Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

A Photo-tunable Membrane Based on Inter-particle Crosslinking for Decreasing Diffusion Rates

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Synthesis and photoreaction of PHCA

The synthesis of PHCA was performed by polycondensation of DHCA and 4-HCA (mol ratio = 1:1). The photoreaction of PHCA is based on the cycloaddition of cinnamic moieties to generate cyclobutane crosslinks. Specially, when PHCA was irradiated in solid state, the generated product is undissolved in DCM which should be the good solvent. This can be attributed to that more closed and compact polymer chains exist in solid state to allow further crosslinking among network.

The photoreaction was triggered under 365nm UV beam from a longwave UV lamp (Blak-Ray® B-100AP/R high-intensity UV lamp, UVP Company, USA). This light source is not a focused laser. Before irradiation, the lamp was warmed up for 15min to reach stability. Samples were placed before the lamp, and light was irradiated horizontally through sample solution. The distance between solution and lamp was 10 cm (<20 mW/cm^2). Typically 20h irradiation was applied before the samples were collected for further analysis. The conditions of lamp and distance were kept constant for all the irradiation processes in this work.

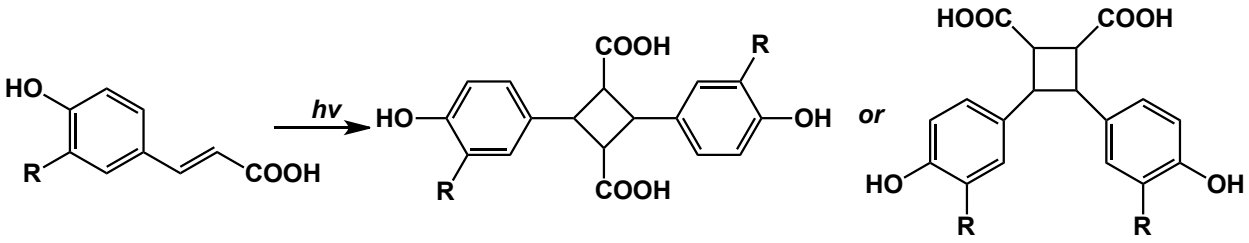

Figure S1. [2+2] cycloaddition of hydroxycinnamic acid derivatives under irradiation.

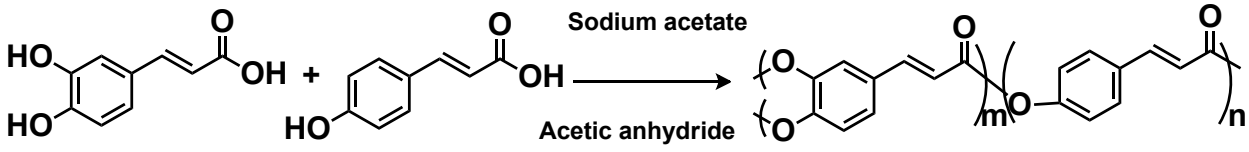

Figure S2. Polycondensation of DHCA and 4-HCA to obtain PHCA.

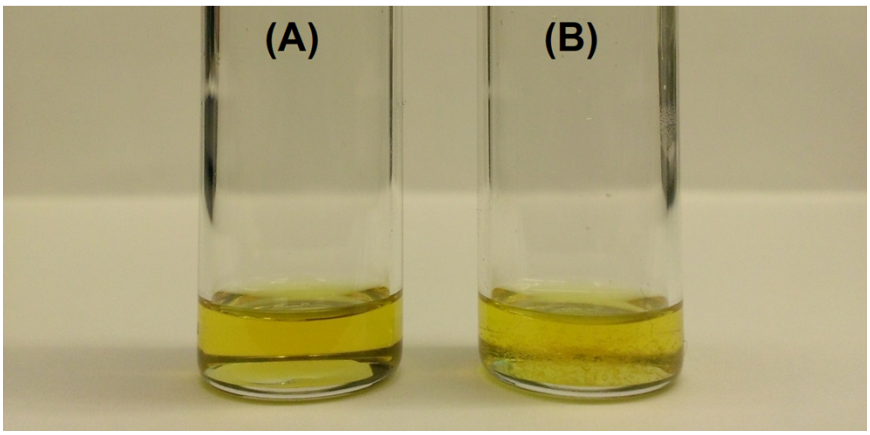

Figure S3. The solubility change of PHCA in DCM between before (A) and after (B) irradiation on its solid state. PHCA solid was irradiated directly to give highly crosslinked product that could not completely dissolve in DCM.

