Electronic Supplementary Information (ESI)

In-Situ Ultrafast Separation and Purification of Oil/Water Emulsions by Superwetting TiO_2 Nanocluster-Based Mesh

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Experimental Section

Fabrication of TiO_2 nanocluster-based Mesh

Copper mesh was chosen as the substrate and TiO_2 clusters were coated on it by solvothermal reactions. Pre-cleaned copper mesh with a mesh number of 400 was immersed in a solution of 2.5 ml tetrabutyl titanate (TBOT), 12.5 ml glycerol and 37.5 ml ethanol, then heated to 180 °C for 24 h. Subsequently, the mesh was taken out, rinsed with deionized water and dried at room temperature.

Preparation of the Oil-in-Water and Water-in-Oil Emulsions

Oil-in-water emulsions were prepared by mixing oil and water according to a volume ratio of 1: 100 with 0.05 g surfactant (namely SDS, CTAB and Tween20) per 100 ml, and stirred for 2 h. Water-in-oil emulsions were prepared by mixing water and oil (namely toluene, gasoline, diesel, n-heptane and n- octane) according to a volume ration of 1:100 with 0.20 g Span80 per 100 ml, and stirred for 2 h. For the contaminated emulsions, 5 mg/L MB aqueous solution was added instead of pure water.

Emulsion Separation and Purification Experiments

The as-prepared mesh was fixed between two polytetrafluoroet hylene (PTFE) clamps, with a glass tube on each side. The emulsions were poured into the glass tube, and the separation was driven by gravity. In the in-situ separation and purifaication process, UV illumination was provided by a 125 W mercury lamp (Philips, Holland). The filtrates water or oil were collected for further test.

Instruments and Characterization

SEM was conducted on a SU-8010 field emission scanning electron microscope (Hitachi, Japan). XRD was measured on a Bruker D8 advanced X-ray diffractometer with a CuK_{α} radiation source (Bruker-AXS, Germany). CAs were performed on an OCA-20 contact angle analyzer (Data-Physics, Germany). Optical microscopy images were taken on an ECLIPSE LV100POL polarizing microscope (Nikon, Japan). Oil concentration was evaluated by an Oil480 infrared spectrometer oil content analyzer (Beijing Chinainvent Instrument Tech. Co. Ltd., China). Oil purity was evaluated by a Karl Fischer titrator (Cou-LoAquamax KF Moisture Meter, UK). TOC was operated on a TOC-Vcph analyzer (Shimadzu, Japan). UV-vis was record on a Lambda-750 UV spectrometer (Perkin Elmer, USA).

Additional Tests and Details

Supplementary Characterization of Composition and Wettability

The XPS was taken to verify the composition of the TiO_2 nanocluster-based mesh. In the XPS pattern (Fig. S1), peaks of titanium, oxygen, and carbon were observed by scanning bonding energy from 0 to 1000 eV. The two main peaks at 458.02 eV and 530.08 eV are marked with Ti 2p and O 1s, and the small peak at 284.87 eV is marked with C 1s, indicating that the original copper mesh was coated by titanium dioxide after the solvothermal reaction.

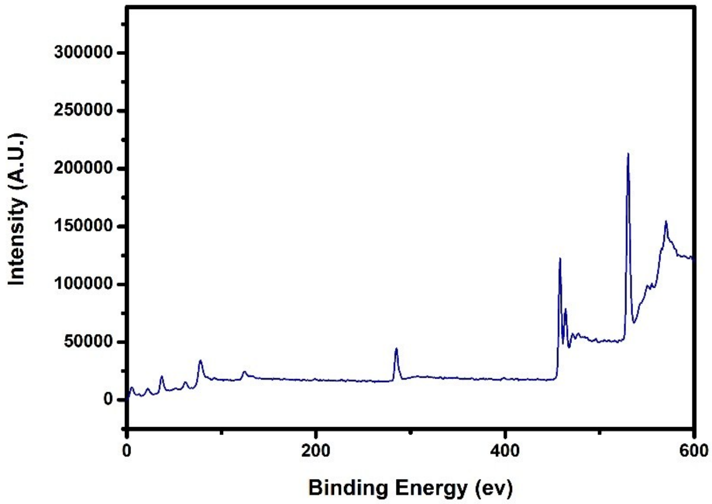

Fig. S1 XPS pattern of the TiO_2 nanocluster-based mesh

The CAs of various oils under water on the mesh are presented in Fig. S2a-d, and the ones of water under various oils are presented in Fig. S2e-h. When the mesh was immersed in the reversed liquid phase, it behaved superlyophobic with the CA value above 150°.

