Supporting Information

A Co$_3$O$_4$ Nano-needles Mesh for High-efficient, High-flux Emulsion Separation

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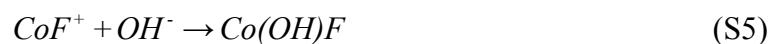## Experimental section

2.1. Materials

Stainless steel mesh was purchased from Guangzhou Ming Wan Screen Mesh Co., Ltd., China, the specific model of mesh is 316 L material, twill weave and 1800 mesh. Al sheet was purchased from Shanghai Kayoon Metal Materials Co., Ltd., China. $Co(NO_3)_2 \cdot 6H_2O$ was purchased from Guangdong Guanghua Sci-Tech Co., Ltd., China. NH_4F and $AgNO_3$ were purchased from Xilong Chemical Co., Ltd., China. Acetone, ethanol, HCl (36-38 wt%), NaOH, NaCl and H_2NCONH_2 were purchased from Beijing Chemical Works, China. All the chemical reagents were analytical grade and used as received without further purification. All the aqueous solutions were prepared with deionized water.
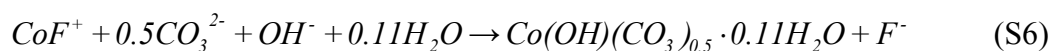
2.2. Preparation of nano-needles stainless steel mesh

The original stainless steel mesh was cut into 3.5×3.5 cm^2 pieces as substrate, then sonicated sequentially in acetone, ethanol, 1 M HCl solution and deionized water for 1 h, and dried at room temperature. 0.87 g $Co(NO_3)_2 \cdot 6H_2O$, 0.37 g NH_4F, and 0.90 g H_2NCONH_2 were dissolved in 60 mL deionized water, and the mixed suspension was magnetically stirred for 1 h. The resulting solution was transferred to a 100 mL Teflon-lined autoclave. A piece of stainless steel mesh was placed vertically in the autoclave. Then, the autoclave was sealed and heated to 120°C for 6 h. After the reaction, the as-obtained pink mesh was picked out of the mixture and rinsed with deionized water and ethanol, followed by natural drying. Finally, the as-obtained pink mesh was put into a muffle furnace at 300°C for 2 h, where it was transformed into a black mesh for further characterizations and experiments.
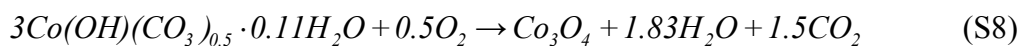
Synthesis of Co_3O_4 nano-needles stainless steel mesh.

(1) Hydrothermal process

$$Co^{2+} + F^- \rightarrow CoF^+ \tag{S1}$$

$$H_2NCONH_2 + H_2O \rightarrow CO_2 + 2NH_3 \tag{S2}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{S3}$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{S4}$$

$$CoF^+ + OH^- \rightarrow Co(OH)F \tag{S5}$$

$$CoF^+ + 0.5CO_3^{2-} + OH^- + 0.11H_2O \rightarrow Co(OH)(CO_3)_{0.5} \cdot 0.11H_2O + F^- \qquad (S6)$$

(2) Subsequent calcination

$$6Co(OH)F + O_2 \rightarrow 2Co_3O_4 + 6HF \qquad (S7)$$

$$3Co(OH)(CO_3)_{0.5} \cdot 0.11H_2O + 0.5O_2 \rightarrow Co_3O_4 + 1.83H_2O + 1.5CO_2 \qquad (S8)$$
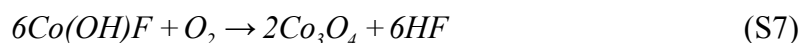
2.3. Instrumentation and Characterization

Scanning electron microscope (SEM) images were collected with a Quanta 250 FEG scanning electron microscope (FEI, Czech Republic). X-ray diffraction (XRD) patterns were collected on an XRD-6000 (Shimadzu). The CA values were obtained by measuring five different positions of the same sample using the sessile drop method with a Dataphysics OCA-20 contact angle analyzer. For underwater optical contact angle (OCA) measurements, the as-obtained mesh was first immersed in water, then a 4 μL oil drop (1, 2-dichloroethane, petroleum ether, cyclohexane, isooctane, xylene, gasoline) was dropped on to the as-obtained mesh, and the OCA was measured. The measurement procedure of the water-reserving ability of the membranes: we first weigh the mass of the original stainless steel mesh and the as-prepared Co_3O_4 nano-needles mesh, and then the two meshes were immerged into deionized water for ten minutes and again weigh the mass of the two membranes respectively. The water capacity of the meshes was characterized by the specific value of the difference value between the mass that before and after water collection and the mass of the original mesh. Droplet size distributions of the oil-in-water emulsion samples and filtrate solutions were obtained by dropping anemulsion droplet on a glass sheet for imaging with an optical microscope (OLYMPUS BX51, Japan). The Tyndall phenomenon was characterized by using a beam of red light to irradiate the emulsion and filtrate. An infrared oil measurement instrument (OIL480) was used to test the separation efficiency of the coated mesh for the oil-in-water emulsions.