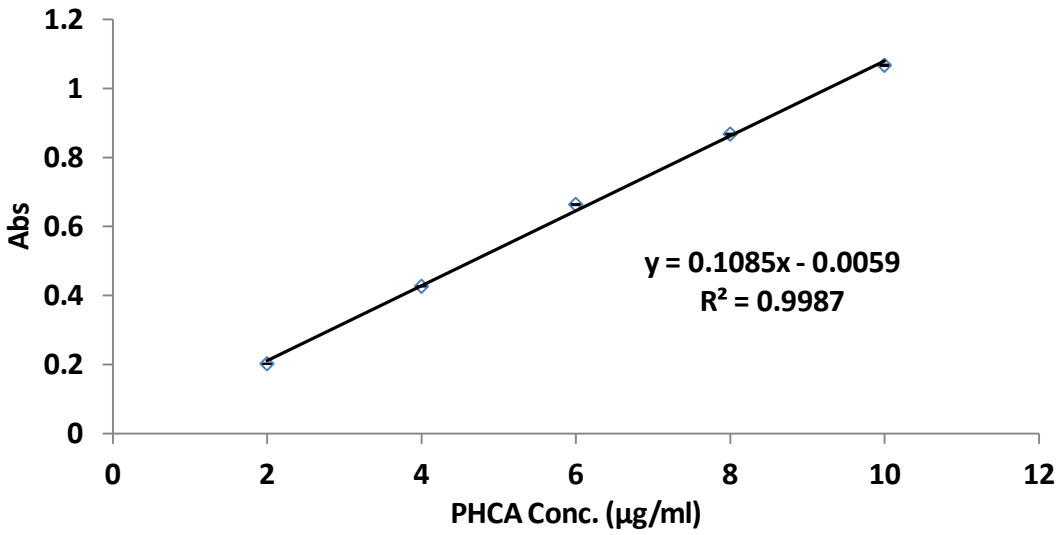

Figure S4. Calibration of PHCA in DCM solution, measured by UV/Vis spectroscopy for quantification.

Photoreaction of PHCA/PVA microspheres

The microspheres were irradiated in 3 different states. In diluted state, intra-particle photoreaction caused the shrinkage of microspheres. In concentrated or dry state, inter-particle photoreaction could occur to crosslink adjacent microspheres to form agglomeration.