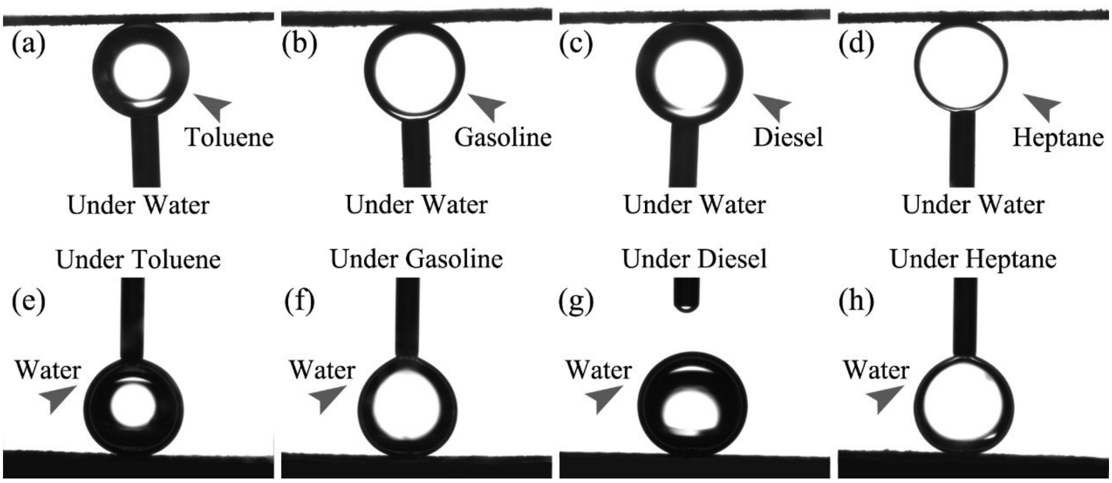

Fig. S2 CA photos of various oils under water and water under various oils. (5 μL deionized water as the water droplet and 5 μL toluene, gasoline, diesel or n-octane as the oil droplet).

The BET test was taken to represent the pore size of the TiO_2 nanocluster-based mesh. The pore width is in the range of 10-50 nm, and the ravage value is 22.07 nm, according to the BET pattern (Fig. S3).

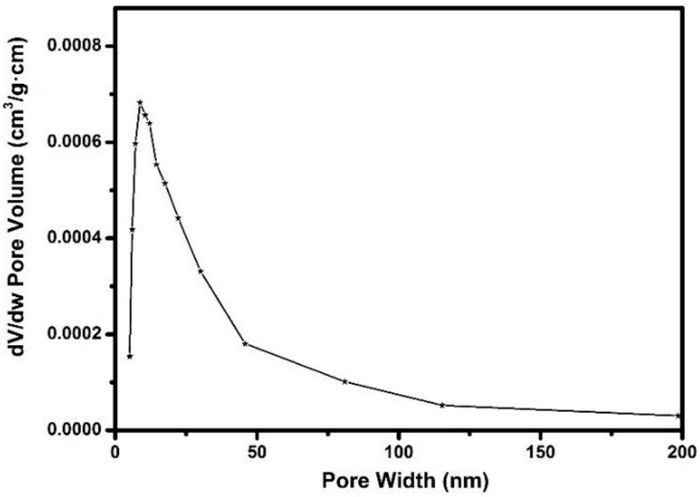

Fig. S3 BET pattern of the TiO_2 nanocluster-based mesh

Separation and Purification Process of Emulsions

The separating experiments were performed using the devices in Fig. S4. The TiO_2 nanocluster-based mesh was fixed by two polytetrafluoroet hylene (PTFE) clamps, and two glass tubes were fixed on each side. There is no need for the mesh to be pre-wetted. The emulsions were poured into the glass tube, and the whole process was driven by gravity only. Clear filtrates could be gathered in the beaker below for further test.

