# Surface Modification of Gold Nanorods by Grafting Fluorene-Based Conjugated Copolymers Containing Thiol-Pendants

Duryodhan Sahu, Hsuan-Chih Chu, Po-Jen Yang, and Hong-Cheu Lin*

Two conjugated surfactants of monomer TF and polymer PTF with pendant thiol groups are synthesized for surface modifications of gold nanorods (GNRs). Cetyltrimethylammonium bromide (CTAB)-GNRs (without surface-modification) in aqueous solutions are prepared, and the original CTAB surfactant is replaced with TF and PTF due to their thiol-gold grafting reactions. Surface-modified TF-GNRs and PTF-GNRs in THF are obtained. UV-visible spectra provide the grafting evidence of TF and PTF. Compared with TF-GNRs, the PTF-GNRs show better solubility and stability against aggregations of nanorods in THF. TEM and XPS confirm the existence of binding bonds between the sulfur groups of PTF and the gold surface in PTF-GNRs. Compared with polymer surfactant (PTF), the faster PL emission decay in PTF-GNRs match well with the PL quenching of PTF-GNRs. Surface modifications are verified by UV-visible, TEM, XPS, PL and lifetime measurements.
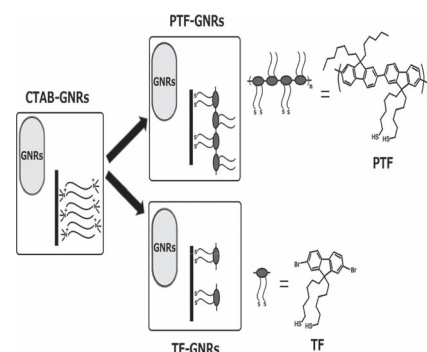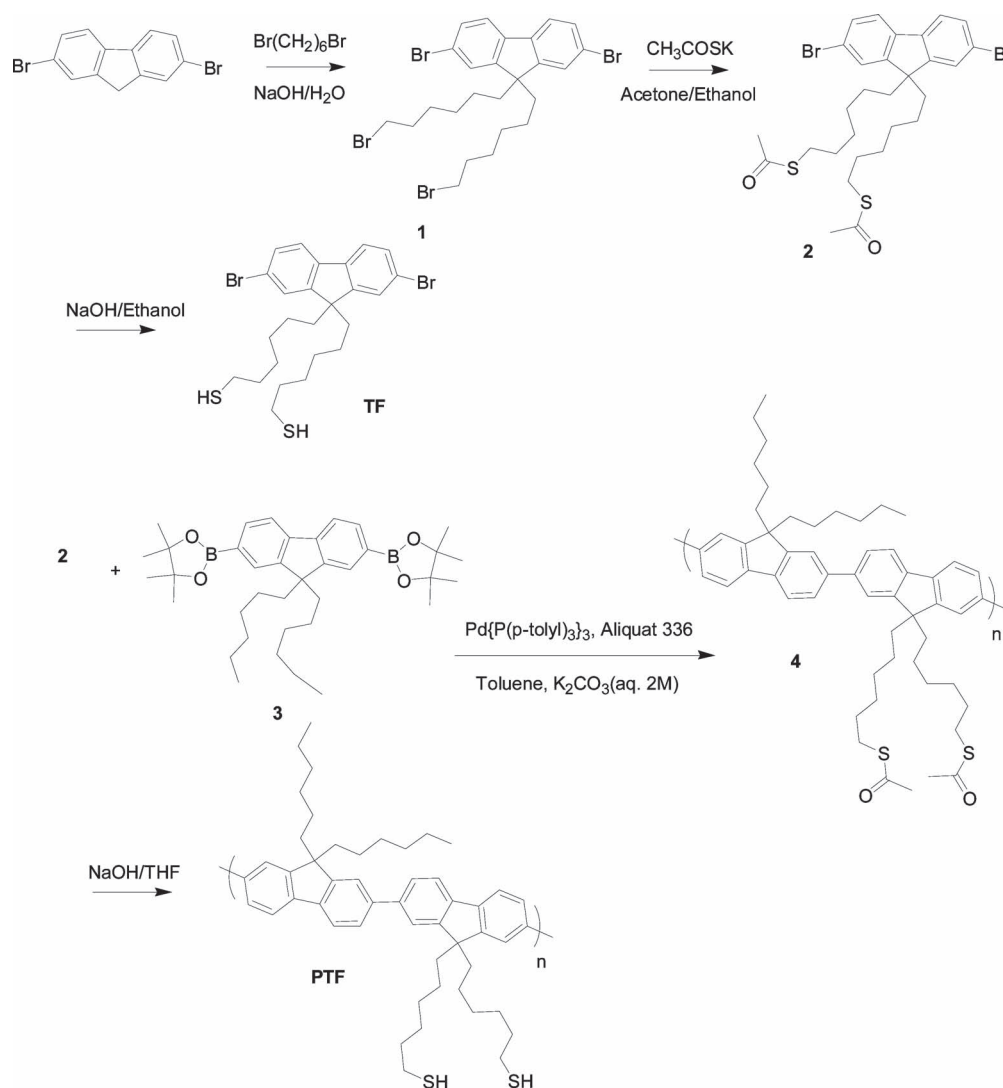
1. Introduction

