Supporting Information

Formation of organic nanoparticles by solvent evaporation within porous polymeric materials

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Experimental Details

Chemical and reagents: Poly(vinyl alcohol) (80 % hydrolyzed, Mw 9,000-10,000,) was purchased from Aldrich. Sodium dodecyl sulfate (95%), Oil Red O and curcumin from *curcuma longa* (Turmeric) were from Sigma. Cyclohexane was obtained from Fisher Scientific. All the aqueous solutions were prepared using distilled water, and normal GPR solvents were used.

Preparation of porous scaffolds: 5 wt % PVA solution in water was firstly prepared. To prepare oil-in-water emulsions, SDS was dissolved in 5 wt % PVA at the concentration of 0.05g SDS/ml solution. Cyclohexane was added into the aqueous phase dropwise while stirring to form an emulsion. The volume ratio of oil phase to the emulsion was varied at 50 v/v % and 75 v/v %. The aqueous solutions or the emulsions were frozen directionally in liquid nitrogen. The frozen samples were placed in a freeze-drier (LyoLab 3000, Heto) for 48 h to remove the frozen solvent and produce the porous materials.

Formation of organic nanoparticles by solvent evaporation within the porous materials: OR or curcumin was dissolved in cyclohexane or acetone to prepare the required organic solutions of 0.15 w/v % OR-ACE, 0.03 w/v % OR-CH and 0.43 w/v % curcumin-ACE solutions. These organic solutions were diluted to obtain the solutions of lower concentrations.

The pre-formed porous materials were soaked into OR-ACE, OR-CH, and curcumin-ACE for 30 minutes to reach saturation. The soaked samples were then filtered and dried in a fume cupboard overnight or in a vacuum oven for about 1 h at room temperature. The organic nanoparticles were formed *in-situ* within the porous scaffolds during solvent evaporation. These porous composites could be dissolved in water rapidly to produce stable aqueous organic nanoparticle dispersions.

Characterization: To measure absorption capacity, the porous materials were soaked in the organic solutions and taken out at different time intervals to assess the mass gains. The soaked samples were cleaned with tissue paper to remove the excess of organic solution on the surface. The degree of absorption was quantified by mass gain ratio as calculated below:

Mass gain ratio=$(W_s - W_d)/W_d$, where W_s is the weight of the porous material after being soaked in the organic solutions, and W_d is the weight of the dry porous material.

Morphology of the porous materials was characterized by a Hitachi S-4800 SEM. The materials were sectioned and adhered to SEM studs, and then coated with gold using a sputter-coater (EMITECH K550X) for 3 min at 35 mA. To image the organic nanoparticles with a STEM detector, one drop of aqueous nanoparticle dispersion was placed onto a TEM grid and allowed to dry. The size and zeta potential of the nanoparticles in aqueous dispersions were measured by dynamic light scattering (DLS) using Malvern Zetasizer Nano S at 25 ^{0}C. The UV-vis spectroscopy measurements were performed using a UV plate reader (μQuant, Bio-Tek instrument Inc.). The photos of nanodispersions were recorded by an Olympus C-5060 wide zoom digital camera.

Key finding summary: A generic method was proposed for the preparation of organic nanoparticles within porous materials. It seemed that the interaction of organic compounds with the polymeric scaffold was critical for the formation of nanoparticles. The size (30–60 nm) and the loading of the organic nanoparticles could be controlled by varying the concentration of organic solutions and the porosity/composition of the porous scaffolds. The nanoparticles could be easily released by dissolution to form aqueous nanoparticle dispersions. Semiconducting and other organic compounds may be also prepared via this approach to obtain organic nanoparticles for potential applications in coatings and optoelectronics. Another advantage was that this method might be easily scaled up to produce a large quantity of organic nanoparticles.

