



Single-walled carbon nanotube-mediated physical gelation of binary polymer blends: An efficient route to versatile porous carbon electrode materials



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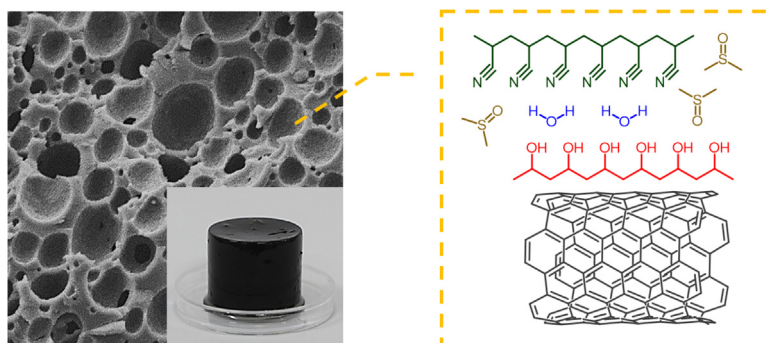
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HIGHLIGHTS

- The effect of co-nonsolvents on the microstructure of the gel was demonstrated.
- The SWNT-mediated physical gelation of binary polymer blends were reported.
- Physically cross-linked gels were converted to versatile electrode materials.

GRAPHICAL ABSTRACT



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ABSTRACT

A non-covalent approach to prepare nanotube-containing gels was developed based on the physical gelation of two polymers, polyvinyl alcohol (PVA) and polyacrylonitrile (PAN), with different microphase behaviors in water/dimethyl sulfoxide (DMSO) mixture. Single-walled carbon nanotubes (SWNTs) were incorporated into the binary-polymer/binary-solvent system to alter the physical gelation behavior and, in turn, to achieve unique physicochemical characteristics of the resulting gels. SWNTs were wrapped with PVA, which extended the binary polymer system to a ternary polymer system consisting of PVA bound to SWNTs, free PVA, and PAN. It was observed that the SWNT/PVA/PAN ensembles gelled with appropriate amounts of water in DMSO and the gelation behavior was reversible. The amounts of water and SWNT were determined to be key parameters affecting the formation of the gels. The SWNT/PVA/PAN gels were successfully converted to carbonaceous gels via heat treatment in an inert atmosphere, which can be extended to several applications such as electrode materials. The macroporous carbonaceous gels were further functionalized via manganese deposition followed by potassium hydroxide activation, which yielded excellent cell performance in a neutral electrolyte with the energy density of 9.6–24.8 Wh kg⁻¹ and power density of 8.0–0.1 kW kg⁻¹.

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1. Introduction

Polymer gels have attracted considerable interest from both academic and industrial points of view for a long time. A substantial amount of research on the gelation of polymers has been carried out to understand its fundamental mechanism, which has provided good solutions to various industrial problems [1–8]. Polyacrylonitrile (PAN) is an invaluable material for industrial applications because it is the best precursor for producing carbon materials via thermal treatment. Therefore, the gelation behavior of PAN has been an important research topic in the past. It was reported that propylene carbonate solvent was favorable to achieve crystalline PAN at high concentration, which led to the physical gelation of PAN [9]. However, PAN is not easily crystallized in common solvents such as dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The crystallinity of PAN may originate from the polymer precipitation accompanying the gelation rather than from the gelation itself. The physical gelation of PAN in DMF–water mixtures has been also reported in the literature [10]. DMF is a good solvent for PAN whereas water is a nonsolvent for PAN. Temperature change and water content are considered to be key variables affecting gelation. Amorphous transparent gels were obtained with 3% water in DMF, and increasing the water content to 10% yielded turbid gels with enhanced polymer chain ordering. In most cases, physical gelation is reversible-controlled [11]. However, it has also been reported that the treatment of PAN with strong bases in DMSO yielded chemically cross-linked gel structures, which might be due to the cyclization of chains owing to a nucleophilic attack on the nitrile carbon [12]. Polyvinyl alcohol (PVA) is also a synthetic polymer widely used in industries owing to its remarkable characteristics such as high water solubility, light polarization, high strength and modulus, and biocompatibility. Physical gelation of PVA has been performed in mixtures of DMSO and water [13,14], in contrast to that of PAN. It was observed that the gelation mechanism was based on spinodal decomposition and crystallization, which was similar to that of PAN. Physical gels constitute three-dimensional networks whose junction points consist of physical bonds between polymer chains. Despite many investigations, there are still controversial issues regarding the physical gelation mechanism of polymers because the nature and structure of the junctions are highly complex.

