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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≡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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