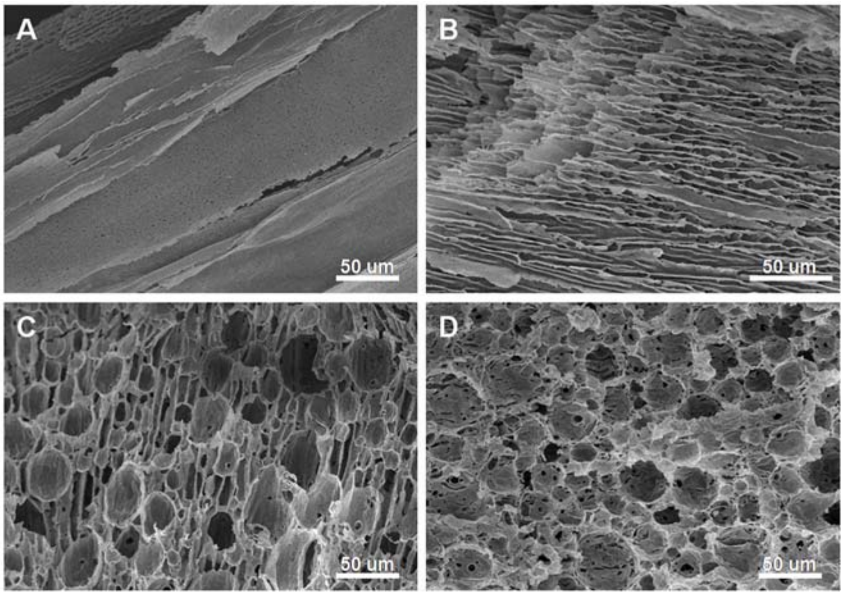

Fig. S1. Porous structures of the scaffolds for the preparation of organic nanoparticles: (A) aligned porous structure produced from PVA solution (S1); (B) aligned porous structure produced from PVA/SDS solution (S2); (C) emulsion-templated porous structure from the emulsion containing 50 v/v% internal phase, both emulsion-templated and ice-templated pore structures observed (S3); (D) highly interconnected porous structure prepared from the emulsion containing 75 v/v % oil phase.