Recently, nanocomposites containing metallic nanoparticles (or nanorods) and organic molecules have emerged as an exciting research area for their applications in optoelectronics, sensors and light energy conversions.[1–5] Hybrid materials (i.e. nanocomposites) composed of organics and nanostructural inorganics with better interactions could be produced by modifications of the functionalities on surfactants. Modification methods on the surfaces of metal nanostructures by organic molecules were significantly developed for the design of biological sensors and optoelectronic devices.[6–8] To promote the application potential of nanocomposites, the specific surface plasmon resonance (SPR) bands of gold nanorods (GNRs) could be improved by increasing the aspect ratios of GNRs properly.[9,10] The longitudinal plasmon band of two distinct surface plasmon resonance bands could be tuned from the visible to the near infrared (NIR) range. Previously, many research groups have reported wet chemical synthetic routes to GNRs,[11,12] in which the most commonly used method is a rod-shaped micelle growth via the surfactant cetyltrimethylammonium bromide (CTAB). Using CTAB as a bilayer surfactant on the surface of GNRs makes them become fairly soluble in the aqueous phase. However, the hydrophilic nature of CTAB surfactants[13,14] limits the further applications of GNRs. Normally, followed by centrifugation, GNRs are purified by several cycles of suspension and then isolated in the precipitate, where the excess CTAB can be removed in the supernatant. However, if the CTAB surfactants could be fully removed from the solution, GNRs would lose their stability in colloidal dispersions and form aggregates. Therefore, considerable interest has arisen in developing techniques to facilitate surface modifications of GNRs to disperse GNRs well in nanocomposites for further applications. Continuous efforts to prepare functional GNRs with novel surfactants, such as organo-soluble photoresponsive azo-thiol monolayer-surfactants, have been reported, with GNRs becoming very stable in both organic solvents and in the solid state without aggregation or decomposition.[15]

D. Sahu, H.-C. Chu, P.-J. Yang, H.-C. Lin
Department of Materials Science and Engineering,
National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu,
Taiwan 300, ROC
E-mail: linhc@cc.nctu.edu.tw

In previous studies, using polymers to modify the surfaces on gold nanorods were reported via a layer-by-layer (LbL) technique with poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) alternately.[16] The method of LbL assembly was a simple way to modify the surfaces of gold nanorods through the alternate adsorptions of cationic and anionic polymers in solutions. The bonding forces of the polymers and nanorods on the interface between the two layers are noncovalent, which can lead to instabilities of the alternative polymeric surfactants.[17] The limitation of this LbL technique is that anionic and cationic polyelectrolytes are required to modify the nanorods, which limits the types of functionalities and LbL systems that can be incorporated into the nanorods. As a result of this, several reports on the surface modification of GNRs with thiol derivatives of polymers were reported,[18–20] in which stronger binding to the surface of nanorods, better control over the thickness

of the polymer layer, and higher stability than polyelectrolyte materials were highly beneficial. In the past decade, fluorene-based conjugated polymers have been demonstrated as a very outstanding class of electron donors with high hole mobilities. In addition, polyfluorenes were also synthesized and investigated for applications in the design of multifunctional chemical sensors and circuit components (such as single electron transistors).[21–24] The thiol end groups provide covalent attachment of the thiol derivative of polymers to gold surfaces.[25] Recently, the surface modification of gold surfaces and nanospheres using well-defined homopolymers and copolymers prepared with thiol functional groups has been reported.[26,27] Herein, the surface modification of GNRs by grafting a conjugated polymer, i.e. a thiol derivative of poly(fluorene) (PTF), is reported. The fluorene units (with and without thiol pendants) and their polymer were synthesized by following the synthetic steps in Scheme 1. The pendant alky chains with

Scheme 1. Synthetic procedures of surfactants for monomer TF and polymer PTF.

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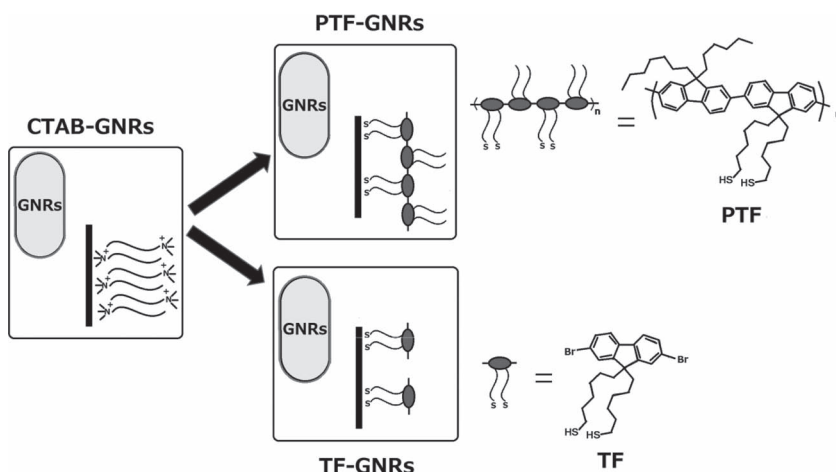
Macromolecular
Journals

