Supporting Information

Immobilization of Polymeric Fluorogen on PDVB Nanotube with Assistance of Supercritical CO₂ for Functional Films

Guiheng Xu^a, Qun Xu^a, Anjun Qin^b, Jingtao Cheng^a, Nan Wang^a, Junyi Wei^a, Chengliang Zhang^c, Zhenzhong Yang^{*c}, Ben Zhong Tang^{*d}

^a College of Materials Science and Engineering, Zhengzhou University, Zhengzhou, China. Fax: +86 371 677678; Tel.: +86 371 67767827; E-mail: <u>gunxu@zzu.edu.cn</u> ^b Department of Polymer Science and Engineering, Zhejiang University, 310027, China; ^c State Key Lab of Polymer Physics & Chemistry, Chinese Academy of Science; E-mail:yangzz@iccas.ac.cn ^d Department of Chemistry The Hong Kong University of Science & Technology Hong

^dDepartment of Chemistry, The Hong Kong University of Science & Technology, Hong Kong, China. E-mail:<u>tangbenz@ust.hk</u>

Experimental Section

Materials: Polydivinylbenzene (PDVB) nanotubes were supplied by the group of Prof. Zhenzhong Yang in the Chinese Academy of Science.²⁰ Poly(aroxycarbonyltriazole) (PACT) $(M_{\rm W} = 15100 \text{ g/mol}, \text{PDI} = 1.4)$ was prepared by our previously reported procedures.¹⁴ DMSO was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Poly (ethylene glycol) (PEG, M_W =10000) was supplied by the Kermal Chemical Reagent Co., Ltd. (China).

Samples Preparation: In a typical experiment, there were three basic steps to fabricate the PDVB/PACT nanocomposite. First, PACT (0.4 mg) was dissolved in DMSO (2 g) at the suitable temperature (25 °C). PDVB nanotubes of 0.3 mg were dispersed in 3 g of DMSO, and the mixture was ultrasonicated for 1 h at 40 °C before being added into the corresponding PACT solution. Second, the hybrid solution was quickly transferred into the \overline{SC} CO₂ apparatus (a 50 ml stainless steel autoclave) as quickly as possible and experimental condition was controlled to reach the determined temperature and pressure. Third, the reaction time was controlled for 3h. At last, CO_2 was slowly released to atmospheric pressure and the sample was collected.

For the preparation of functional film: 1 mg of PACT/PDVB nanocomposite was added into the 1 ml 5 wt % PEG₁₀₀₀₀/DMSO solution and ultrasonicated for 10 min at room temperature to form a homogeneous mixture. The mixture was then dropped on silicon wafer to fabricate nanocomposite/PEG films by spin coating. The films were then annealed in weighing bottle containing 3 ml volatile polar solvents (THF, DCM, and chloroform) for about 30 minutes at room temperature. The films were also immersed in organic solvent (THF, DCM, and chloroform) for 30 seconds.

Characterization: Transmission electron microscopy (TEM FEI Tecnai G2 20) experiments were conducted with an accelerating voltage of 200 kV to characterize the morphologies and microstructures of the polymer-modified PDVB nanotube. Fourier transform infrared spectra (FTIR) were recorded on a TENSOR 27 FTIR spectrometer (Bruker) in the absorption mode with 32 scans at a resolution of 2 cm⁻¹ intervals. UV-vis spectra were performed on a Hitachi U-3010 with a 200 nm/min scanning speed and a bandwidth 0.1 nm. Photoluminescence (PL) spectra were measured on a FluoroMax-p fluorescence spectrometer (FluoroMax-p Jobin Yvon). Fluorescence emission of the nanocomposite was also examined by a confocal laser scanning microscopy system (CLSM, FV-1000-IX81Olympus).