

## Supporting Information

# Underwater superoleophobic Carbon Nanotubes/Core-Shell Polystyrene@Au Nanoparticles Composite membrane for Flow- Through Catalytic Decomposition and Oil/Water Separation

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## **Material and methods**

**1. Materials.** Chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ , 99.9%) and Poly (N-vinylpyrrolidone) (Mw 550, 000) were purchased from Sigma-Aldrich. 3-Aminopropyltrimethoxysilane (ATPES) was provided by the Alfa Assar. Sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ , 99.8%), styrene and azoisobutyronitrile (AIBN) were obtained from Aladdin Company in Shanghai, China. Styrene was refined by distillation under reduced pressure before using. AIBN was recrystallized three times in methanol. Mixed cellulose ester membrane was obtained from Sea Peninsula Industrial Co., Ltd.. The raw multiwall carbon nanotubes (diameter about 10-30 nm and length about 10-30  $\mu\text{m}$ , -COOH % about 1.5%) with a purity of over 90% was purchased from Chengdu Organic Chemistry Co., Ltd. Other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd in Shanghai, China and used as received. Milli-Q-grade water (18.2  $\text{M}\Omega \cdot \text{cm}$ ) was used for all experiments.

**2. Synthesis of 25 nm citrate-stabilized AuNPs.** The AuNPs were synthesized according to our previous reports.<sup>1</sup> Briefly, 100 mL of  $2.5 \times 10^{-4}$  M  $\text{HAuCl}_4$  aqueous solution was heated to 120 °C in an oil bath. Subsequently, 10 mL of 1% sodium citrate solution was added into above solution and stirred vigorously for about 30 min. Meanwhile, the colour of the solution was changed from light yellow to ruby red, indicating the formation of AuNPs. 20 mL of synthesized Au NPs were centrifuged at 8000 rpm for 20 min to remove excess sodium citrate.

**3. Synthesis of 3-5 nm citrate-stabilized AuNPs.**<sup>1</sup> 0.22 mL of sodium citrate (1 wt%) aqueous solution was added into 15 mL of  $\text{HAuCl}_4$  aqueous solution (0.3 mM). 0.65

mL of ice-cold NaBH<sub>4</sub> solution (0.1 M) was added quickly into above mixed solution under vigorous stirring. The solution turned from orange colour to brownish-red, indicating the formation of AuNPs.

**4. Preparation of Amino-functionalized PS microspheres.** PS-NH<sub>2</sub> microspheres were prepared by dispersion polymerization:<sup>2, 3</sup> Briefly, 6.5g of styrene monomer and 0.75 g of steric stabilizer PVP were added into 20 mL of ethanol containing 16 mM of AIBN. The mixture was stirred at 70 °C for 10 h under nitrogen. After the reaction finished, the resultant mixture were refined by centrifugation at 6000 rpm and washing with ethanol before drying at 40°C under vacuum. Then 20 mg of purified PS microspheres were dispersed in 20 ml of ethanol. 0.4 ml of APTES solution (8.5×10<sup>-2</sup> M) in anhydrous ethanol was added into above solution and stirred for 2 h at 25 °C. Then the APTES-functionalized PS microspheres were washed respectively with ethanol and water for three times by repeated centrifugation and finally re-dispersed in 20 ml of water. The PS-NH<sub>2</sub> microsphere dispersion (1 mg/mL) was stay for at least 20 h before using.

**5. Preparation of high-density PS@AuNPs hybrid microspheres.** 5mL of PS-NH<sub>2</sub> microsphere dispersion (1 mg/mL) was mixed with 20 mL of AuNP dispersion and stirred lightly for 10 h at room temperature. Then the resultant mixture was centrifuged three times at 5000 rpm for 10 min to remove excess AuNP. The pink colour precipitated was re-dispersed in 5 mL of water and achieved high-density PS@AuNPs hybrid microspheres.

