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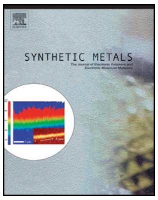

A facile fabrication of polydiacetylene nanowires and their response to aqueous solutions with basicity

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ABSTRACT

Polydiacetylene nanowires composed of 10, 12-docosadiynedioic acid (DCDDA) were fabricated simply by solution reprecipitation method with diameter of 50–150 nm and length of several micrometers. As the DCDDA nanowires are exposed to aqueous solutions of pH less than 7, there is no fluorescence emission observed. In contrast, we observed the a red-fluoresce response of the nanowires as they exposed to solutions of pH ranging 8–10, reflecting the degree of ionization of carboxylate head groups.

1. Introduction

In recent years, one-dimensional nanostructures such as wires, rods, belts, and tubes are attracting considerable interest due to potential applications in electronic devices [1–3], chemical sensors [4–7], and biosensors [7–9]. In particular, one-dimensional nanomaterials have been described as a good candidate for a sensitive sensing system owing to the high surface-to-volume ratio of the nanostructures. For example, since carbon nanotubes (CNTs) were discovered by Iijima in 1991 [10], the CNTs-based gas sensors have attracted intensive research interest because of they have high sensitivity towards gas molecules, fast response time, and relatively low operating temperature. Kong et al. demonstrated the first gas sensors based on single-walled carbon nanotubes (SWNTs) [4]. Since then, many techniques have been developed to improve the performance of CNT gas sensors [5,11].

In addition, many researchers have studied chemical sensors based on semiconductor nanowires, such as silicon nanowires, SnO_2 nanowires, ZnO nanowires, and In_2O_3 nanowires. These sensors usually work via a change in the surface charge of the nanowires in the presence or absence of target molecules [6,8]. In this system, target molecules are detected only by a change in the electronic conductance. Nevertheless, the control of doping concentrations in semiconducting nanostructures remains a challenge.

Conjugated polymers (CPs) that are characterized by a delocalized electronic structure have attracted much attention due to their potential in chemical and biological sensing applications [12]. In comparison to small molecule-based sensors, π-conjugated polymer-based sensors show enhanced detection capability due to a transferring signal along the backbone of the CPs [13]. Of the various CPs, polydiacetylenes (PDA) have been studied as an active platform for chemical and biological sensing because they undergo a visible color change from blue to red and a fluorescent change from non-fluorescent to red-fluorescent in response to a variety of external stimuli, such as temperature [14–16], pH [16,17], chemical solvent [18], and ligand-receptor interaction [19–23]. This phase transition occurs when external stimuli impose stresses that altering the delocalization length of π-electrons along the backbones of PDA. Various one-dimensional PDA nanostructures have been fabricated by self-assembly of highly ordered diacetylene monomers [24,25]. In addition, a number of researchers have suggested that hydrogen bonding, hydrophobic interactions, and π-π stacking act as the driving force of the self-assembly [24,26].

In this paper, PDA nanowires with a highly organized state were fabricated by the reprecipitation method. A bolaamphilic diacetylene monomer was adopted in order to facilitate the formation of nanowires. The nanowires were treated with various pH

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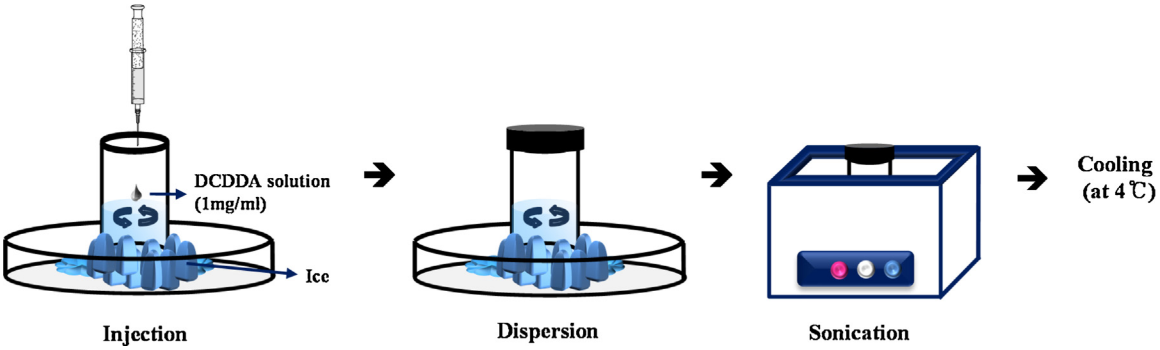

Fig. 1. General procedures for the preparation of DCDDA nanowires.

solutions and corresponding fluorescent change of nanowires was observed.

2. Experimental

2.1. Materials

10,12-Docosadiyndioic (DCDDA) monomers was purchased from GFS chemicals.