2.4. Oil-in-Water Emulsion Separation Experiments

Oil-in-water emulsions were prepared by injecting oil (namely, isooctane, cyclohexane, petroleum ether, xylene and gasoline) into water or strong alkali and high-concentration salt aqueous solution (1 mol L^{-1} NaOH and 1 mol L^{-1} NaCl) in a ratio of 1:100 v/v under ultrasonication, which was continued for 1 h at 250 W to obtain a homogeneous white emulsion. Commonly, the as-obtained petroleum ether-in-water emulsion could remain stable

for 1 h, while the isooctane-in-water, cyclohexane-in-water and xylene-in-water emulsions could remain stable for 6 h, and the gasoline-in-water emulsion could remain stable for 24 h when stored under ambient conditions. The as-prepared mesh was placed on a filtration apparatus with a diameter of 20 mm, and then a certain volume of oil-in-water emulsion was added into the apparatus. The separation processes were respectively carried out under a suction vacuum pressure of 0 KPa and 5 KPa. The filtrate water was collected, and the oil content in the water was determined by an infrared spectrometer oil content analyzer.
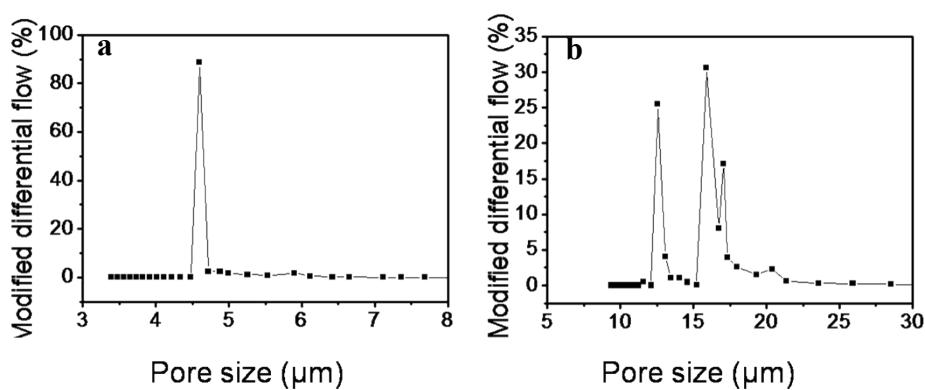