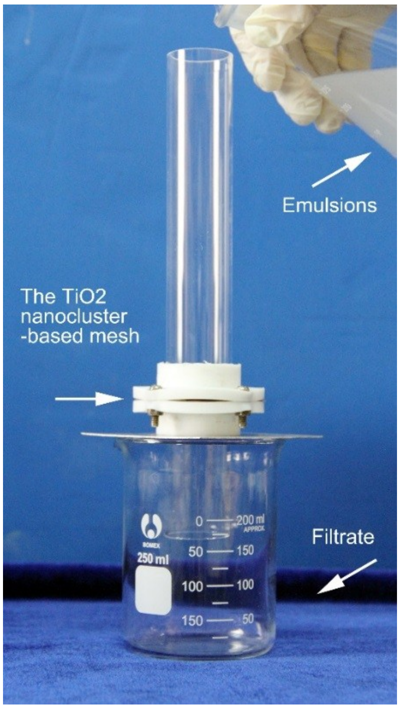

Fig. S4 The device for emulsions separation and purification treatment.

The water-retention capacity of the mesh was illustrated in Fig. S5. It was measured by calculating the ratios of the increased weight and the initial weight for the original copper mesh and the TiO_2 nanocluster-based mesh respectively. The mesh coated with TiO_2 could maintain water more than 65% of its weitht, whereas the bare mesh could only maintain 25%, indicating that the growth of titanium dioxide has significantly increased the mesh's water-favoring property.

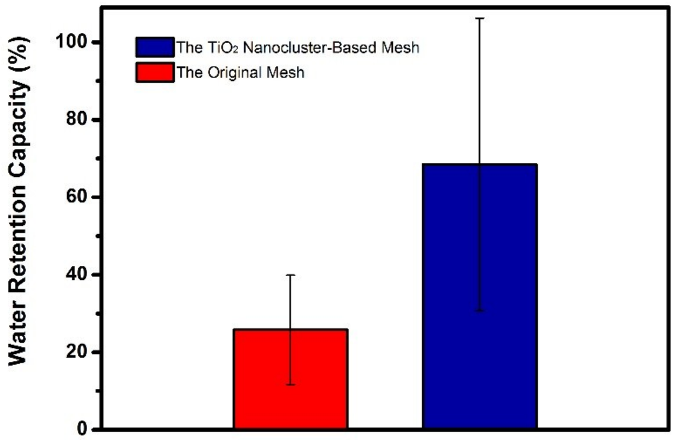

Fig. S5 Water Retention capacity of the TiO_2 nanocluster-based mesh.

The TOC test of 120 min for the SDS-stabilized (n-octane)-in-water emulsion is given as a contrast in Fig. S6. After decreased by nearly 95 percent within 60 mins, it tended to be steady and almost no change.

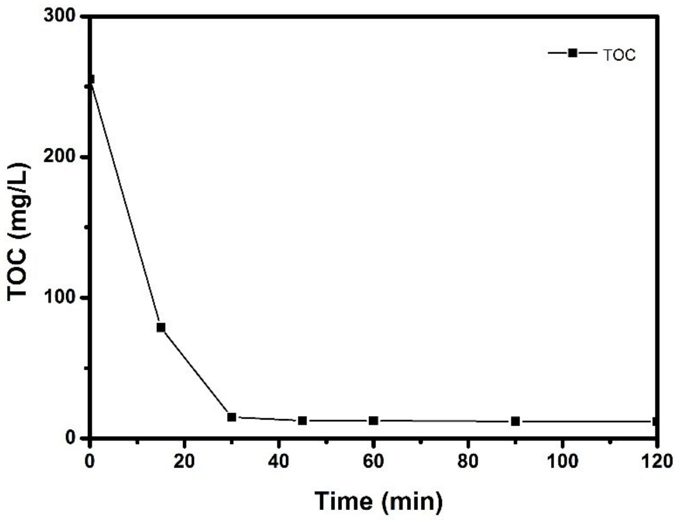

Fig. S6 TOC evolution during the degradation process.