2.2. Preparation of polymeric DCDDA nanowires

We prepared PDA nanowires using DCDDA containing two carboxylic groups by the reprecipitation method. A 1 mg/ml tetrahydrofuran (THF) solution of DCDDA was injected into stirring deionized (DI) water at 4 °C using a micropipette. After stirring for 10 min, the resulting solution was sonicated for 5 min and the solution dispersed DCDDA nanowires were stored in the refrigerator at 4 °C for 4 h (Fig. 1). The nanowires were polymerized by exposure to 254 nm UV light at an intensity of 1 mW/cm^2 for 30 min.

2.3. Immobilization of DCDDA nanowires on amine modified glass slide

0.1 mM DCDDA nanowire solution was reacted with 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)/N-hydroxysuccinimide (NHS) solution in a volume ratio of 10:1. After being allowed to shaking for 30 min, the resulting solution was dropped on the amine—modified glass slide glass, and then incubated for 100 min under controlled humidity.

2.4. Characterization

The morphology of the nanowires was observed through a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4300) and a high-resolution transmission electron microscope (HR-TEM, Tecnai G2, Fei). The visible absorption spectra of the DCDDA nanowires were obtained using an HP 8453 UV–vis spectrophotometer (Agilent Technologies, Waldbronn, Germany). The fluorescent images of the nanowires were recorded using a fluorescence microscope (BX51, Olympus, Japan).

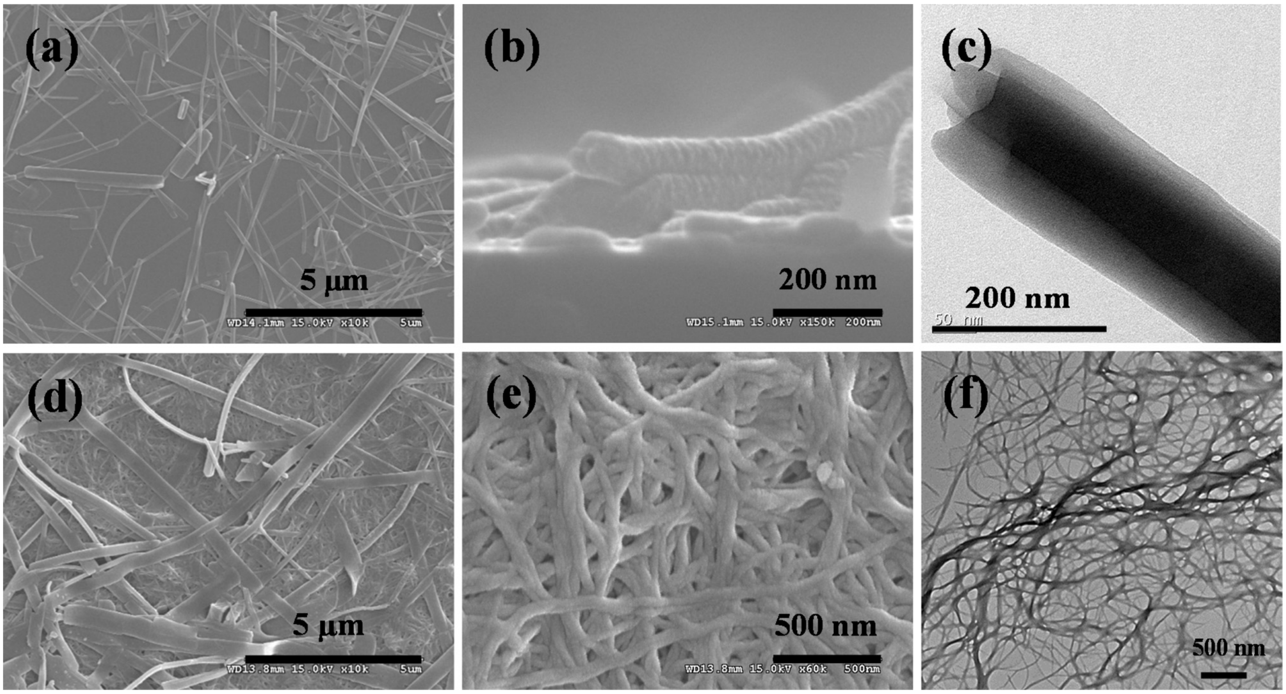

Fig. 2. The morphology of self-assembled DCDDA nanowires. (a) SEM image of polymeric DCDDA nanowires. (b) Cross-sectional SEM image of polymeric DCDDA nanowires. (c) Magnified TEM image of DCDDA nanowire. (d), (e) SEM images of heated polymeric DCDDA nanowires and (f) TEM image of heated polymeric DCDDA nanowires.