1551

Figure 1. Surface modification processes of gold nanorods GNRs by monomer TF and polymer PTF (i.e. surface-modified gold nanorods TF-GNRs and PTF-GNRs, respectively).

thiol functional groups could proceed the surfactant place exchange reaction. The thiol pendants of the polymeric surfactants could provide covalent attachments to the gold surfaces. As shown in Figure 1, the binding of conjugated polymer PTF on the metal surface of GNRs resulted in the quenching effect of excited PTF by the process of energy transfers to GNRs, which are the main deactivation channels for the excited molecules on the metal surfaces.[28,29] Easier surface modifications on gold nanorods, along with higher efficiencies and reproducibility of the surfactant exchange reactions, make our approach promising. The generality of this approach opens up new nanomaterials for the conjunction of different organics (or polymers) and nanostructural inorganics into nanocomposites for different applications in nanomaterials.

2. Experimental Section

2.1. Materials

All chemicals were purchased from Aldrich and used without further purification. Ultrapure filtered water with a resistivity of 18.2 MΩ was used in all experiments. Compound 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (3) was synthesized according to known literature procedures.[30] The conjugated polymer with two side-chain thiol groups was also synthesized following previous a literature method.[31] The polymerization was performed by a Suzuki coupling reaction. CTAB-GNRs were synthesized by the seed-mediated growth method (via HAuCl$_4$).[32,33] The gold nanorods were prepared by a seed-mediated growth method with slight modifications. Specifically, the spherical gold nanoparticles used as seeds were prepared first. The solutions were mixed with 5.0 mL of an aqueous HAuCl$_4$ (0.5 × 10^{-3} M) and 5.0 mL of CTAB (0.2 M). 0.6 mL of an aqueous ice-cold NaBH$_4$ solution (0.01 M) was added and vigorously stirred. Then, 5.0 mL of an aqueous solution (0.2 M CTAB

and 4 × 10^{-3} M silver nitrate) was gently mixed with 5.0 mL of HAuCl$_4$ (1 × 10^{-3} M). The solution at this stage appeared bright brown-yellow, then became colorless upon addition of 70 µL of ascorbic acid (0.1 M). Finally, 12 µL of a seed solution was injected, and the reaction mixture was gently stirred and kept at 25 °C. Upon cooling, excess CTAB was crystallized and separated by filtration. The filtrate contained monodisperse Au nanorods and was used directly in subsequent studies. The formation of gold nanorods and their aspect ratios were confirmed by UV-visible absorption spectra and TEM analyses.

2.2. Measurements and Characterization

^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using CDCl$_3$ solvent. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. The molecular weight and polydispersity data were determined by gel permeation chromatography (GPC) using polystyrene as a standard. UV-visible absorption spectra were recorded in water solution using a Jasco V-670 spectrophotometer, and photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer. Measurements were performed in quartz cells with a 10 mm optical path. The PL spectra were measured at the excitonic emission. Transmission electron microscopy (TEM) analyses were performed using a JEOL 2100 electron microscope with an acceleration voltage of 200 keV. A drop of a dilute solution of gold nanorods was allowed to dry on a carbon coated copper grid and then probed using TEM imaging. The samples were prepared from solutions collected on copper TEM grids (200 mesh/carbon films) and allowing the solvent to evaporate. X-ray photoelectron spectra (XPS) were obtained using an ESCA ULVAC-PHI spectrometer in constant analyzer energy mode with a pass energy of 50 eV and Al-K$_\alpha$ (280 eV) radiation as the excitation source. XPS analysis was performed at room temperature and at pressures under 5 × 10^{-10} Torr. The take-off angle used in XPS was 45°, and the sputter ratio was 8.5 nm min^{-1}. Time-resolved photoluminescence spectra were utilized to measure lifetime using a home-built single photon counting system. Excitation was performed using a 375 nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 MHz). The signals collected at the excitonic emissions of solutions (λ = 480 nm) were connected to a time-correlated single photon counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with bi-exponential kinetics in which two decay components were derived.

2.3. Synthesis of Monomer TF

2.3.1. 2-Bromo-9,9′-bis(6,6″-bromohexyl)fluorene (1)

2,7-Bromofluorene (1 × 10^{-3} mol) was added to a mixture of aqueous sodium hydroxide (50 mL, 50%), tetrabutylammonium bromide (1 × 10^{-3} mol) and 1,6-dibromohexane (10 × 10^{-3} mol) at 75 °C. After 4 h, the mixture was cooled to room temperature.

After extraction with CH_2Cl_2, the combined organic layers were washed successively with water, aqueous HCl (0.5 M), water and brine, and then dried over $MgSO_4$. The excess 1,6-dibromohexane solvent was removed by vacuum distillation, and the residue was purified by silica gel column chromatography using hexane and dichloromethane (10:1) as the solvent. Compound 1 was obtained as a white solid in a yield of 59%. ^{1}H NMR ($CDCl_3$, δ): 7.52 (m, 2H), 7.45 (m, 2H), 7.43 (m, 2H), 3.26-3.28 (t, 4H), 1.91-1.99 (m, 4H), 1.54-1.71 (m, 4H), 1.07-1.21 (m, 8H), 0.60-0.65 (m, 4H).