Emulsions containing different kinds of surfactants (anionic surfactant like SDS, cationic surfactant like CTAB, nonionic surfactant like Tween20) were also took in the measurement and got the similar results of photodegradation efficiency.

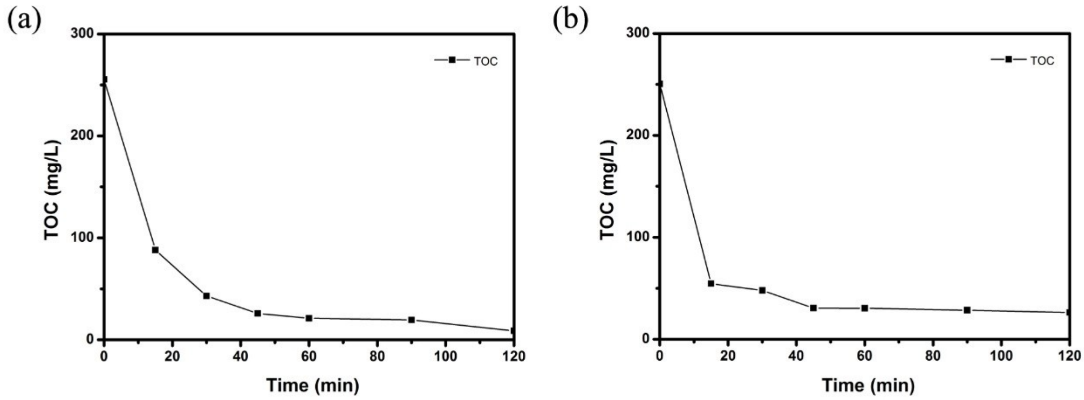

Fig. S7 TOC evolution during the degradation process of emulsions with different surfactant. (a) Emulsion with CTAB. (b) Emulsion with Tween20.

For the blank test of emulsions stability, we put the stabilized emulsions with MB under UV illumination for 2 h. It could be observed that there was no significant changes in the emulsion (Fig. S8), and the UV-vis pattern in Fig.S9 showed the concentration decline.

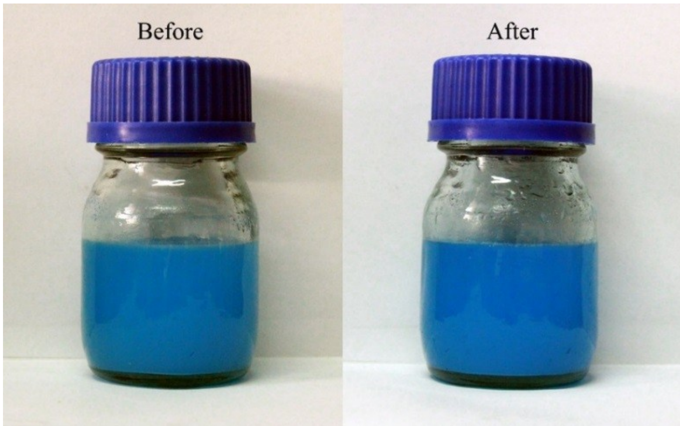

Fig. S8 Blank test of MB stability under UV light.