Fig S1 The pore sizes of the stainless steel mesh (a) and Co_3O_4 nano-needles coated stainless steel mesh (b) are 16.3 μm and 4.6 μm respectively, which were measured by Membrane Pore Size Analyzer.
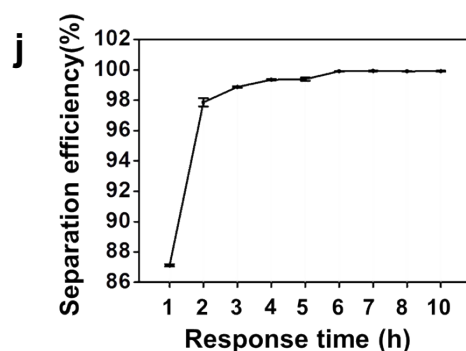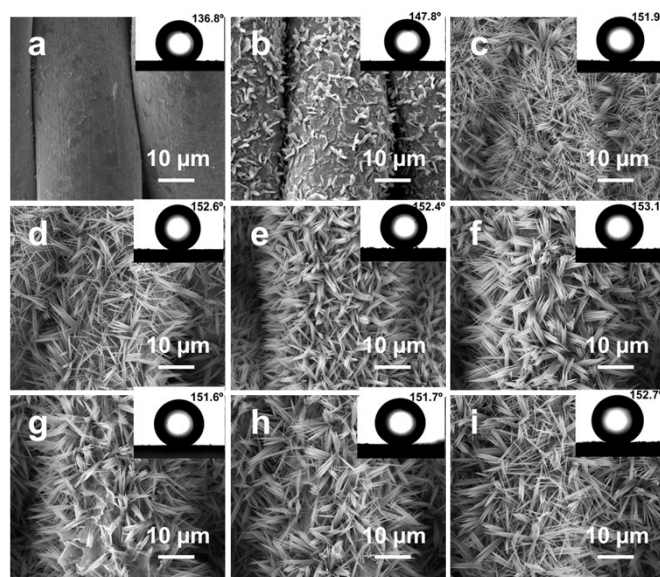
Fig S2 a-i) SEM images of Co_3O_4 nanostructures growing on stainless steel mesh with different hydrothermal reaction time: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h, (e) 5 h, (f) 6 h, (g) 7 h, (h) 8 h, (i) 10 h and subsequent calcination respectively. The insets show the photographs of oil contact angles under water on Co_3O_4 nanostructures surface. When the reaction time was less than 3 h, oil contact angles were lower than 150°. When the reaction time was more than 3h, the SSM with a layer of uniform Co_3O_4 nano-needles arrays perform superoleophobic (above 150°) under water. j) The corresponding cyclohexane-in-water emulsion separation efficiency with the above meshes. Before 6 hours, the separation efficiency increased with the extension of the hydrothermal reaction time. While, when we extended the time to 10 hours, separation efficiency has no obvious change. Specifically, the emulsion separation efficiencies were 87.12% ± 0.08% for 1 h, 97.86% ± 0.27% for 2 h, 98.88% ± 0.05% for 3 h, 99.35% ± 0.04% for 4 h, 99.39% ± 0.10% for 5 h, 99.90% ± 0.01% for 6 h, 99.92% ± 0.02% for 7 h, 99.90% ± 0.01% for 8 h and 99.91% ± 0.03% for 10 h, respectively.
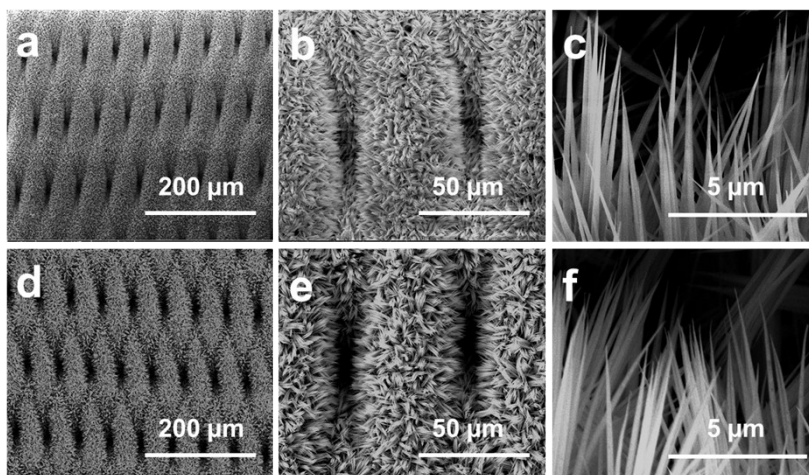
Fig S3 a, b, c) SEM images of Co_3O_4 nano-needles mesh before calcination. d, e, f) SEM images of Co_3O_4 nano-needles mesh after calcination. The diameter of the nano-needles coated steel wire slightly decreased after calcination (before calcination: 48.2 ± 0.8 μm; after calcination: 46.6 ± 0.9 μm), that is to say, the length of the nano-needles has slightly decreased. But, the morphology of nano-needles has no obvious change before and after calcination.
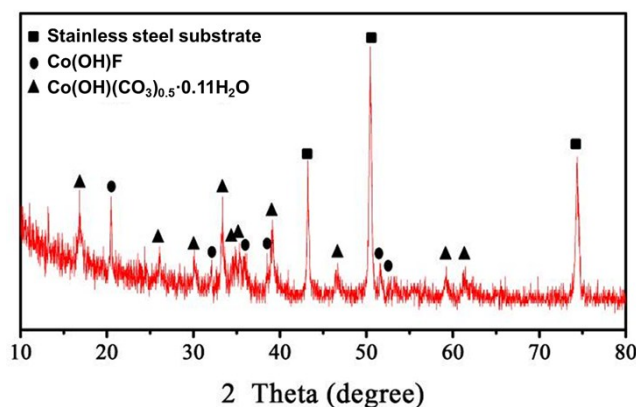