**6. Preparation of freestanding CNTs/PS@AuNPs hybrid film.** 3mg of CNT was

dispersion in 60 mL of ethanol/water mixed solution (1/1, v/v) under continuous sonication. A certain volume of PS@AuNPs hybrid microsphere dispersion was dropped slowly into above mixed solution under vigorous stirring and then sonicated for 5 min. 15 mL of achieved uniformed mixed solution was then filtrated on the mixed cellulose ester (CE) membrane with the vacuum degree at 0.09 MPa to form smooth black hybrid film. The surface black film on the CE membrane can be peeled off to obtain freestanding SERS-active CNTs/PS@AuNPs hybrid film.

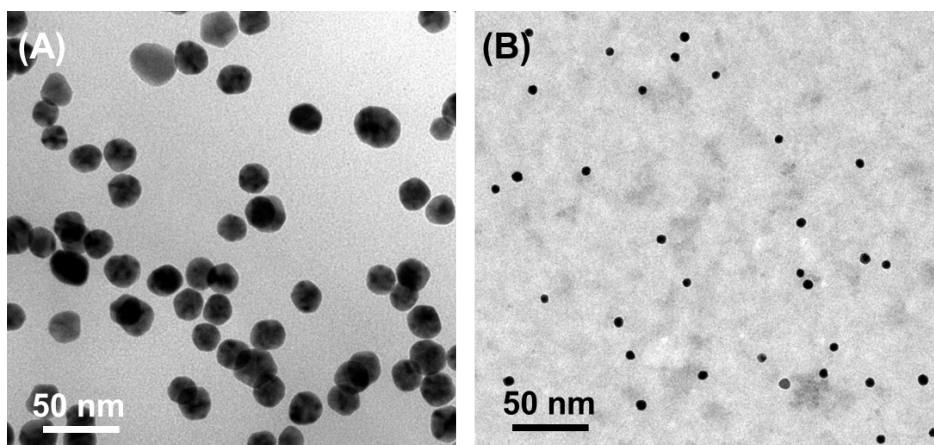
**7. Catalytic reactions using PS@AuNPs hybrid microspheres monitored by successive UV/vis spectra.** For testing the catalytic performance of PS@AuNPs hybrid microspheres (2  $\mu\text{m}$  PS microsphere and 3-5 nm AuNP) were employed as catalyst. 1 mL of PS@AuNPs dispersion in water (about 5.0 mg composite microspheres with 1.1 wt% Au) was added to 1 mL of mixed solution of 4-nitrophenol (5 mM) and  $\text{NaBH}_4$  (500 mM) aqueous solution. The reaction process was recorded by successive UV/vis spectra at 0.5 min interval.

**8. Preparation of the Oil-in-Water.** Oil-in-water emulsions:<sup>4</sup> 1.2 g of emulsifier tween 80 (HLB = 15) was added into 120 mL of water, and then 4 mL of soybean oil or other organic solution (dichloromethane and chloroform) was added. The mixture was stirred for 3 h before standing for 24 h, and no de-emulsification was observed.