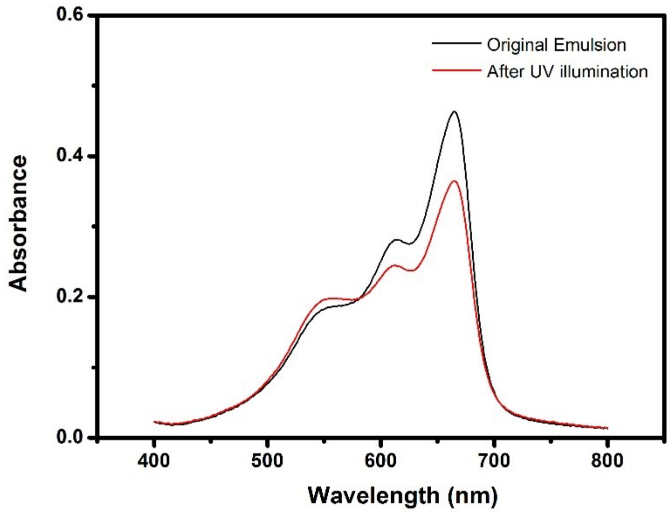

Fig. S9 Blank test of MB stability under UV light.

For the complementary test of absorption effect for TiO_2, emulsions separation process was operated without UV light, while the devices and other conditions were the same. The UV-vis pattern in Fig. S10 reveals that there was a small decline of absorption but imitated.

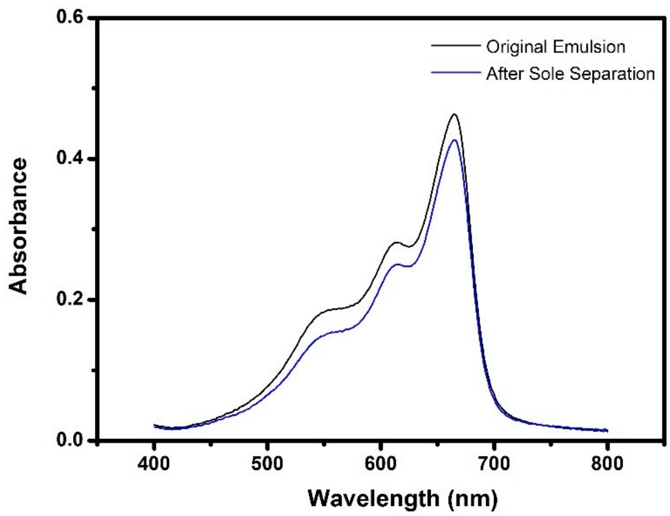

Fig. S10 Blank test of MB absorption of the mesh.

Fig. S11 diaplays the separating of water-in-oil emulsion. The original feed emulsion is milky white before treatment, while the collected filtrate is transparent. The optical microscopy photos could also prove the separation results.

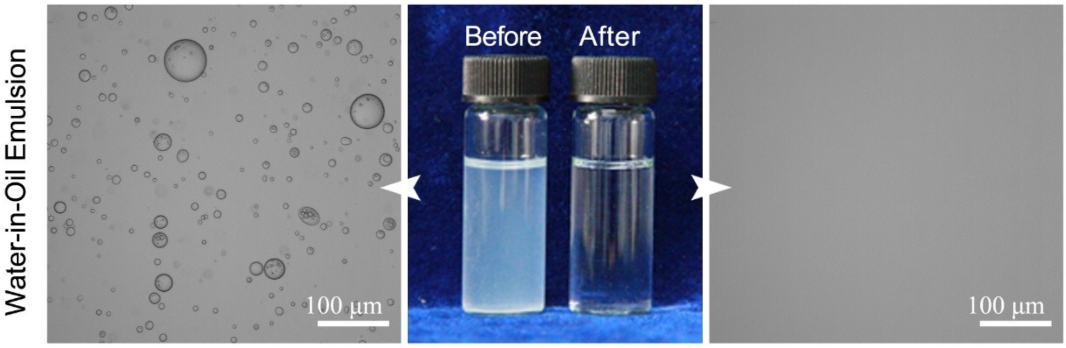

Fig. S11 Optical microscopy photographs of water-in-oil emulsion before and after separation.

An additional separation experiment was taken using the original copper mesh without TiO_2 to testify the function of the TiO_2 nanoclusters on the mesh. It was found that emulsion flowed through the mesh quickly and remained its emulsified state (Fig. S12), which indicated that the original copper mesh doesn't have demulsification ability and separation capacity.