Fig S4 XRD pattern of the cobalt compound precursors nano-needles mesh. ■, ● and ▲ represent the speaks of the stainless steel substrate, Co(OH)F and $Co(OH)(CO_3)_{0.5} \cdot 0.11H_2O$ respectively. The diffraction peaks match well with the standard cards of Co(OH)F (JCPDS Card No: No. 50-0827) and $Co(OH)(CO_3)_{0.5} \cdot 0.11H_2O$ (JCPDS Card No: No. 48-0083).
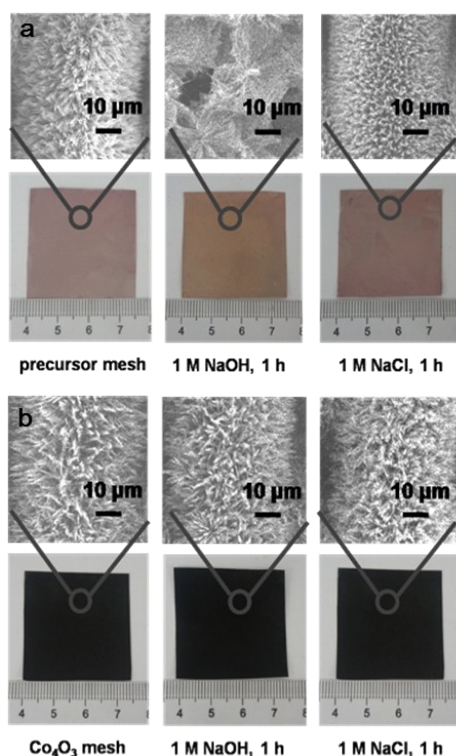
Fig S5 (a) From left to right, the photographs are of the original precursor mesh and its corresponding results after 1 mol/L NaOH and NaCl aqueous solution immersion for 1 h, respectively. (b) From left to right, the photographs are of the as-prepared Co_3O_4 nano-needles mesh and its corresponding results after base and salt (1 mol/L aqueous solution) immersion for 1 h, respectively. The top of them are the corresponding SEM images.
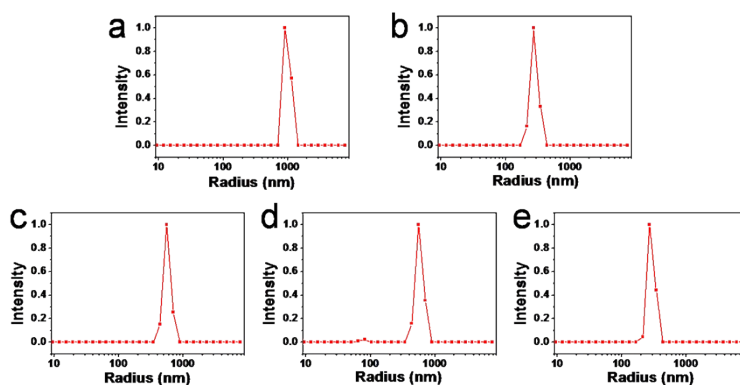

Fig S6 Dynamic light scattering (DLS) of (a) petroleum ether-in-water emulsion, (b) xylene-in-water emulsion, (c) cyclohexane-in-water emulsion, (d) isooctane-in-water emulsion and (e) gasoline-in-water emulsion. The average radius of the dispersed phase were 983 nm for petroleum ether, 279 nm for xylene, 566 nm for cyclohexane, 573 nm for isooctane and 288 nm for gasoline, respectively.
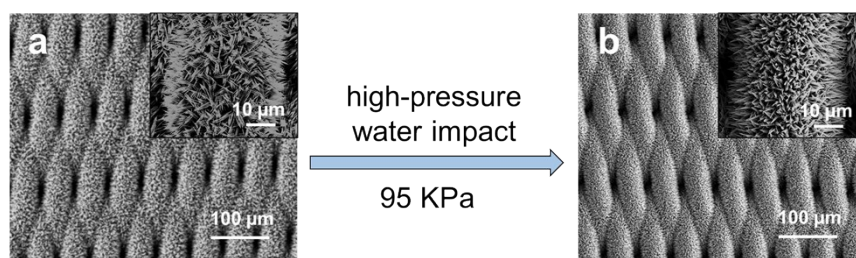
Fig S7 The high-pressure water impact test for our Co_3O_4 nano-needles mesh. a) SEM images before test. b) SEM images after test. Specifically, the Co_3O_4 nano-needles mesh was placed on a filtration apparatus with a diameter of 20 mm, and then the water was added into the apparatus under a suction vacuum pressure of 95 KPa. The test lasted for one hour and the water flux was 80266 ± 121 L m^{-2} h^{-1}. The morphology of as-prepared Co_3O_4 nano-needles mesh had no obvious change after high-pressure water impact test.
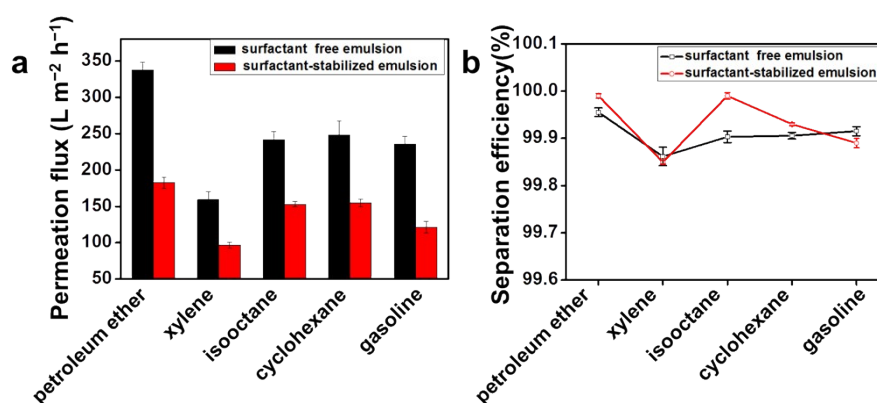