2.3.2. Thioacetic Acid 6-[9-(6-acetylsulfanyl-hexyl)-2,7-dibromo-9H-fluoren-9-yl]-hexyl ester (2)

The bromide (1) (1×10^{-3} mol) and potassium thioacetate (2.5×10^{-3} mol) were stirred in 25 mL of acetone and 25 mL of ethanol to reflux for 24 h, and then the solvent of the mixture solution was removed on a rotary evaporator. After extraction with CH_2Cl_2, the organic layer was washed with water several times and dried over $MgSO_4$. The resulting thioacetate was used without purification. The yield was 92%. ^{1}H NMR ($CDCl_3$, δ): 7.52 (m, 2H), 7.45 (m, 2H), 7.43 (m, 2H), 2.85 (t, 4H), 2.28 (s, 6H), 1.91-1.98 (m, 4H), 1.54-1.65 (m, 4H), 1.07-1.22 (m, 8H), 0.61-0.65 (m, 4H).

2.3.3. 6-[2,7-Dibromo-9-(6-mercapto-hexyl)-9H-fluoren-9-yl]-hexane-1-thiol (TF)

The thioacetate (2) (1×10^{-3} mol) was dissolved in 50 mL of absolute ethanol and the solution was degassed for 1 h with nitrogen. After 1 h, potassium carbonate (K_2CO_3) was added to the flask and the mixture was gently warmed to ~35 °C. After stirring under N_2 for 4 h, the solution in the flask was poured into 50 mL of an aqueous solution of saturated ammonium chloride and extracted with CH_2Cl_2. The organic layer was washed with water 5 times, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography using hexane and dichloromethane (2:3) as the solvent to give a light gray solid in a yield of 68%. ^{1}H NMR ($CDCl_3$, δ): 7.52 (m, 2H), 7.45 (m, 2H), 7.43 (m, 2H), 2.51 (quin, 4H), 1.91-1.98 (m, 4H), 1.02-1.65 (m, 14H), 0.61-0.65 (m, 4H); Anal. calcd for [$C_{25}H_{32}Br_2S_2$]: C 53.96, H 5.80; found: C 54.45, H, 5.76.

2.4. Synthesis of Polymer PTF

The polymerization of compound 4 was carried out through palladium (0)-catalyzed Suzuki coupling reactions. Into a 50 mL two-neck flask, 1 equiv. of monomer 2 and 1 equiv. of compound 3 were added in 10 mL of THF. The Pd(0) complex, Pd{P(p-tolyl)3}3 (1 mol%), was transferred into the mixture in a dry environment. Then, 2 M aqueous potassium carbonate and the phase transfer catalyst, i.e. aliquat 336 (several drops), were subsequently transferred via cannulas into the previous mixture under nitrogen. The reaction mixture was stirred at 75 °C for 3 d. The reaction mixture was cooled to 50 °C and added slowly into a vigorously stirred mixture of 300 mL methanol. The polymers were collected by filtration and reprecipitation from methanol. The polymer with thioacetate (2×10^{-3} mol) was dissolved in 50 mL of THF, and sodium hydroxide solution (10 mL, 50 wt%) was added under nitrogen and stirred overnight. The reaction mixture was neutralized by adding acetic acid, and then poured into 25 mL of water. The organic layer was extracted with CH_2Cl_2 and washed with water

5 times, dried over $MgSO_4$ and concentrated to give a light gray solid. According to literature procedures,[30] the thiol group is one of the functional groups that could not be tolerated in the Suzuki reaction. We had to use a protective group, such as thioacetate, to polymerize first and then hydrolyze to PTF. The number-average molecular weight of PTF was 8420 and the polydispersity index (PDI) was 1.2. The yield was 49%. ^{1}H NMR ($CDCl_3$, δ): 7.62-7.38 (m, 12H), 2.51-2.45(m, 4H), 2.20-1.91 (m, 4H), 1.83-0.16 (m, 38H).

2.5. Surface Functionalization of Gold Nanorods with Thiol-Terminated Monomer TF and Polymer PTF

Place-exchange methods have been widely employed to functionalize gold nanoparticles with thiol derivatives of organic molecules.[18,25] The surface of gold nanorods can be modified with the thiol-terminated monomer TF from the original CTAB surfactant. The phase exchange from the aqueous phase to organic solvent was followed by the following steps. First, 10 mL of aqueous gold nanorod solution and 10 mL of 25×10^{-3} M TF in toluene were mixed with vigorous stirring. Then, 15 mL of acetone were added. The mixture was reacted at room temperature with constant stirring for 5 h. We extracted the upper layer solution of the mixture. The pink color was transferred from the lower aqueous phase to the upper toluene solvent, and the upper layer was collected. The formation of covalent bonds with thiol groups facilitated the phase transfer of gold nanorods. The modified gold nanorods could be easily dispersed in THF. GNRs from the aqueous phase were directly extracted by thiol-group-ligands in a mixture of 1:1:2 (water:thiol:acetone) stirring for 3 h. The gold nanorods were transferred from water into toluene, and gold nanorods could be dispersed in THF. The same method was used for the surface modication of gold nanorods GNRs with polymer PTF.

