



Unusual enhancement of fluorescence and Raman scattering of core-shell nanostructure of polydiacetylene and Ag nanoparticle

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ABSTRACT

The colorimetric and fluorescent properties of polydiacetylene (PDA) have been assessed for chemosensors and ultrafast biosensor applications. The low quantum efficiency, however, has delayed the further development of PDA based practical devices. Here, we synthesized a hybrid nanostructure of PDA with Ag nanoparticles of core. A core-shell type Ag@PDA blue phase nanoparticles showed significantly enhanced Raman scattering, whereas it dramatically decreased after the thermal treatment inducing phase transition of PDA to red. On the other hand the Ag@PDA red phase nanoparticles showed an evidently increasing fluorescence accompanying with the shortened lifetime. These unusual reinforced optical properties is attributed to the core Ag nanoparticles providing the surface selection rule and the surface enhancement effects by the localized surface plasmon. Consequently, our result demonstrates the hybrid structure of PDA with metal nanoparticles to be an alternative to overcome the limit of PDA for high performance devices.

1. Introduction

Polydiacetylene (PDA) undergoes a distinctive chromatic change during the phase transition of its structure [1,2]. Environmental stimuli cause a sub picosecond level occurring phase transition of PDA, which results in structural changes in the side chains or π -system on the main chain [3]. The chromatic properties such as thermo-, mechano-, and chemo-chromic property of PDA have been studied by examining its response with temperature, pH, mechanical stress, and bio or chemical interactions [4–8]. Interestingly, red phase PDA has shown a fluorescence property, whereas blue phase PDA is non-fluorescent [9,10]. The colorimetric and fluorescent properties of PDA have attracted considerable attention for the application of chemosensors and ultrafast biosensors [9,11–13]. However, the further development of practical PDA-based devices has been delayed due to the low quantum efficiency in both of red and blue phase. Therefore, it is necessary a significant enhancement of the fluorescence signaling process for high performance PDA-based devices.

One of the distinguishing optical properties of PDA is the Raman scattering [14,15]. The intensity of resonant Raman spectroscopy of PDA is related to the change in the conjugation path length on the PDA backbone. As the π -electron delocalization length affects the electronic excited state, the varying intensity of the resonant Raman signal is used as an indicator for not only the distribution of π -electron delocalization lengths [16], but also the electronic structure of the PDA [17]. The change from C=C to C \equiv C (or vice versa) occurs on the polymorphic organic chains while interacting with other nanomaterials or due to the chemical or biological reactions [18]. For example, the charge delocalization length of PDA changing the photochromic properties varies with the chemical reaction, incorporation of biomolecules, and embedding metal nanoparticles (NPs) [19–21].

In this study, we examined the non-linear Raman and photoluminescence (PL) properties of core-shell type hybrid nanostructure of PDA with Ag nanoparticles (NPs). Ag NPs provide an effective platform for surface-enhanced optical properties [22]. Therefore, it is interesting to examine whether the Ag NPs can synergistically enhance the Raman

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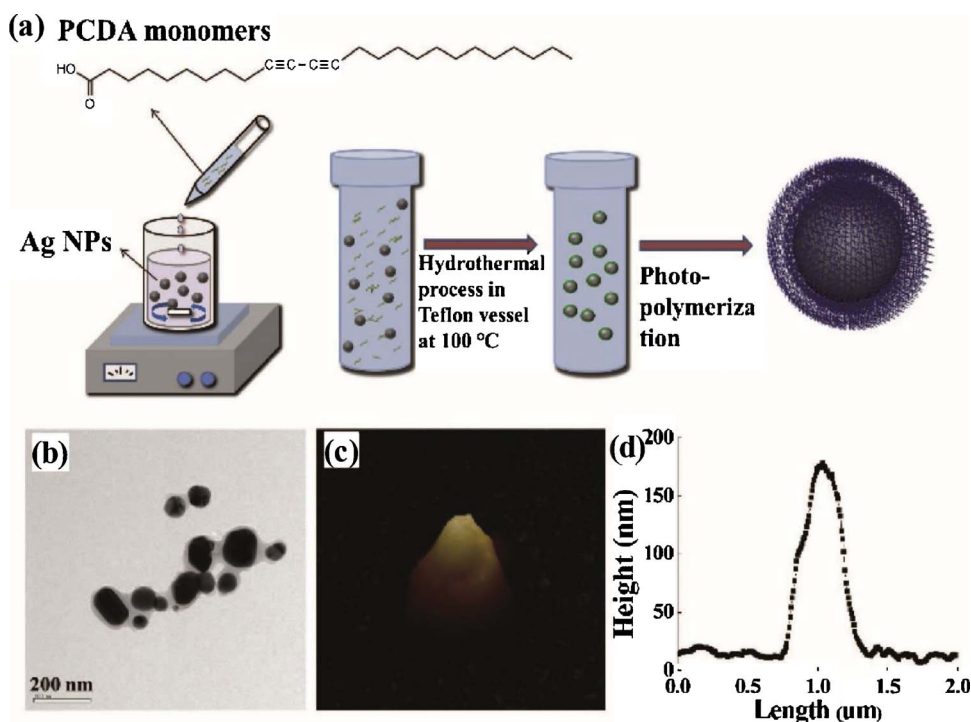