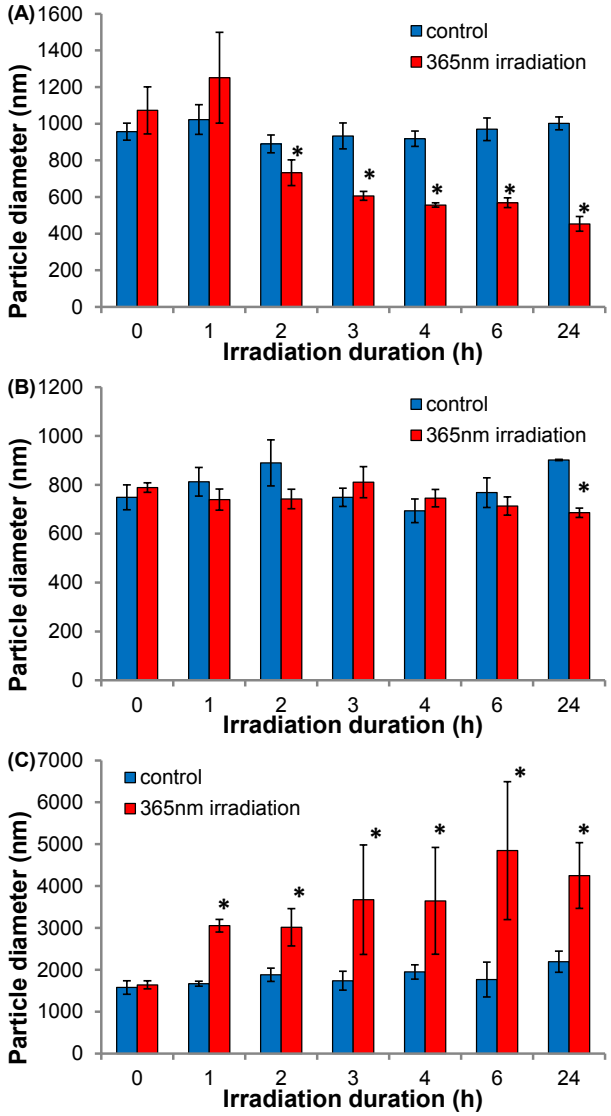

Figure S5. The size change of microspheres under 365nm light irradiation. (A) 20 μg/ml microspheres in water suspensions, size decreased indicating the shrinkage of particles; (B) 10^3

μg/ml microspheres in water suspensions; (C) 4×10^4 μg/ml dry microspheres on glass slides, size increased indicating the agglomeration of particles. The increased size was not accurate due to the significant agglomeration. (Data shown as mean ± SD of 3 samples. * $p<0.05$, compared with data at 0h of each group, respectively)

Morphologies and permeability of composite membranes

The embedment of PHCA/PVA microspheres endowed the membrane with the yellow color of PHCA. It also increased the thickness since the microspheres occupied space in matrix. Practically, the thickness of membrane could be simply controlled by setting desired original blade height, and it directly influence the diffusion ability as well as the photosensitive controllability of membranes. To achieve a better controllability (a smaller $P_{relative}$), a thicker membrane, such as > 25μm, was preferred.

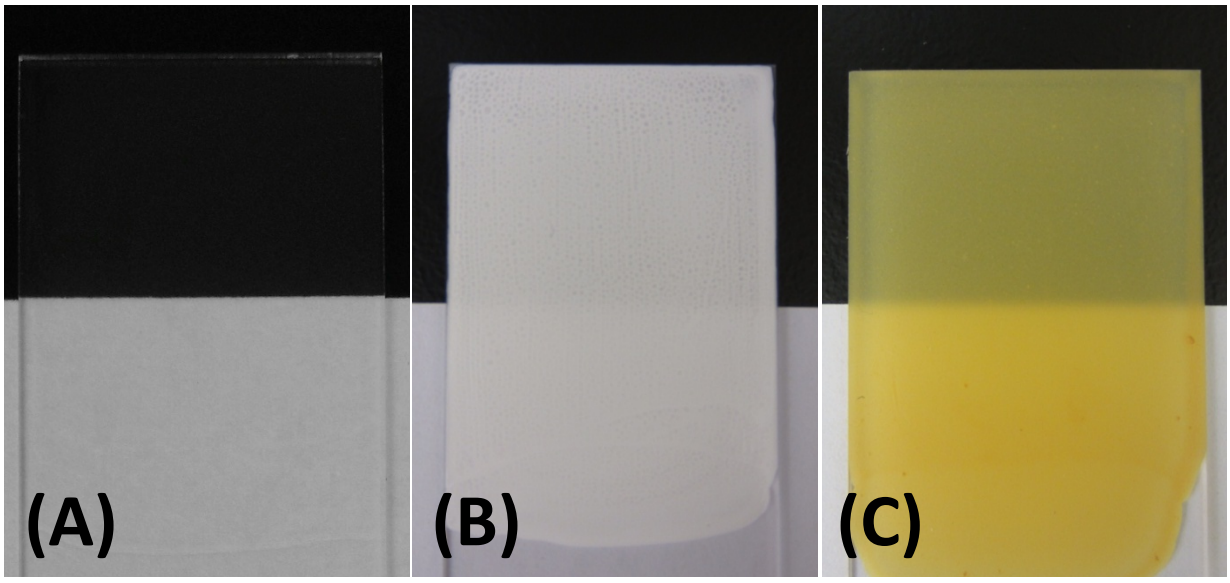

Figure S6. Photographs of EC (A), EC/PVA (B) and EC/PHCA/PVA (C) membranes. A piece of white paper was put behind the bottom of membranes for contrast.