3. Results and Discussion

3.1. GNRs Surface-Modified with Monomer TF and Polymer PTF

As shown in Figure 2, the UV-visible absorption spectrum of CTAB-GNRs (without surface-modification) in the aqueous solution exhibited transverse and longitudinal surface plasmon resonances at 512 nm and 778 nm, respectively. In addition, as revealed by the TEM image in Figure 3a, the gold nanorods possessed an average length and diameter of 25.0 and 7.0 nm, respectively, featuring an average aspect ratio of 3.6. The thiol derivatives of TF and PTF were immobilized onto the surface of the gold nanorods using a ligand-exchange technique, so the original CTAB surfactant on the gold surface could be replaced by thiol groups due to the thiol-gold grafting reactions of TF and PTF (see Figure 1). The binding of the thiol derivatives onto the gold nanorod surface was characterized by TEM and UV-visible measurements. As we know, it has previously been proven that UV-visible spectroscopy is a powerful tool to monitor the coating of gold nanorods with polyelectrolyte multilayers.[15–17] The UV-visible absorption
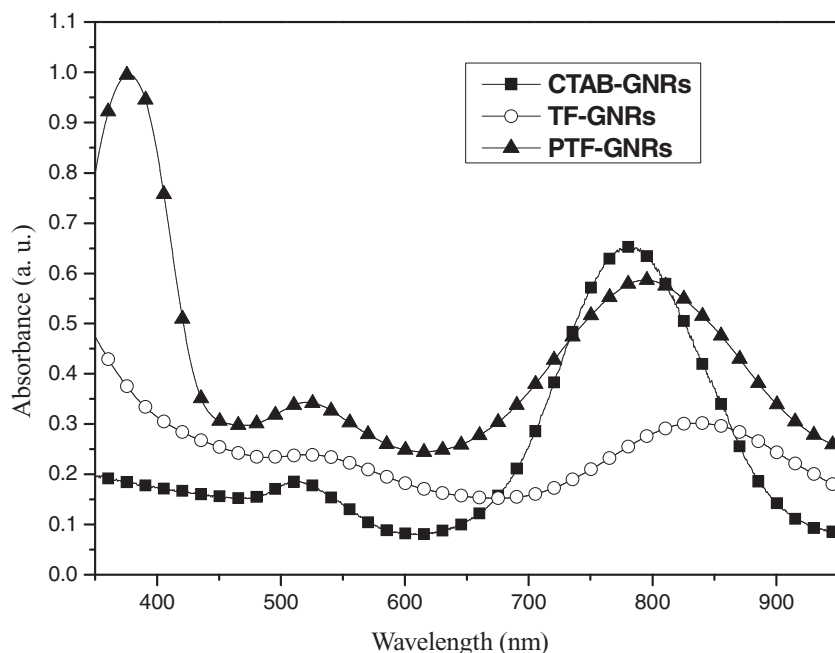
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Journals

1553

Figure 2. UV-visible absorption spectra of CTAB-GNRs (in aqueous solution), TF-GNRs (in THF solution) and PTF-GNRs (in THF solution).

spectrum of CTAB-GNRs illustrates that the absorption maximum for the transverse surface plasmon band of the ungrafted nanorods occurred at a wavelength of 512 nm in Figure 2. When gold nanorods (GNRs) are further surface-modified with monomer TF and polymer PTF, Figure 2 shows small red shifts in the transverse surface plasmon bands of 528 nm and 530 nm, respectively. These phenomena demonstrate that the red-shifted absorptions are
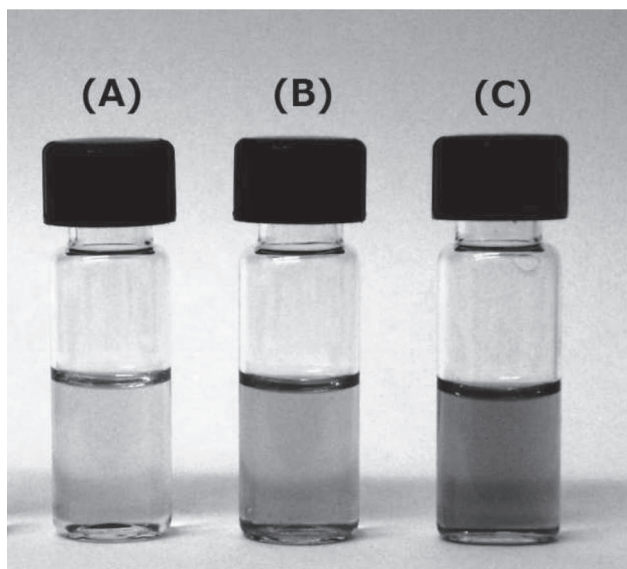

Figure 3. Photographs of GNRs dispersed in THF after place exchange reaction: TF-GNRs (a); PTFs-GNRs in THF (b); CTAB-GNRs in aqueous solution (c).

