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Preparation of Surface dendrimer-modified gold nanorods by Round-Trip Phase Transfer Ligand Exchange

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Abstract. In this work we firstly used partially thiolated polyamidoamine (PAMAM) dendrimer to replace CTAB molecules on the surface of gold nanorods (GNRs) by round-trip phase transfer ligand exchange, thus eliminating their cytotoxicity and improving their biocompatibility. The dendrimer-modified gold nanorods (dGNRs) were characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), UV-vis spectrometer, thermogravimetric analysis (TGA) and Fourier transformation infrared (FTIR) spectroscopy. The results indicate that dGNRs were successfully prepared.

1. Introduction
Gold nanorods (GNRs), because of their small size, strongly light enhanced absorption in near infrared region (NIR), and plasmon resonance enhanced properties, have tremendous applications such as photothermal therapy, cell imaging, and gene delivery [1]. However, cetyltrimethylammonium bromide (CTAB) is one of the widely used surfactant for the synthesis of GNRs. The double layer of CTAB on the surface of GNRs is problematic for bioconjugation, nonspecific adsorption of DNA, cytotoxicity, and stability. Therefore, it has been an extensive interest in modification of the surface of GNRs [2].

Dendrimers are a relatively novel class of polymers with highly ordered structure. The accretion of functional groups, symmetry perfection, nanosize, and internal cavities provide these novel dendritic nanocomposites many potential applications in biochemistry, gene therapy, and nanomedicine. Dendrimer coating of nanoparticle surfaces can alter the charge, functionality, and reactivity, as well as enhance the stability, dispersion and biocompatibility of the nanoparticles [3]. Hence, we develop a novel method to use partially thiolated polyamidoamine (PAMAM) dendrimer to replace CTAB molecules on the surface of GNRs by round-trip phase transfer ligand exchange, thus eliminating their cytotoxicity and improving their biocompatibility.

2. Experiments
Chloroauric acid (HAuCl\textsubscript{4}•3H\textsubscript{2}O), Cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH\textsubscript{4}), and ascorbic acid were obtained from the Aldrich Company. Methyl mercaptoacetate,
dodecanethiol (DDT), and mercaptoundecanoic acid (MUDA) were obtained from the Alfa Aesar Company. G4.0-PAMAM dendrimers with surface amine groups were stored in our lab. GNRs were synthesized according to the seed-mediated template-assisted protocol [4]. Functional PAMAM dendrimers, with a small number of thiol groups were prepared by reacting G4.0 PAMAM dendrimers with methyl mercaptoacetate[5].

Ligand exchange was achieved by a two phase extraction, which was performed according to reference [2]. First, CTAB was removed from the GNR-CTAB by extracting the GNRs into an organic phase via the ligand dodecanethiol (DDT). Then, the GNR-DDT was extracted into an aqueous phase by mercaptoundecanoic acid (MUDA). Ligands can be further customized to partially thiolated polyamidoamine (PAMAM) G4.0 dendrimer. Free unreacted dendrimers were removed by filtration with a 100K MWCO microcon device. The unreacted thiol groups on the GNRs were quenched with N-ethylmaleimide to minimize the dimer formation.

3. Characterization

HR-TEM (Hitachi H-700H) was used to confirm particle size and observe dendrimer coating. UV–vis spectra were measured at 20°C with a Shimadzu UV-2450 UV-visible spectrophotometer equipped with a 10-mm quartz cell. The 400–1100 nm wavelength region was scanned, since it includes the absorbance of the GNRs. TGA measurement was performed by a TGA 2850 thermogravimetric analyzer (TA Instruments) under N₂ in the temperature range of 30-700°C with an increasing rate of 5°C/min. The fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer Paragon-1000 FTIR Spectrometer.

4. Results and Discussion

![Figure 1. (A)TEM and (B)HRTEM images of dGNRs.](image)

Figure 1 shows the results of G4.0 PAMAM dendrimer functionalized GNRs characterized by TEM and HRTEM. As shown in Figure 1A, synthesized dGNRs are 42 nm in length, and 10 nm in width, indicating no significant size change after dendrimers modified. HRTEM imaging has been carried out to investigate the crystal structure of individual dGNRs in Figure 1B. It showed that the GNR with [110] orientation is single crystalline without twin planes and exhibited good crystalline and clear lattice fringes. The experimental lattice fringe spacing is consistent with the interplanar spacing of the [001] plane of GNRs.
Figure 2. UV–vis absorbance spectra of GNRs before and after dendrimers modification.

Figure 2 shows the UV–vis absorbance spectra of GNR-CTAB and dGNRs in the 400–1100 nm wavelength range, using deionized water as the solvent. The spectrum of GNR-CTAB showed that GNRs-CTAB have two absorption bands, a weak short-wavelength band around 520 nm and a strong long-wavelength band around 821 nm. Moreover, we found that the plasmon peaks of dGNRs exhibited no significant changes in peak width or position.

The G4.0 dendrimer coating layer on the surface of GNRs can be further confirmed by TGA analysis as shown in Figure 3. The grafted dendrimer content (%) of the dGNRs was calculated by TGA from the weight loss between 20°C and 800°C. For comparison, the TGA curve of GNR-CTAB without dendrimer coating is also shown. In the case of the GNR-CTAB, between 200°C and 800°C there was a continuous but not very obvious decrease (~4%) in weight, which is a typical weight loss for the CTAB layer on the surface of GNRs. The quantity of dendrimer attached to the GNRs is also shown in Figure 3. There has been a weight loss of ~17% for the dGNRs. All of these reveal the existence of G4.0 PAMAM dendrimer on the surface of GNRs.
To further study the replacement of CTAB molecules on the surface of GNRs by G4.0 dendrimer, the FT-IR spectra of (a) pure G4.0, (b) GNR-CTAB, and (c) dGNRs were determined. The IR peaks of pure G4.0 at 3288, 3070, 1644, 1546 cm\(^{-1}\) are assigned to the stretching vibration of –OH, amide A (mainly –NH stretching vibration), amide I (mainly C=O stretching vibrations) and amide II (the coupling of bending vibrate of N-H and stretching vibrate of C-N) bands, respectively. The difference between the IR spectrum of pure G4.0 and that of GNRs is obvious. Comparing the IR spectra of dGNRs with those of pure G4.0, the characteristic peak of –OH groups shifts to a high wavenumber of about 144 cm\(^{-1}\) and the other characteristic peaks are negligible variations. The results also indicate that the existence of G4.0 PAMAM dendrimer on the surface of GNRs.

5. Summary

The partially thiolated polyamidoamine (PAMAM) G4.0 dendrimer modified GNRs were prepared by round-trip phase transfer ligand exchange. The synthesized dGNRs were 42 nm in length, and 10 nm in width, whose plasmon peaks exhibited no significant changes in peak width or position. TGA curves and FT-IR spectra revealed the existence of G4.0 PAMAM dendrimer on the surface of GNRs. The novel nano-composite has potential versatility in biological applications such as therapy, sensing, and imaging.

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