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Porous PEDOT–SiO_2 hybrid conductive micro particles prepared by simultaneous co-vaporized vapor phase polymerization

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ABSTRACT

Porous PEDOT–SiO_2 particles were successfully prepared using simultaneous co-vaporized vapor phase polymerization (SC-VPP). By controlling the TEOS content, the morphologies of the obtained particles could be tuned from appearance of hollow egg shells aggregates to the hybrid particle composed of microspheres. Despite only having up to 40% of TEOS in the SC-VPP process, SiO_2 accounts for over 90% of the resulting hybrid particle, because the hydrolysis/condensation reactions of TEOS would be much faster as compared with the PEDOT polymerization. The specific capacitance of a single hybrid particle decreased with increasing SiO_2 portion, owing to changes in its external/internal structures.

Introduction

Since the discovery of polyacetylene as the first conductive polymer (CP) in 1977 [1], several CPs such as polyaniline, polypyrrole (PPy), and poly(3,4-ehtylenedioxythiophene) (PEDOT) are gaining much attentions owing to their high electrical conductivity and stability in the natural state. CPs have been widely applied in the fields of "green" electronics [2], biomedical materials [3,4], displays [5,6], and energy science [7,8,9]. In particular, PEDOT is among the most successful conjugated polymer, with excellent conductivity, good ductility, and high flexibility [10–13]. However, organic CPs have fundamental limitations [14–16]. In long-term practical applications, the poor physicochemical properties including pencil hardness, anti-scratching property, solvent-, mechanical-, and wear resistance of organic CP layer could deteriorate device reliability. Organic–inorganic hybridization could be a potential route to overcome such drawbacks of organic CPs. For example, PEDOT–SiO_2 composites have been reported to enhance the device performance in energy applications [17–20]. A highly transparent and efficient counter electrode was easily fabricated using PEDOT–poly-(styrenesulfonate) (PEDOT–PSS)–SiO_2 inorganic/organic composite, and used in bifacial dye-sensitized solar cells [17]. Composite films consisting of PEDOT–PSS and SiO_2 particles were prepared via the simple method of direct vacuum filtration to increase the thermoelectric power factor [18]. Electrodes based on (PEDOT–PSS)–SiO_2 particles slurry could be used in electrochemical flow batteries with high energy density and scalable storage capacity [19,20]. Despite the successes in the applications using PEDOT and SiO_2 particle mixture, it is difficult to completely disperse the CP and the inorganic material at the molecular level. It can be expected that an interpenetrating network structure, which contains a homogenous mixture of PEDOT and SiO_2 molecular chains, might be required to further enhance the performance of the aforementioned devices.

Several of our previous papers showed that organic–inorganic hybrid CP films could be simultaneously polymerized in the vapor phase with the co-vaporization of the monomer for CP and metal oxide precursors [21–25]. The simultaneous co-vaporized vapor phase polymerization (SC-VPP) would be a approach to prepare

Abbreviations: CP, conductive polymer; CT, computerized tomography; DCM, dichloromethane; EDOT, 3,4-ethylenedioxythiophene; EDS, energy dispersive X-ray spectroscopy; FIB, focused ion beam; FTS, iron (III)-ρ-toluenesulfonate; LCR, Inductor/Capacitor/Resistor; PCM, phase change material; PEDOT, poly(3,4-ehtylenedioxythiophene); PPy, polypyrrole; PS, polystyrene; PSS, poly-(styrenesulfonate); SC-VPP, simultaneous co-vaporized vapor phase polymerization; SEM, scanning electron microscopy; TEOS, tetraethylorthosilicate.

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versatile organic–inorganic composites homogeneous at the molecular level, which could not be easily accomplished by using simple solution–solution and/or solid–solution mixing. The mixing of various species in the gas phase can effectively overcome the solubility limitation in the liquid/solid mixtures. As a result, the thus fabricated PEDOT–SiO_2 and PPy–SiO_2 hybrid films had much higher conductivity than the pristine PEDOT film, due to smoother surface endowed by the SiO_2 component in the hybrid film [22–24]. Moreover, the PEDOT and SiO_2 composite shell could be coated onto golf ball-shaped poly(D,L-lactide-*co*-glycolide) microparticles while retaining their complex surface morphology, resulting in the modulation of both the chemical and physical properties of the microparticles [25]. This is because of a non-invasive (i.e., with no change in the surface morphology) nanoscale conformal coating of PEDOT–SiO_2 hybrid material. Up to date, we have prepared 2-dimensional (2D) PEDOT–SiO_2 hybrid coated films on surfaces with various morphologies (i.e., flat film, microspheres, and golf ball-shaped microspheres having nano-sized dimples).