Recent progress in nanotechnology has allowed the combination of various nanomaterials with gels, providing unique opportunities to achieve promising characteristics of materials for advanced applications. For

example, single-walled carbon nanotubes (SWNTs) were incorporated into a biocompatible hydrogel matrix, which allowed the detection and imaging of a small molecule target using pressure-sensitive fluorescence change in a mouse tissue model [15]. In addition, graphene flakes were embedded into hydrogel nanofibers and the resulting graphene hydrogel nanofibers showed the ability to selectively uptake and recognize cationic dye molecules in an aqueous solution [16,17]. Most of the gels were chemically cross-linked, and therefore, they were brittle and lacked the ability to self-heal. In this work, we report, for the first time, the physical gelation behavior of an SWNT-containing binary polymer (PVA and PAN) blend in the presence of water. PVA-wrapped SWNTs were introduced as a dispersed phase to the continuous phase PAN, in which the concentration of the SWNTs was varied to control the microstructure and properties of the resulting products. Notably, the PVA bound to SWNTs can result in distinct chain conformation and mobility of the polymer chains in the presence of water compared with free PVA chains. Subsequently, appropriate amounts of water were added to the SWNT-containing binary blend systems, which allowed the gelation of the SWNT-containing binary polymer blends. Water acted as a porogen to enable the control of the porosity of the gels. Furthermore, the SWNT-in-binary-polymer gels (SbPGs) were successfully converted to carbon structures, SWNT-in-carbon gels (SbCGs), via heat treatment under an inert atmosphere. The electrochemical properties of the SbCGs were tuned by tailoring the microstructure of the polymer precursors i.e., SbPGs.

2. Results and discussion

Two polymers with different solubilities in DMSO, i.e., PVA and PAN, were used to prepare SWNTs-containing gels with water. First, SWNTs were wrapped with PVA chains in DMSO solution (Fig. S1). The PVA-wrapped SWNTs were mixed with appropriate amounts of PAN and water in DMSO at 90 °C and the subsequent cooling of the mixture solution to 25 °C resulted in a gel structure, namely SbPG. The SbPG was molded into shape-persistent, freestanding objects, such as films and columns, by virtue of its good mechanical strength (Fig. S2). The amounts of water (relative to DMSO) and SWNTs were the key parameters affecting the formation of the gels. The formation of the gel was sensitive to the amount of water added, as typically illustrated in Fig. 1a and b. The gelation was not occurred at the water/DMSO volume ratio of 6×10^{-2} , which is less than 7×10^{-2} . There was a range of water amounts to generate the gel (see Fig. S3), indicating that water plays an essential role in the formation of the gel structure. The chemical

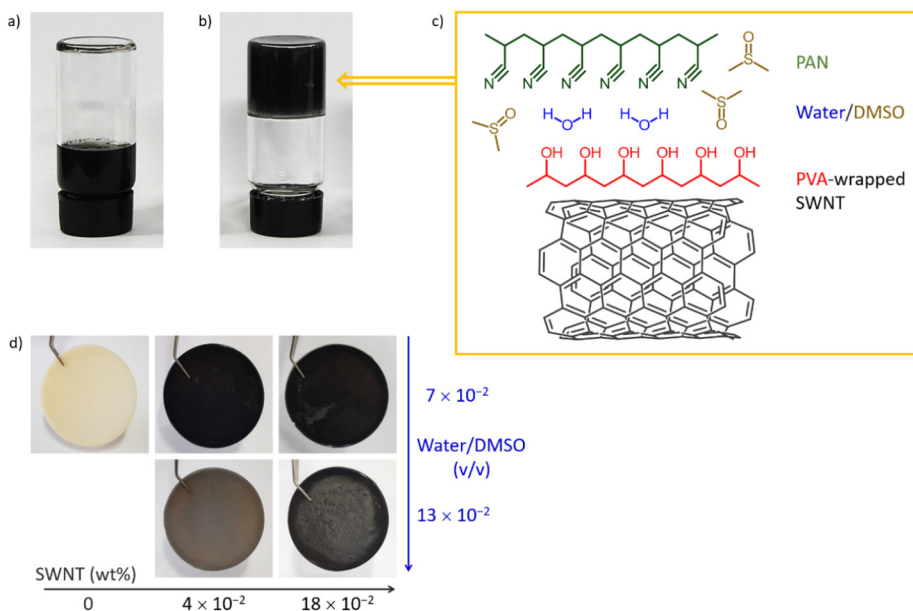


Fig. 1. Formation of gels depending on the water content (water/DMSO volume ratio): a) 6×10^{-2} and b) 13×10^{-2} (0.04 wt\% SWNT). c) Scheme illustrating the microstructure of the gels comprised of SWNT, PVA, PAN, and water. d) Photographs showing the aerogel films prepared with different amounts of SWNT and water (the aerogel was obtained via freeze-drying).

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