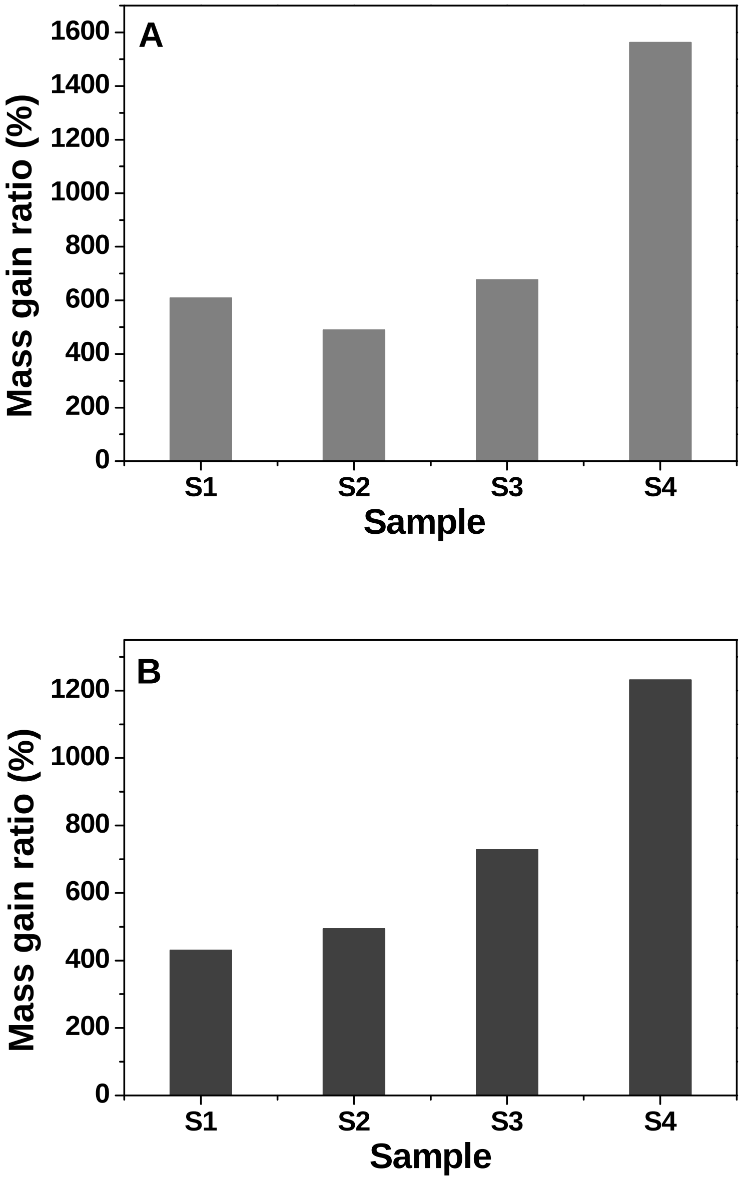

Fig. S2. The mass gain ratios of porous materials (samples S1-S4) when soaked in the OR-ACE solutions (A) and OR-CH solutions (B). The saturation time is 10 min for samples S1-S3 and 30 min for sample S4 in the OR-ACE solution, and 10 min for samples S1-S2, 20 min for sample S3 and 30 min in the OR-CH solution. The absorption capacities were observed to be around 430%, 490%, 720% and 1220% for samples S1–S4 respectively.

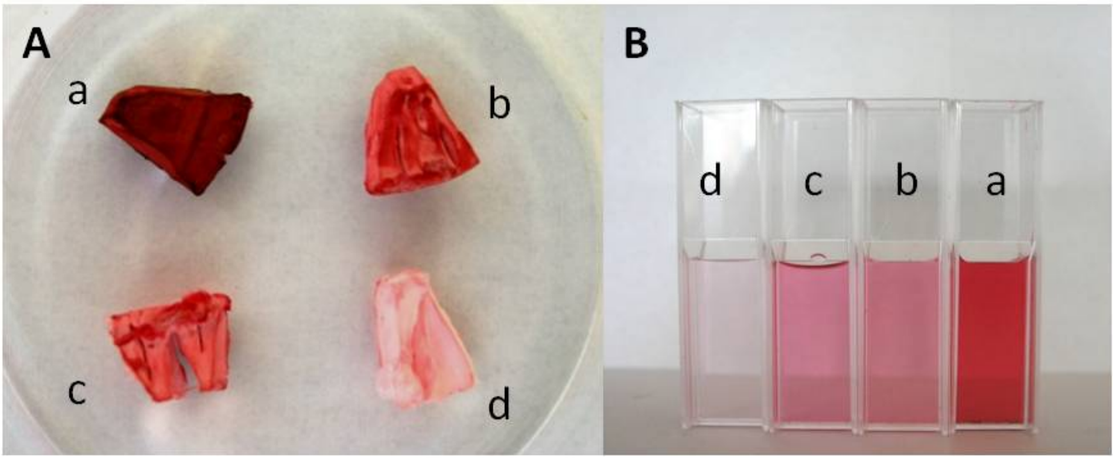

Fig. S3. (A) The photo of nanocomposites made by soaking sample S4 in the OR-ACE solutions at the concentration of 0.15 (a), 0.025 (b), 0.015 (c) and 0.0015 (d) w/v % and then removing acetone under vacuum. (B) The corresponding photos of OR nanoparticles dispersions obtained by dissolving the composite materials in water.