In this work, we further expand this approach to fabricate 3D porous PEDOT–SiO_2 particles. This novel conductive 3D structure can be used in biomedical applications [26–28] as well as energy applications as previously mentioned. The synthesis of CP-based spherical, conductive nano- and/or micro-particles has been extensively researched by using self-assembly-assisted chemical polymerization [29,30], or by the template method using silica and polystyrene (PS) particles [31,32]. On the other hand, the use of microfluidic devices can achieve a high homogeneity of the droplets and control the particle size from the microscale to the nanoscale. It also provides control over the shape of the particles via using a wide range of materials, including hydrogels, metals, polymers, and polymers doped with functional additives [33–35]. Moreover, golf ball-shaped polymer particles with internal pores can be easily fabricated by using a microfluidic device with phase change material (PCM) [36–38]. However, to the best of our knowledge, there have been no reports concerning the fabrication of porous PEDOT microspheres using SC-VPP combined with porous PS template prepared by droplet microfluidics. The morphology and pore characteristics of the produced porous PEDOT–SiO_2 particles were investigated for varying SC-VPP conditions, and confirmed by scanning electron microscopy (SEM) and micro-computerized tomography (CT). Their chemical compositions were characterized by energy dispersive X-ray spectroscopy (EDS) analysis. The electrical properties of a single porous PEDOT–SiO_2 particle were also measured by a LCR meter combined with a test vehicle prepared by focused ion beam (FIB)-assisted Pt deposition.

Material and methods

Chemicals

In order to produce the porous PS template, PS (Sigma–Aldrich, M_n = 170,000) was dissolved in dichloromethane (DCM, JUNSEI, Japan), and then mixed with 2-methylpentane (M_w = 86.18, TCI, Japan) as an organic PCM. Since the template was manufactured by the microfluidic device as shown in Fig. S1 in the online version at doi:10.1016/j.jiec.2018.02.003, poly(vinyl alcohol) (Sigma–Aldrich, Mw = 9000–10,000) was dissolved in distilled water to obtain a solution for the continuous flow. A solution of iron(III)-ρ-toluenesulfonate hexahydrate (FTS, Sigma–Aldrich) was used as an oxidizing agent of PEDOT polymerization, and was impregnated into the porous PS microspheres. In the SC-VPP process, the oxidant-impregnated particles were exposed to gas-phase 3,4-ethylenedioxythiophene (EDOT, MD Bros., Japan) as the monomer of PEDOT and tetraethylorthosilicate (TEOS, SAMCHUN, Korea) as the monomer of SiO_2. After the polymerization, the oxidant and unreacted monomers were washed off with ethanol (SAMCHUN, Korea).

Preparation of porous polystyrene template

PS (pellet type) was dissolved at 5 wt% in DCM for 20 min. To produce pores in the PS microspheres, 10 wt% of 2-methyl pentane was added to the solution and mixed for 10 min. When the dissolution was complete, it was placed in a syringe-PTFE tube assembly that was mounted on a syringe pump. Then, the syringe was connected to the inner line (discontinuous oil phase) of the microfluidic device as shown in Fig. S1 in the online version at doi:10.1016/j.jiec.2018.02.003. Another assembly of a tygon tube and syringe was filled with 1 wt% aqueous solution of PVA and mounted on another syringe pump. Then connected the syringe to the outer line of the device where the continuous flow will occur. The flow rate of the syringe pump was set to 1 ml/h for the inner line and 15 ml/h for the outer line. At the outlet of the device, a PTFE tube was used to immerse the droplets produced inside the device in 1 wt% PVA solution. This solution containing droplets was stored for one day. Afterwards, the droplets became porous solid PS particles and floated on the top of PVA solution. After washing the particles with vacuum filtration, they were treated with a sonicator for 30 s for effective cleaning. This cleaning process was repeated three times. Finally, the filtered particles were dried in a vacuum oven at 60 °C for 1 h. The dried porous PS microspheres were used as a template for the SC-VPP process to make the porous conductive particles.

Preparation of porous PEDOT-based hybrid particles

FTS was dissolved at 20, 30, or 40 wt% in 1-butanol. The prepared porous PS templates in the previous step were impregnated with this FTS solution by stirring. After four days, the impregnated particles were separated using a vacuum filtration device without washing, and then dried in a vacuum oven at 60 °C for 10 min. The FTS-impregnated particles were transferred to a small mesh pocket, and placed in the middle of the glass reactor where the SC-VPP will occur. A few drops of liquid EDOT and/or TEOS were placed in a petri dish located at the bottom of the reactor. Then, the reactor was closed by a lid and sealed using sealing film. A schematic diagram of the SC-VPP chamber can be seen in our recent paper [9] TEOS was co-evaporated with EDOT by 10, 20, 30, 40 wt% in the monomer mixture in order to prepare the porous PEDOT–SiO_2 hybrid particles. After polymerization for 24 h, the particles were and immersed in distilled water for 2 h, and then filtered and washed with distilled water and ethanol using a vacuum filter. After washing, the particles were dried in an oven at 60 °C and immersed in DCM for 2 h in order to remove the PS template. Then, the PS-removed particles were separated using vacuum filtration to obtain PEDOT-based particles having an inverted pore shape.

Characterization of porous PEDOT–SiO_2 particles

The surface and cross section of the particles were observed using an optical microscope (Nano Inside, MSDM-1250, Korea), and a normal scanning electron microscope (TESCAN, VEGA3, Czech) in order to confirm the pores of the PS template prepared by a syringe pump (KD Scientific, LEGATO 200) and a microfluidic device. The morphologies of the surface and cross section were also confirmed using another optical microscope (Nano Inside, MSDM-1250), normal SEM (TESCAN, VEGA3, Czech), and FE-SEM systems (TESCAN, MIRA LMH, Czech). Micro-CT (SkyScan 1272, Bruker AXS), which is non-destructive tool for visualizing the interior of an object, was used to image and characterize the pores in the 3D

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