Table S1. Thickness of different membranes

Composition	EC	EC/PVA	EC/PHCA/PVA		
Original blade height	300 μm	300 μm	150 μm	300 μm	450 μm
Thickness / μm	9.93 ± 0.26	28.59 ± 0.36	10.79 ± 1.44	25.63 ± 2.37	37.42 ± 0.98

Data are presented as mean ± SD by measuring 8-10 positions along the cross-sections on SEM images.

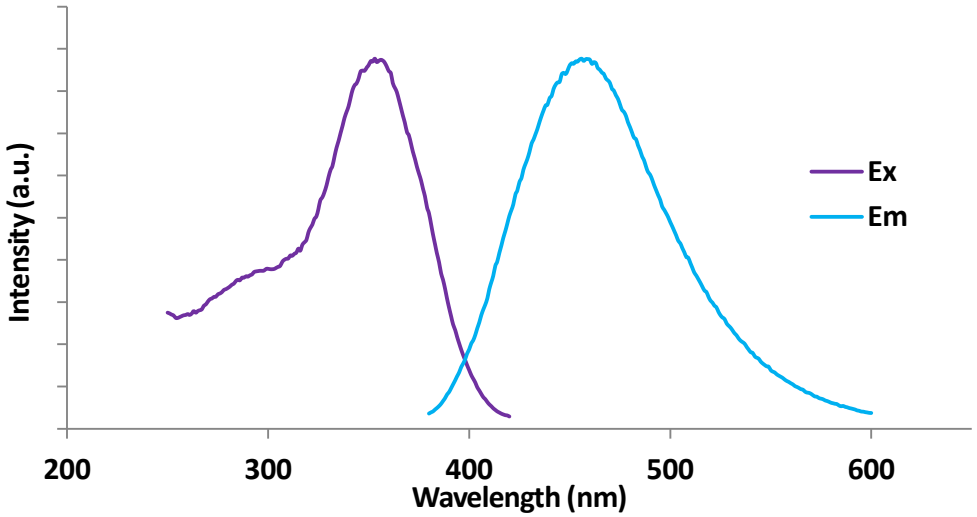

Figure S7. Excitation and emission spectrum of PHCA (λ_{Ex} = 354nm, λ_{Em} = 456nm).

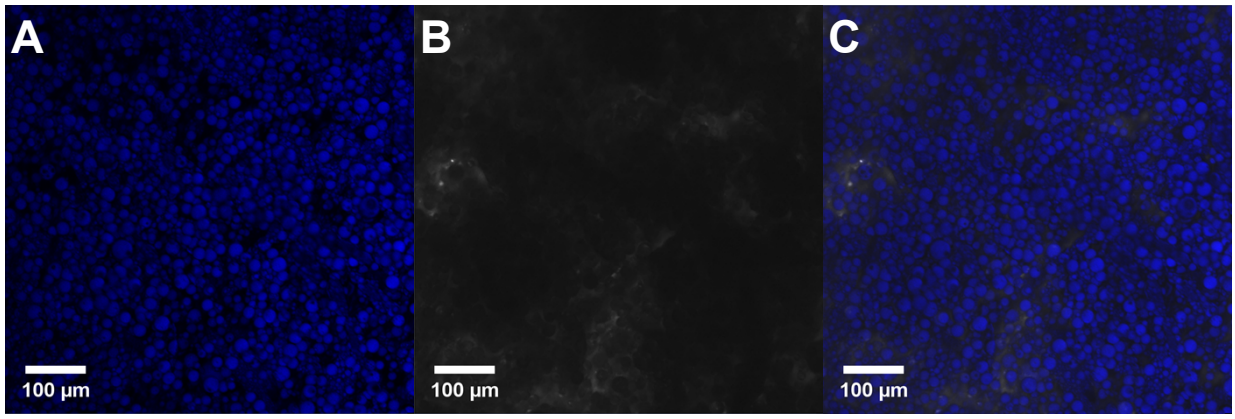

Figure S8. CLSM images of EC/PHCA/PVA composite membrane from top view, showing the dense distribution of microspheres. A: DAPI channel showing PHCA microspheres; B: bright channel; C: combination.