due to the transverse surface plasmon band of the gold nanorods upon grafting of monomer TF and polymer PTF to the nanorod surface. Due to the modifications on the surfaces of GNRs, these shifts in adsorption maxima were attributed to changes in the local refractive indexes at the surfaces of the rods,[32] resulting in increases in the local dielectric function values. Moreover, it shows that the red shifts in the absorption wavelengths for the transverse surface plasmon bands are associated with the surfactants adsorbed on the nanorod surfaces. In addition, the interactions between gold nanorods and TF and PTF molecules resulted in dampening and broadening of the plasmon absorption bands of longitudinal absorptions, which are highly sensitive to the surfactant type (i.e. monomer TF and polymer PTF). For example, gold nanorods surface-modified with polymer PTF (i.e. PTF-GNRs) have narrower and higher absorbance in contrast to those surface-modified with monomer TF (i.e. TF-GNRs). Compared with CTAB-GNRs, the longitudinal absorption of TF-GNRs (surface-modified with monomer) possessed the largest red-shifted absorption from 778 nm to 818 nm. In addition, the longitudinal absorption of PTF-GNRs (surface-modified with polymer) also showed a red-shifted absorption to a lesser extent at 803 nm. The characteristic red-shifted spectra in the transverse and longitudinal plasmon absorptions correspond well with the observations of previous research groups,[33] who demonstrated that the increase in the wavelength of the surface plasmon band matched the nanometer thickness of different surfactants adsorbed on the surfaces of GNRs. It should also be mentioned that the longitudinal plasmon absorptions after surface-modification appear to have broader absorptions with less absorption intensities, which indicates that aggregations of nanorods do occur upon grafting of thiol derivatives (such as monomer TF and polymer PTF) to the surfaces of nanorods. To evaluate the contributions from the monomer and polymer surfactants, the UV-visible absorption spectra of TF-GNRs and PTF-GNRs were compared after surface-modification. In TF-GNRs, the transverse surface plasmon band of the nanorods red shifted to 530 nm, and the longitudinal surface plasmon band tranformed into a broader band absorption, which indicates a clear aggregation of nanorods. Because PTF is a fluroene-based copolymer containing pendant thiol groups and alkyl side-chains, upon grafting PTF on the surfaces of GNRs, the resulting surface-modified gold nanorods PTF-GNRs showed better solubility and stability against their aggregations of nanorods
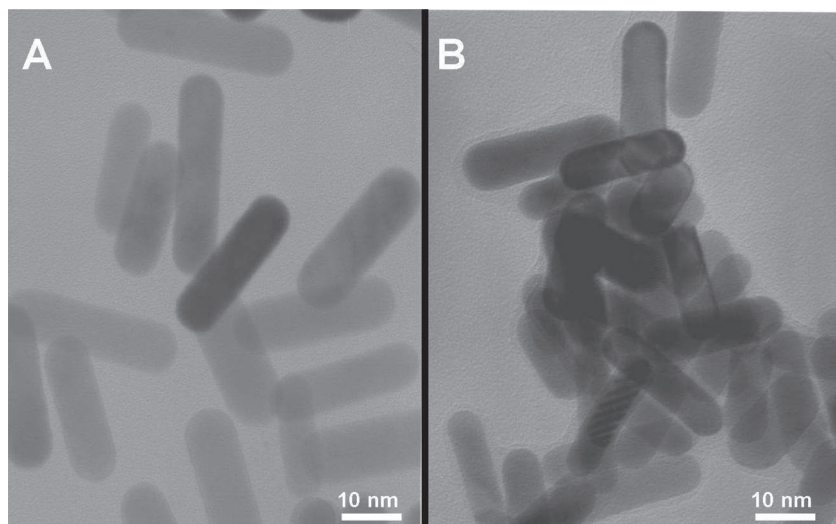
Figure 4. TEM images of (a) CTAB-GNRs and (b) PTF-GNRs after the surface modification.

in THF due to the stronger longitudinal surface plasmon band. Figure 3a, 3b and 3c show photographs of TF-GNRs and PTF-GNRs dissolved in THF and CTAB-GNRs dispersed in aqueous solution, respectively. The colors of those solutions could be also observed clearly due to the surfactant exchanged reaction.

The red-shifted phenomena in the absorption wavelengths upon the coating of nanorods with thiol derivatives (including monomer TF and polymer PTF) could also be investigated by transmission electron microscopy (TEM). The TEM micrograph of CTAB-GNRs in Figure 4a indicates that the surfactants of CTAB attached to the surfaces of the nanorods are too thin to be observed. However, as shown in Figure 4b, the TEM image of PTF-GNRs verifies that polymer surfactants (PTF) with an average thickness of 1–3 nm were grafted to the surfaces of GNRs in layered forms. Since non-grafted surfactants (PTF) on the surfaces of GNRs could be removed by numerous THF washing and centrifugation cycles, the layered polymer (PTF) of PTF-GNRs detected by TEM should be covalently attached to the surface of the nanorods (GNRs), which was also confirmed by the previous results of UV-visible spectra with red-shifted characteristic absorptions. TEM micrographs demonstrated that PTF as a new surfactant for GNRs also facilitated them to disperse well in THF solutions. The TEM results provide another source of evidence of PTF-GNRs in which the surfaces of gold nanorods (GNRs) were modified with PTF. Therefore, the TEM images confirm the red-shifted UV-visible absorptions, which also provide direct evidence that the thiol derivatives are covalently attached to the surfaces of GNRs. To demonstrate the presence of thiol pendant groups in polymer PTF is vital for their covalent attachments to the gold nanorods. Hence, due to weaker dipole interactions