Fig S8 The permeation flux and separation efficiency of surfactant free emulsions and surfactant-stabilized oil-in-water emulsions with our as-prepared Co_3O_4 nano-needles mesh. a) The permeation flux of surfactant free emulsions and surfactant-stabilized oil-in-water emulsions under gravity. Specifically, for surfactant free oil-in-water emulsions (the oil named petroleum ether, xylene, isooctane, cyclohexane and gasoline), the permeation fluxes were 338 ± 11 L m^{-2} h^{-1}, 159 ± 10 L m^{-2} h^{-1}, 242 L ± 11 m^{-2} h^{-1}, 248 ± 19 L m^{-2} h^{-1} and 236 ± 11 L m^{-2} h^{-1}, respectively. For surfactant-stabilized oil-in-water emulsions (the oil named petroleum ether, xylene, isooctane, cyclohexane and gasoline), the permeation fluxes were 183 ± 8 L m^{-2} h^{-1}, 97 ± 4 L m^{-2} h^{-1}, 153 ± 4 L m^{-2} h^{-1}, 155 ± 5 L m^{-2} h^{-1} and 122 ± 8 L m^{-2} h^{-1}, respectively. The separation efficiency of surfactant free emulsions and surfactant-stabilized emulsions (all above 99.8%).

I   II

IV   III

Stainless steel mesh(SSM)

Co(OH)F and Co(OH)(CO$_3$)$_{0.5}$·0.11H$_2$O crystal seeds

Co(OH)F and Co(OH)(CO$_3$)$_{0.5}$·0.11H$_2$O nano-needles@SSM

Co$_3$O$_4$ nano-needles@SSM

Scheme S1 The formation process of of Co$_3$O$_4$ nano-needles mesh. The composition of 316 L stainless steel mesh substrate contains Cr (16-18%), Ni (10-14%) and Mo (2-3%). The reaction processes are as follows, the surface of 316 L stainless steel in air generally is of an oxide layer. This oxide layer would form hydroxyl groups when immerses in basic solution (I); these hydroxyl groups combines with the crystal seeds of Co(OH)(CO$_3$)$_{0.5}$0.11H$_2$O and Co(OH)F formed in reactive solution (II); Co(OH)(CO$_3$)$_{0.5}$0.11H$_2$O and Co(OH)F further grow on the basis of the original seed and form nano-needles (III); after calcination, Co(OH)(CO$_3$)$_{0.5}$0.11H$_2$O and Co(OH)F nano-needles turn into Co$_3$O$_4$ nano-needles (IV). [1-3]

References:

1. Y. Wang, H. Xia, L. Lu J. Lin, *ACS Nano*, 2010, **4**, 1425.
2. J. Jiang, J. Liu, R. Ding, J. Zhu, Y. Li, A. Hu, X. Li X. Huang, *ACS Applied Materials & Interfaces*, 2011, **3**, 99.
3. J. Xu, K. Wang, S.-Z. Zu, B.-H. Han Z. Wei, *ACS Nano*, 2010, **4**, 5019.