm and 435 nm, respectively.

Then the steady-state fluorescent spectra of PEN/silver NPs were shown in Fig. 8, the fluorescent emission wavelength of PEN solution when excited at 365 nm was obviously red-shifted as loading content of smaller luminescent silver nanoparticles increased (Fig. 8a), the gradual red-shift and decreasing of fluorescent emission intensity was attributed to the interplay of radiative and non-radiative energy transfer between PEN/luminescent Ag NPs pair. On the contrary, the fluorescent emission of PEN was basically quenched in the presence of larger sized non-fluorescent silver nanoparticles (Fig. 8b), which was mainly due to the fact that non-radiative energy transfer channel from PEN to large Ag nanoparticles played an dominative role in this case, as the fluorescent emission of PEN was partly overlapped with the absorption spectra of large silver nanoparticles. The variation of PEN/Ag nanoparticles fluorescent emission was also unambiguously reflected by the colouring and brightness changes under UV light illumination (see Fig. 8c).

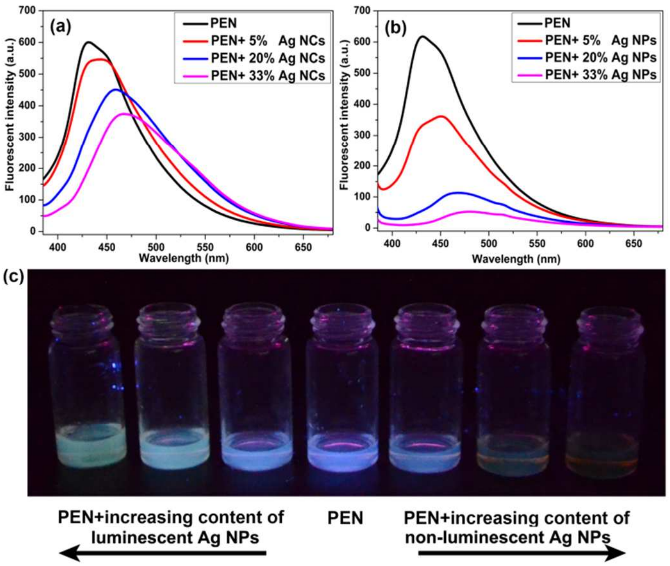

Fig. 8 The fluorescent emission spectra of PEN solution in the presence of different contents of small luminescent silver nanoparticles (a) and larger non-fluorescent silver nanoparticles (b) and photos of vials containing PEN solution and PEN solution mixed with Ag NPs of different sizes under 365 nm UV light excitation (c).

Conclusions

In this contribution, the fluorescent silver nanoparticles with average size of 6 ±2 nm were synthesized *via* a one-step reduction of silver nitrate with mild reductant of organic solvent DMF in the presence of colloid stabilization agent of PVP under N_2 protection, followed by a high speed centrifugation. The fluorescent emission of obtained silver nanoparticles is mainly attributed to the ultra-small sized domains on the surface of silver NPs and/or the particle-supported silver nanoclusters that are created by the chemical etching of pre-formed large-sized silver nanoparticles. In addition, the fluorescent emission of the obtained silver nanoparticles is dependent on the excitation wavelength. Furthermore, their fluorescent emission profile (intensity and shape) can be readily modulated *via* the resonant energy transfer from an intrinsic blue-emitting fluorescent polymer of polyarylene ether nitriles in the uniform solution phase, which is confirmed by the time-resolved fluorescent lifetime measurement. Meanwhile the fluorescent emission of PEN can be modulated by the silver nanoparticles as well, indicating the strong fluorescent interactions existed between luminescent silver nanoparticles and fluorescent polymer (PEN).

Acknowledgements

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Notes and references

[a] Research Branch of Advanced Functional Materials, High Temperature Resistant Polymer and Composites Key Laboratory of Sichuan Province, School of Microelectronics and Solid-States Electronics, University of Electronic Science and Technology of China, Chengdu, 610054, P. R. China. E-mail: jiakun@uestc.edu.cn (K. Jia), liuxb@uestc.edu.cn (X. B. Liu), Tel: +86-28-83207326, Fax: +86-28-83207326.

[b] School of Resources and Environment, University of Electronic Science and Technology of China, Chengdu, 610054, China.

[c] Kun Jia and Pan Wang contribute equally to this work.

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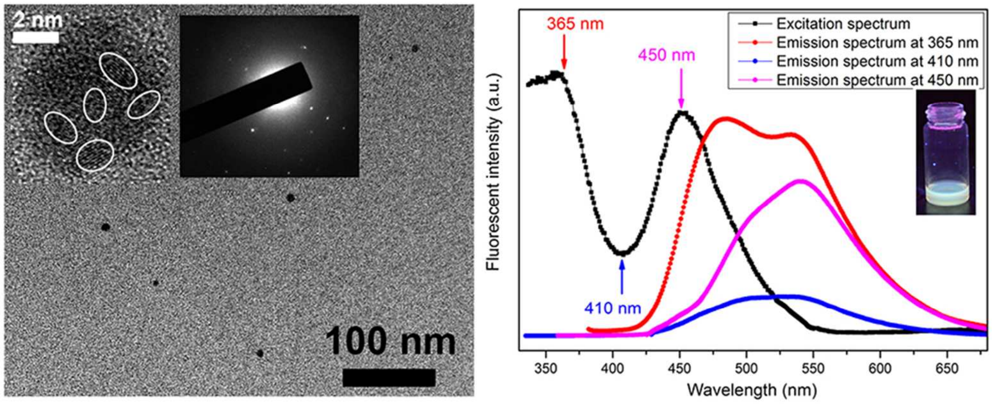

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