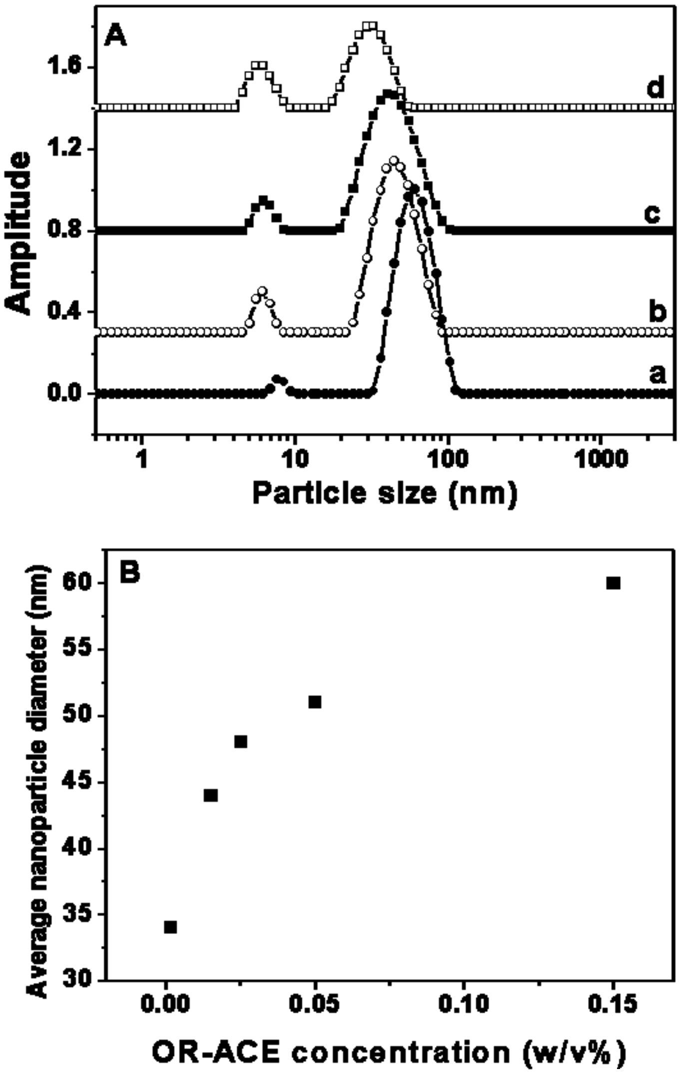

Fig. S4. (A) DLS curves of OR nanoparticle dispersions prepared by soaking sample S4 in the OR-ACE solutions at the concentration of 0.15 w/v % (a), 0.025 w/v % (b), 0.015 w/v % (c), and 0.0015 w/v % (d). Although the possibility of small OR nanoparticles can not be excluded, the small peaks around 6 nm are likely from aggregates of surfactant SDS or PVA.[14] (B) The relationship between the average nanoparticle sizes and the OR concentrations (the concentration of 0.05 w/v% included).