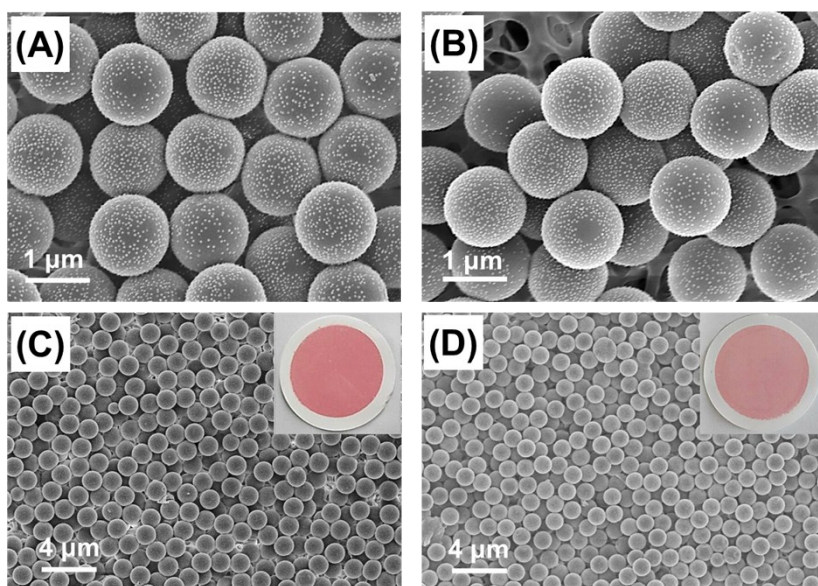
**9. Catalytic reactions using CNTs/PS@AuNPs composite membrane monitored by successive UV/vis spectra.** Preparation of the oil-in-water: 1.2 g of emulsifier tween 80 (HLB = 15) was added into 120 mL of water, and then 4 mL of soybean oil was added. The mixture was stirred for 3 h before standing for 24 h, and no de-

emulsification was observed. For testing the catalytic performance of CNTs/PS@AuNPs composite film (2 mg of PS@AuNPs microsphere, 4×4 cm area),<sup>5</sup> 30 mL of oil/water mixed solution containing 4-nitrophenol (2.5 mM) and NaBH<sub>4</sub> (250 mM) was added onto the composite membrane using a vacuum filtration setup. The content of 4-nitrophenol in the filtrate solution was characterized by UV/vis spectra.

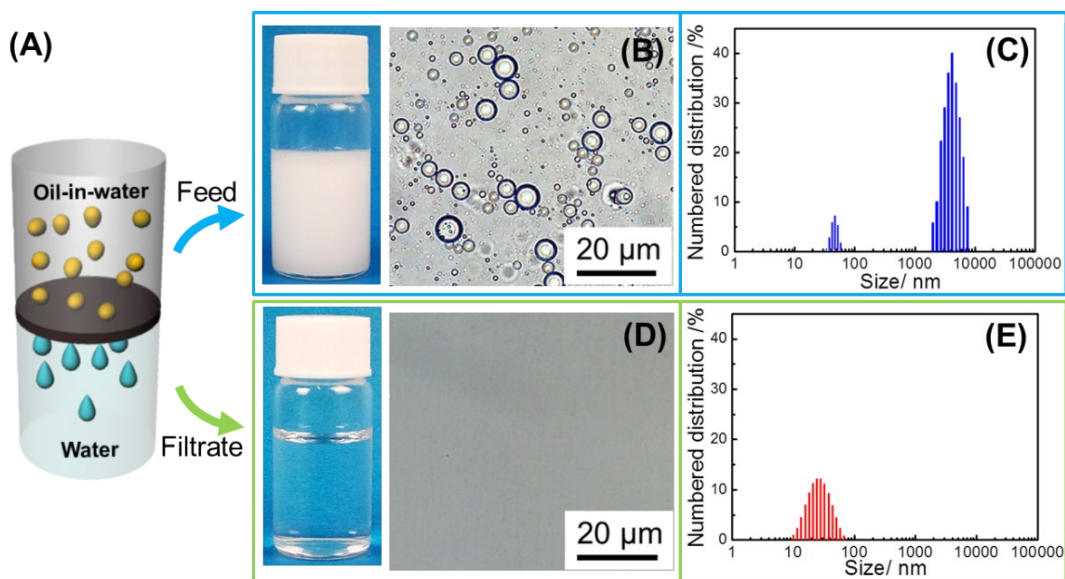
**10. Characterizations.** The microstructures of PS@AuNPs and the composite membrane were characterized mainly by scanning electron microscopy (JEOL JMS-6700F scanning microscope) and transmission electron microscopy (JEOL JEM2010 electron microscope). The UV/vis absorption of filtrated solution was recorded by LAMBDA 950 UV-Vis spectrometer. Static water and oil contact angles measurements were performed on an OCA-20 DataPhysics instrument at room temperature. 3 μL of liquid droplet volume was dropped on the membrane and an average of three measurements was made to determine the surface wettability. The oil/water emulsion and filtrate was observed by BX 51TF Instec H601. Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS.