Fig. 1. (a) Schematic illustration of the fabrication procedure for the Ag@blue phase PDA NPs. (b–d) TEM image (b) and AFM image (c) of the core-shell structure of the Ag@PDA NPs, and cross sectional profile (d) of a single Ag@PDA NP.

or fluorescence characteristics of PDA. PDA synthesized on the Ag NPs (Ag@PDA NPs) were fabricated using conventional re-precipitation and hydrothermal methods. The Ag@PDA NPs exhibited an enhanced Raman signal when PDA was in the blue phase, whereas the PL intensity dramatically increased in the red phase.

2. Experimental section

2.1. Preparation of the Ag@PDA NPs

10,12-Pentacosadiynoic acid (PCDA) powder (purity 98%) was purchased from the Sigma Aldrich Company and used as received. The pristine PCDA NPs were prepared using a conventional re-precipitation method [18]. The PCDA powders were dissolved in tetrahydrofuran (THF) to a concentration of 1 mg/ml. The solution was then stirred vigorously for 10 min. The PCDA materials then formed spherical-shaped NPs in a deionized (DI) water solution. The solution was then stirred for 10 min, and ultrasonicated for an additional 10 min. The PCDA NPs solution was stored at 4 °C for 4 h. To fabricate the core-shell type Ag@blue phase PDA hybrid NPs, spherical-shaped Ag NPs were first prepared using the wet chemical reduction of silver nitrate (AgNO_3) with trisodium citrate based on a DI water solution. The Ag NPs were obtained from the DI water solution using a centrifuge. The as-prepared Ag NPs in DI water were then dispersed by a sonication process, which formed a stable dispersion in DI water without additional chemical modification. The PCDA monomers were dissolved in THF and injected rapidly into the Ag NP dispersed already in DI water. The same amount of PCDA monomers was used for each case. Subsequently, the complex solution with the dispersed PCDA and Ag NPs was placed into DI water in a hydrothermal chamber (Parr Instrument Acid Digestion Bombs, 4744 general-purpose bomb) and the mixture solution was heated to 100 °C in a vacuum oven for 5 h. During the hydrothermal process, a high pressure was applied to the PCDA and Ag NPs. The high affinity of the carboxylic groups of PCDA molecules favored the anchoring of the molecules, which caused the attached PCDA molecules to aggregate densely on the surface of the Ag NPs. After the hydrothermal treatment, the hydrothermal chamber was allowed to cool naturally to room temperature (RT). The pristine blue phase PDA

NPs and Ag@blue phase PDA NPs were obtained after drying on a glass substrate in a vacuum oven at RT and irradiated with 254 nm UV light for 15 min to induce photo-polymerization.

2.2. Characterization of the Ag@PDA NPs

The formation and surface morphology of the pristine PDA NPs and Ag@PDA NPs were investigated by scanning electron microscopy (SEM; JEOL JSM-5200) and a high-resolution transmission electron microscopy (HR-TEM; JEOL, JEM-3010). The nanoscale Raman and PL spectra for the pristine PDA and Ag@PDA single NPs were measured using a homemade laser confocal microscope (LCM) built around an inverted optical microscope (Axiovert 200, Zeiss GmbH). The incident laser was controlled carefully during sample loading to avoid unnecessary polymerization and color transition. The 633 nm line of a He-Ne gas laser was used for Raman excitation. The 488 nm line of an unpolarized Ar ion laser was used for PL excitation. The spot size of the focused laser beam on the sample in the LCM experiment was estimated to be approximately 200 nm. For the LCM Raman mapping experiments, the scanning area was tens of μm squares, consisting of 128 by 128 pixels containing 16384 spectra in a single mapping image. Each pixel contained the corresponding Raman spectrum of a single NP. Owing to the limited dispersion region of the spectrometer grating at 633 nm excitation, bands for the C–C–C, C=C, and C≡C stretching modes were not observed in the same spectral window. Therefore, the spectra were divided into 2 areas and the Raman signal was measured carefully to escape the modification of PDA. The LCM Raman mapping of the Ag@PDA NPs was analyzed using WITec project software for the scanning probe data. The PL signal was focused on a multimode fiber that acted as a pinhole for confocal detection. The other end of the multimode fiber was connected to a photomultiplier tube for PL imaging for the PL spectral measurements. The laser power incident was fixed on the sample, and the acquisition time was fixed for each PL spectrum in the LCM PL measurements at 35 μW and 1 s, respectively. Detailed methods for the LCM Raman and PL experiments are reported elsewhere [23]. PL decay characteristics were observed using a fluorescence lifetime spectrometer (FL920, Edinburgh Instruments, Wales) which was operated based upon time correlated single photon counting

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