of polymer surfactants with gold surfaces, it has previously been shown that there is a blue-shift in the transverse surface plasmon band of nanoparticles if polymer unwrapping occurs on gold surfaces.[34] Even after repeated washing of gold surfaces with a good solvent (such as THF) to remove the unreacted polymer surfactants on gold surfaces, there was no further change in the red-shifted absorptions on the surface-modified gold nanorods, which illustrates that polymer unwrapping from the surface of the nanorods does not occur.

The binding bonds for sulfur groups of polymer PTF on the gold surface could be determined by X-ray photoelectron spectroscopy (XPS). Moreover, after surface-modification of GNRs by polymer PTF, the presence of a sulfur signal detected by XPS measurements gives valuable information about the chemical bonding of the surfactant head (S) to the gold surface. The XPS spectrum of PTF-GNRs is shown in Figure 5, which revealed the presence of sulfur from polymer surfactants (PTF) and the absence of nitrogen from CTAB surfactants on the surfaces of gold nanorods. The binding bond for the sulfur group on the gold surface could be determined by XPS. In fact, the S2p core level region for the alkanethiol chain on a variety of metals can be fitted with different components.[35,36] The $S2p_{3/2}$ peak could be fitted with two components, with average binding energy values of 162 and 163–164 eV, as observed in Figure 5. The inset of Figure 5, with a higher resolution of XPS spectrum, shows that each component consists of a doublet with spin–orbit
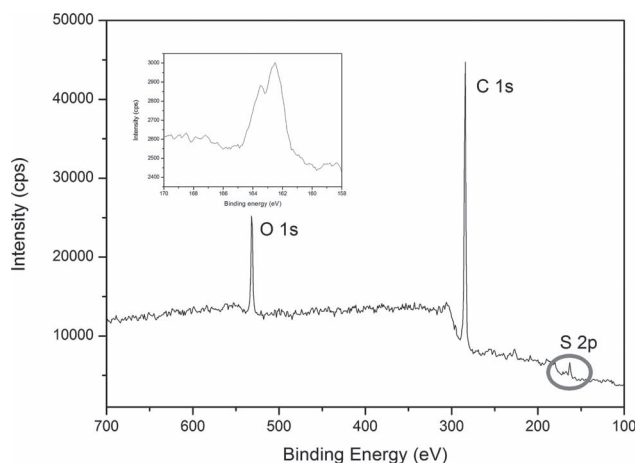

Figure 5. XPS spectrum of surface-modified gold nanorods PTF-GNRs. Inset: higher resolution of the sulfur component comprising a doublet with spin–orbit splitting.

splitting of 1.2 eV. The component at 162 eV is usually the most important one, which is related to S chemisorbed on the Au surface through a thiolate bond.[37] Thus, the XPS result further confirms the successful replacement of CTAB surfactants with polymer surfactants (PTF) on gold nanorods. Although thiol-bearing conjugated polymer may function as a crosslinker (via disulfide bonds among PTF) to crosslink the gold nanorods, as illustrated in Figure 3b, the crosslinking density is not high enough to let PTF-GNRs precipitate out from the solution due to the major reaction of thio groups with GNRs. This can also be proven by the TEM image of PTF-GNRs in Figure 4b, which demonstrated thin film coatings of polymers on GNRs. However, this possible and minor crosslinking density of PTF-GNRs (caused by disulfide bonds among PTF) will not affect the solubility of PTF-GNRs in organic solvents as well as the miscibility of PTF-GNRs in polymer composites.

