

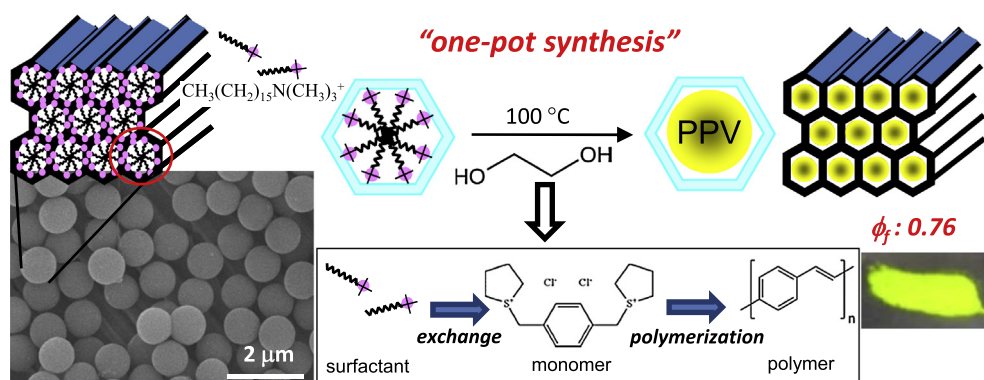
In situ green synthesis of fluorescent monodispersed mesoporous silica spheres/poly(*p*-phenylenevinylene) composites



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GRAPHICAL ABSTRACT



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ABSTRACT

A facile one-pot synthesis for the composite materials fabricated from conjugated polymer, poly(*p*-phenylenevinylene) (PPV), and monodispersed mesoporous silica spheres (MMSS) is demonstrated. Composite materials having superior photoluminescence properties are easily obtained using ethylene glycol as a reaction solvent in which PPV monomers are effectively exchanged with cationic surfactants in MMSS and subsequently polymerized in the solution. The method can prevent serious reduction of photoluminescence properties which occurs inevitably during thermal treatment (200 °C) to polymerize PPV. In our method, the temperature of 100 °C is enough to obtain the fully polymerized PPV, which is confirmed in Fourier transform infrared (FT-IR) spectrum. Reaction mechanism is verified through direct observation of its distinguishable color changes in the reaction solution and the measurement of surface electrical potential (ζ -potential). The obtained results strongly support that PPV chains are impregnated within mesopores in isolated condition, leading to high fluorescence quantum yield (nearly 80%). Compared to the conventional route, this method reduces multistep synthesis to one-step and eliminates high temperature and high vacuum process, leading to the facile eco-friendly procedure.

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Abbreviations: MMSS, monodispersed mesoporous silica spheres; PPV, poly(*p*-phenylenevinylene); PPV-monomer, *p*-xylylenebis (tetrahydrothiophenium chloride).

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1. Introduction

After poly(*p*-phenylene vinylene) (PPV) was firstly applied as an active layer in an organic light-emitting diode (OLED) [1] in 1990, a number of π -conjugated polymers have attracted a great deal of

attention to fabricate photonic devices. A considerable amount of research has been devoted to PPV because it exhibits superior optoelectronic properties [2–4]. In spite of these attractive features, its inherent insolubility endows poor processability which can be a major drawback for the potential applications. To conquer this problem, either employment of a soluble precursor, or modification of the polymer backbone by adding functional groups is plentifully reported. Up until now, the latter method generates variety of soluble PPV-derivatives, such as poly[2-methoxy-5-(20-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) [5–7] and poly(*p*-phenylene-ethynylene)-alt-poly(*p*-phenylene-vinylene) [8]. However, some intrinsic problems still remain that PPV-derivatives are likely to form chain aggregations, causing the generation of interchain excimers which gives negative impact on the photoluminescence properties. In addition, the existence of C=C bonds within polymer backbone impairs the stability due to oxidative degradation. Impregnation of PPV-derivatives within porous host materials is the possible solution to prevent the chain aggregation as well as to enhance the stability.

Wolf et al. employed the deprotonated surface of the mesoporous silica MCM-41 and demonstrated that PPV was distributed throughout the meso channel, revealing the isolation of polymer chains [9]. Garcia and co-workers reported that incorporation of MEH-PPV within internal space of montmorillonite can serve a positive effect on stabilization against the attack of oxygen and moisture [10]. Impregnation of PPV-derivatives into inorganic host materials is emerging research area due to the potential advantage, which cannot be achieved in unencapsulated conjugated polymers. Such composite materials should be available for the application of high performance devices as well as for the fundamental study which brings us new scientific possibilities.