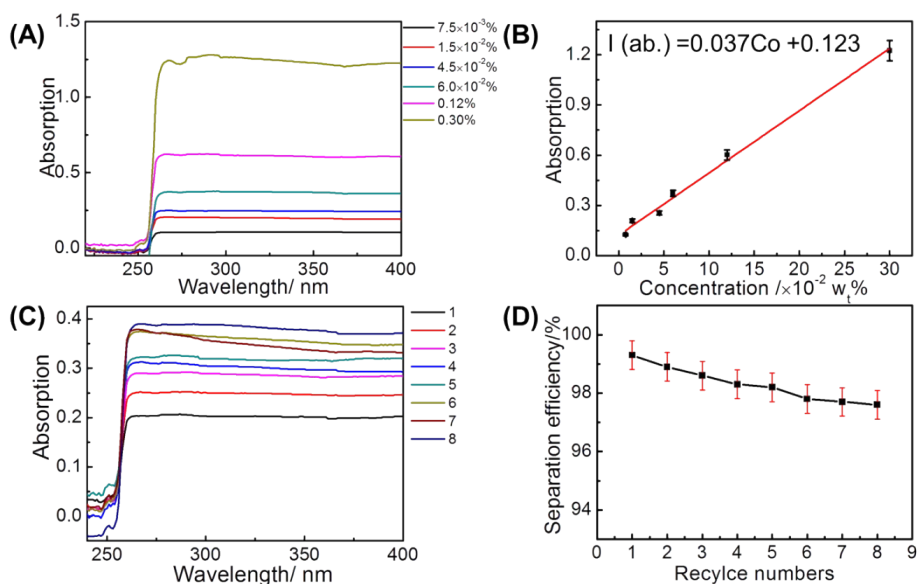
**Fig. S1.** TEM image of citrate-stabilized AuNPs with averaged diameter of 18 nm (A) and 6 nm (B).



**Fig. S2.** SEM images of different densities of PS@AuNP (18 nm size of AuNP) hybrid microspheres deposited on the mixed CE membranes. The density in image (A, C) is higher than that of (B, D). The inset pictures show the photographs of corresponding membranes samples.



**Fig. S3.** (A) Schematic illustration of the superhydrophilic CNT/PS@AuNP membrane for separating oil-in-water emulsions toward feed emulsions. (B) the microscopic pictures and (C) size distribution of oil-in-water emulsions. (D) The microscopic pictures and (E) size distribution of filtrate emulsions after separation.



**Fig. S4.** (A) The UV/vis absorption of soybean oil-in- water emulsion with different concentration. (B) The absorption intensities at 264 nm are plotted against the oil concentration. A normalized line is fitted and the equation between oil concentration and absorption intensity is achieved. (C) The UV/vis absorption and calculated oil contents (D) of filtrates after several recycle separation processes.

## References

1. Y. Huang and D. H. Kim, *Langmuir*, 2011, **27**, 13861.
2. J. W. Kim and K. D. Suh, *J. Ind. Eng. Chem.*, 2008, **14**, 1.
3. J. W. Kim and K. D. Suh, *Polymer*, 2000, **41**, 6181.
4. J. C. Gu, P. Xiao, J. Chen, J. W. Zhang, Y. J. Huang and T. Chen, *ACS Appl. Mater. Interfaces*, 2014, **6**, 16204.
5. J. T. He, W. J. Ji, L. Yao, Y. W. Wang, B. Khezri, R. D. Webster and H. Y. Chen, *Adv. Mater.*, 2014, **26**, 4151.