3.2. PL and Lifetime Analyses of Surface-Modified Gold Nanorods (PTF-GNRs)

To explore the excited-state interactions of polymer PTF with gold nanorods GNRs, the emission behavior of surface-modified gold nanorods PTF-GNRs was monitored by PL spectra and lifetime analyses. As shown in Figure 6a, where the PL spectra are excited at concentrations of the fluorene moieties with the same absorption intensity in both PTF and PTF-GNRs, in contrast to a stronger PL emission of polymer surfactant (PTF) at 423 nm, the PL emission of surface-modified gold nanorods PTF-GNRs was quenched due to the energy transfer of polymer surfactant (PTF) to gold nanorods GNRs. Previous studies also reported that chromophores bound to gold nanoparticles underwent excited-state deactivation by energy or electron transfer processes.[38,39] The excited polymer PTF emission at 423 nm was further analyzed by comparing the PL emission decay (lifetime) of polymer surfactant (PTF) with that of surface-modified gold nanorods PTF-GNRs. As shown in Figure 6b, polymer PTF shows a mono-exponential fluorescence decay with a lifetime of 3.2 ns in THF. The emission decay of surface-modified gold nanorods PTF-GNRs exhibited an additional fast deactivation pathway to have a much shorter lifetime of 0.42 ns. The fluorescence decay of PTF-GNRs was analyzed by a bi-exponential kinetic fit, and the slower component had a lifetime (2.7 ns) similar to that of unbound polymer PTF. The faster PL emission decay component of surface-modified gold nanorods PTF-GNRs matched well with the excited-state quenching in its PL emission spectrum. On the other hand, the slower PL decay component of PTF-GNRs represented the unquenched PL component of the bound polymer PTF. As discussed in earlier studies, smaller metal particles cannot quench all the bound chromophores. It was reported that the energy
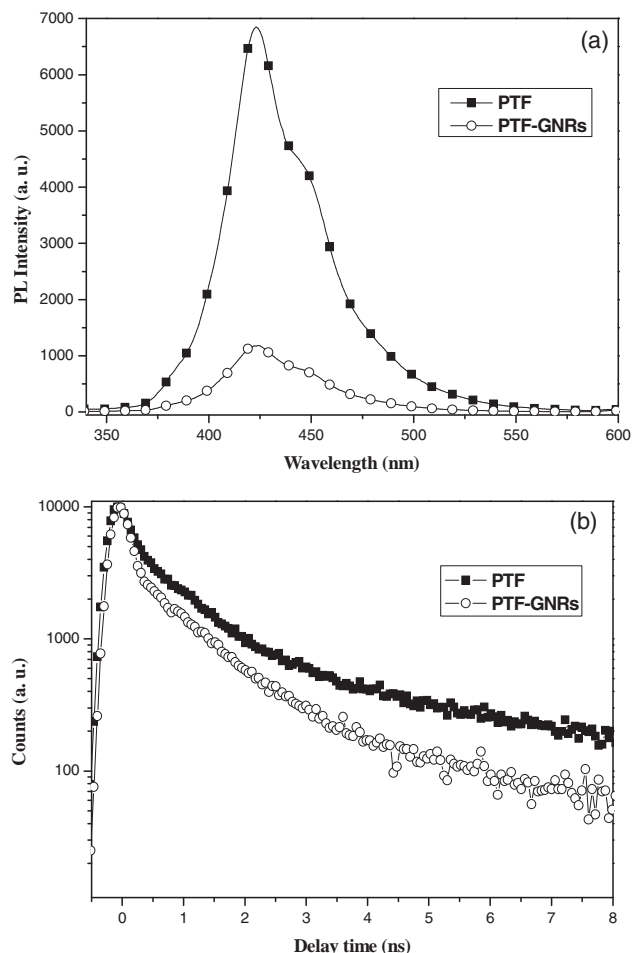

Figure 6. (a) PL spectra (excited at the maximum absorption 379 nm) of polymer PTF and surface-modified gold nanorods PTF-GNRs in THF, which are excited at the concentrations of the fluorene moieties with the same absorption intensity in both PTF and PTF-GNRs. (b) PL lifetime spectra of polymer PTF and surface-modified gold nanorods PTF-GNRs.

or electron transfer pathways dominate as the gold nanostructures are on the nanoscale.[16,31] In addition, the ability to accept and store electrons (i.e. electron transfer) in noble nanoparticles has been demonstrated.[40–42] The other pathway for the excited-state deactivation involves direct energy transfer to metal nanoparticles. The results of PL and lifetime analyses demonstrated that the deactivation of the excited chromophore (PTF) in surface-modified gold nanorods PTF-GNRs could occur via energy transfer processes to gold nanorods GNRs.

4. Conclusion

In conclusion, two conjugated surfactants of monomer TF and polymer PTF with pendant thiol groups were successfully synthesized for surface-modifications of gold nanorods GNRs. A seed-mediated process to produce gold

nanorods CTAB-GNRs (without surface-modification) in aqueous solutions was employed, in which the original CTAB surfactant on the gold surface could be replaced with TF and PTF due to their thiol-gold grafting reactions. Then, gold nanorods surface-modified with monomer TF and polymer PTF (i.e. TF-GNRs and PTF-GNRs, respectively) were obtained and well dispersed in THF. After surface modification, due to consistent red-shifts in the absorption maxima of surface plasmon bands, both UV-visible spectra of TF-GNRs and PTF-GNRs provided evidence of the grafting of TF and PTF to the surfaces of gold nanorods GNRs. Compared with TF-GNRs, the resulting PTF-GNRs (gold nanorods surface-modified with polymer) showed better solubility and stability against the aggregations of nanorods in THF due to the stronger longitudinal surface plasmon band. Moreover, both TEM and XPS analyses confirmed the binding bonds for sulfur groups of polymer PTF on the gold surface in surface-modified gold nanorods PTF-GNRs. The PL emission of surface-modified gold nanorods PTF-GNRs was quenched due to the energy transfer of polymer surfactant (PTF) to gold nanorods GNRs. Compared with polymer surfactant (PTF), the faster PL emission decay (with a shorter lifetime of 0.42 ns) in surface-modified gold nanorods PTF-GNRs matched well with the excited-state quenching in its PL emission spectrum. Finally, surface modifications of gold nanorods by grafting fluorene-based conjugated copolymers (containing thiol-pendants to react with gold surfaces) were newly developed and verified by UV-visible spectroscopy, TEM, XPS, PL and lifetime measurements in this study.

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