We have developed a novel synthetic route for the fabrication of composite materials from mesoporous silica spheres and PPV through a new ion-exchange method [11]. Mesoporous silica spheres containing cationic surfactant species which act as structure-directing agents are processed in a methanolic solution of *p*-xylylenebis-(tetrahydrothiophenium chloride), followed by thermal treatment in vacuo. Insoluble PPV polymer chains are encapsulated within mesopores of host silica spheres, leading to the prevention of chain aggregations, thus improving the fluorescence quantum yield. The obtained yield is about 0.8 under an argon-degassed dispersion, which is much higher than those previously reported values. Sharma et al. has obtained a fluorescence quantum yield of 0.2 for unencapsulated PPV [12] and the value of 0.27 have been reported by Greenham's group for the unprotected pristine PPV [13]. However, the strategy in the previous paper needs a two-step synthesis process; First, PPV monomer is incorporated into mesoporous channels via ion exchange process in methanolic solution. Second, the material is processed in the furnace for the following thermal treatment to eliminate tetrahydrothiophenium group from monomer, leading to polymerization within mesopores. This elimination process is quite common among the previous reports with respect to the synthesis of PPV relatives. Kumar and co-workers prepared PPV/silica composite by sol-gel reaction from the ethanol solution of PPV monomer, followed by the thermal elimination up to 250 °C under an inert condition [14]. Herold et al. conducted the thermal treatment in Ar atmosphere after the precursor was prepared [15]. In all cases, the thermal elimination process of the tetrahydrothiophenium group from monomer under an inert atmosphere is inevitable to obtain the fully polymerized PPV. However, during the thermal treatment process, deterioration of photoluminescence properties with increasing the temperature was inevitably observed. Decreasing the synthesis temperature, preferably weeding out the thermal treatment under the specific atmosphere is suggested to facilitate the reaction process as well as to enhance the photoluminescence

properties at the same time. In addition, with the growing awareness for environmental protection and resource conservation, one-pot synthesis is much more desirable as a green chemistry strategy.

In this study, ethylene glycol is chosen as a solvent during ion exchange reaction instead of methanol. Ethylene glycol is typical dihydric alcohol with higher boiling point than methanol and can act as a good solvent both for the PPV monomer (*p*-xylylenebis-(tetrahydrothiophenium chloride) and for the cationic surfactant [16]. It is often reported that methoxy (or ethoxy) groups are attached on the surface of mesoporous silica during the methanol (or ethanol) extraction of the cationic surfactant [17]. The small organic groups of monohydric alcohols promote the hydrolysis between the silanol groups on the silica surface, which might cause the prevention of effective ion exchange reaction of PPV monomer. On the other hand, ethylene glycol with higher boiling point enables to polymerize PPV by eliminating tetrahydrothiophenium group in situ during ion exchange reaction. The larger molecular size and higher boiling point of ethylene glycol can allow us to design the more facile one-pot route towards the fabrication of composites with high quantum yield from PPV and mesoporous host materials. The validity of our proposed synthesis mechanism is further clarified.

2. Experimental section

2.1. Materials

Tetramethyl orthosilicate (TMOS) and cetyltrimethylammonium chlorides [C₁₆H₃₃(CH₃)₃NCl, CTMACl] were obtained from Tokyo Kasei Kogyo Co., Ltd. Methanol, ethanol, 48% hydrofluoric acid solution, 1 M sodium hydroxide solution, ethylene glycol were purchased from Wako Pure Chemical Industries, Ltd. *p*-xylylenebis (tetrahydrothiophenium chloride), abbreviated as PPV-monomer, was prepared by established procedure [18] at NARD Chemical Industries Co., Ltd. These chemicals were used without further purification.

2.2. Synthesis of monodispersed mesoporous silica spheres (MMSS) impregnated with PPV

Monodispersed mesoporous silica spheres (MMSS) was synthesized via a surfactant-templating method using CTMACl as a template agent. In this study, as-made MMSS, which contains cetyltrimethylammonium ions (CTMA⁺) inside the mesopores, was used as host materials. The synthesis procedure for MMSS has been described in elsewhere [19]. The experimental procedure of the template ion exchange method for the synthesis of PPV@MMSS is schematically illustrated in Fig. 1. A 0.652 g of PPV-monomer was first dissolved in 40 mL of ethylene glycol with magnetic stirring. Then, as-made MMSS (0.503 g) was added to this solution. The mixture was heated at various temperatures ranging from 80 to 120 °C at ambient atmosphere to exchange CTMA⁺ ions with PPV-monomer cations as well as to polymerize PPV simultaneously. The reaction was continued from 3 to 15 h, resulted in bright yellow powder. The powder was collected by filtration and washed with ethanol repeatedly, followed by drying at ambient temperature. The obtained sample was denoted as PPV@MMSS – (x) °C – (y) h, where x and y stand for the synthesis temperature, and time, respectively (Route (a) in Fig. 1). As a control, we also prepared PPV@MMSS material from methanol solution (Route (b) in Fig. 1) at 65 °C for 5 h according to the previous report [11]. In this case, subsequent heating process to eliminate the tetrahydrothiophene group is inevitable and the elimination was conducted at 200 °C in vacuo. The prepared control sample was

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