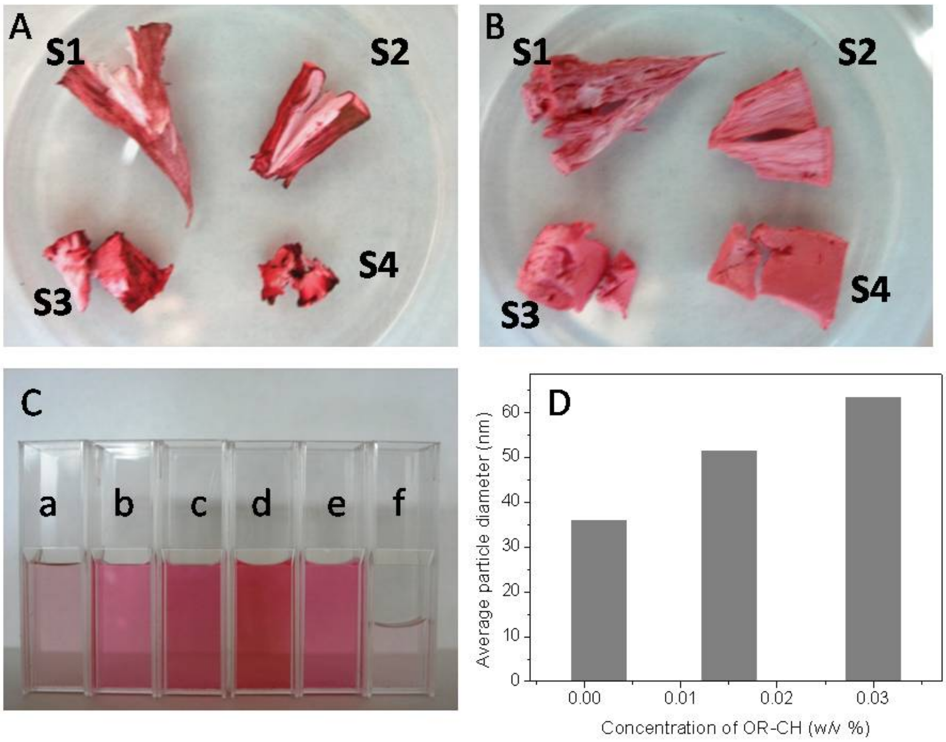

Fig. S5. Photo of nanocomposites prepared by soaking porous materials in 0.03 w/v % OR-CH and then evaporating the solvent in a fume cupboard overnight (A) and in a vacuum oven for 1 h (B) at room temperature. (C) Photos of OR nanosuspensions from the nanocomposites of S1-S4 (a-d) from 0.03 w/v % OR-CH and from 0.015 w/v % (e) & 0.0015 w/v % (f) by solvent evaporation under vacuum. (D) Relationship of average particle sizes with the concentration of OR-CH. The sizes of OR nanoparticles increased with the increasing OR concentration from 0.0015 to 0.03 w/v%. The average zeta potential of resulting OR nanoparticles from samples S1-S4 dried under vacuum was -2.93, -35.2, -35.2 and -33.5 mV.

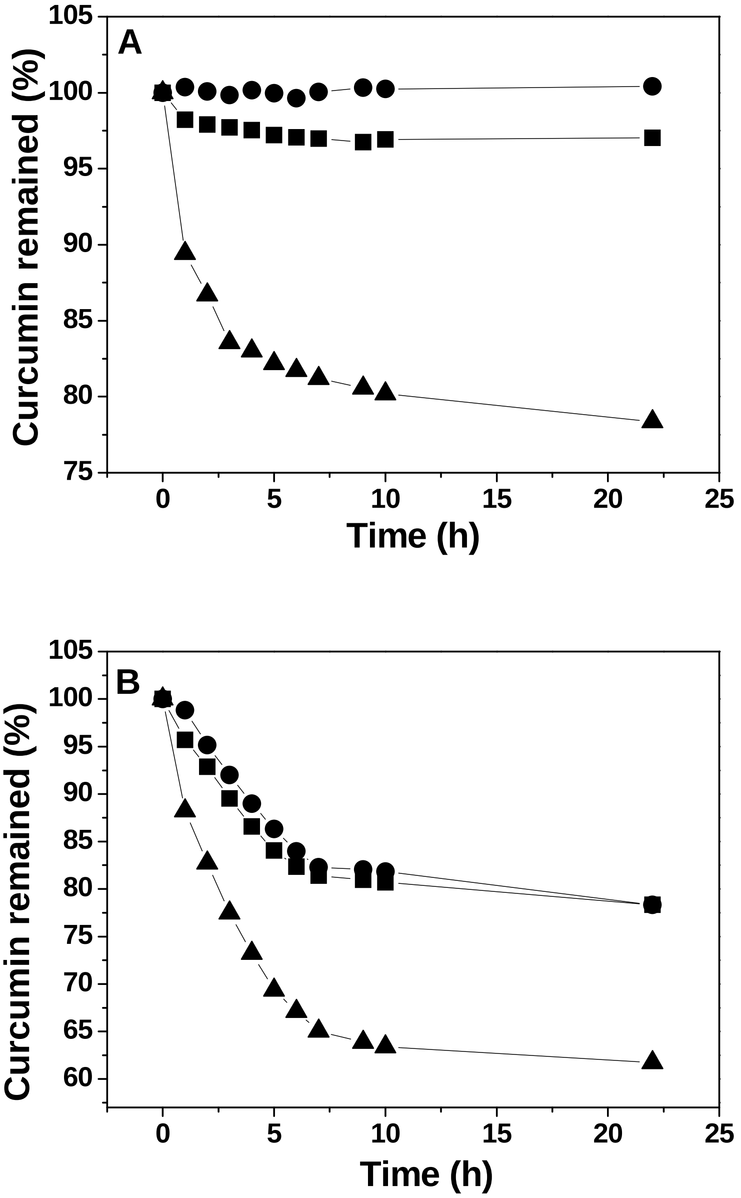

Fig. S6. Curcumin degradation monitored by UV-Vis in dark (A) and with daylight (B). Curcumin (40 µg/ml) in water/acetone (▲); curcumin (40 µg/ml) in water/acetone with 0.5 mg/ml PVA and 0.5 mg/ml SDS (■); curcumin nanosuspension (●), estimated to be 40 µg/ml curcumin, 0.5 mg/ml PVA, and 0.5 mg/ml SDS.