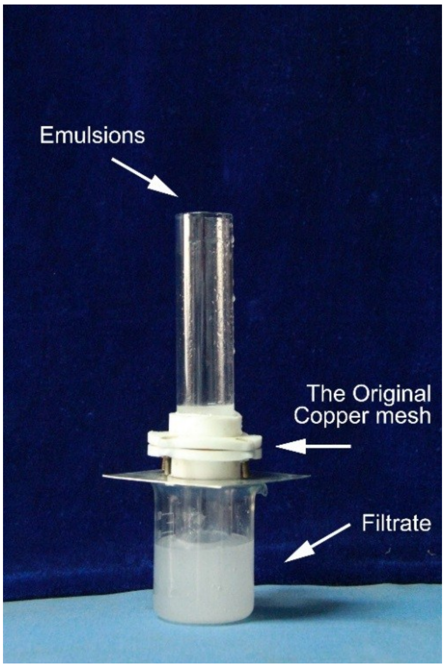

Fig. S12 Emulsion separation by the original copper mesh. The mesh could hardly sustain the emulsion, and single phase of water or oil was not separated out.

The Harsh Condition Test for Stability and Recyclability

Fig. S11 shows the SEM image and Fig. S12 presents the CA photos of the TiO_2 nanocluster-based mesh after a series of testing, including many-time recyclability, pH-stability, solvent-stability, thermal-stability and so on. The flower-like nanoclusters structures remain intact and the special wettability keeps well.

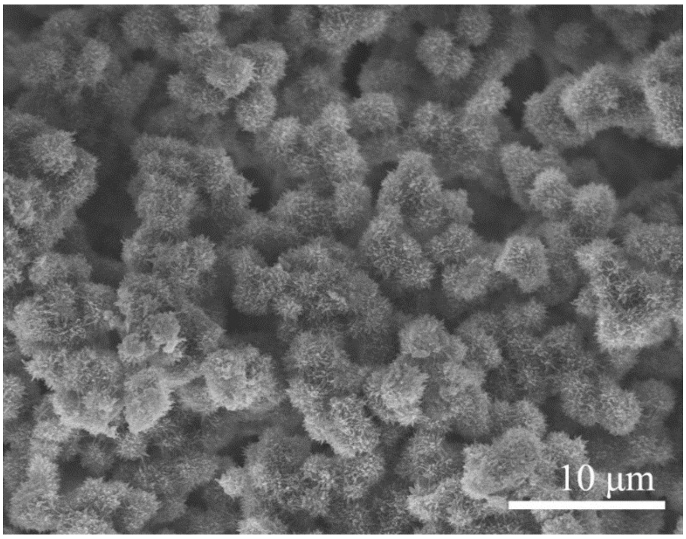

Fig. S13 SEM image after cycling quality test and stability test.

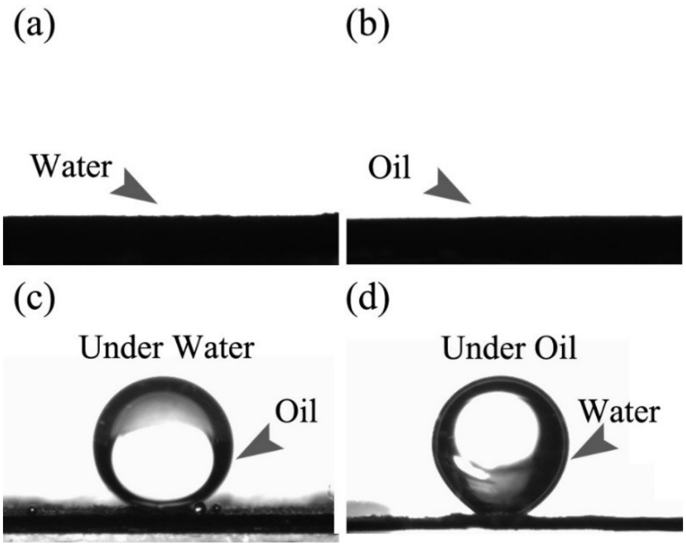

Fig. S14 CA photos after cycling test and stability test (5 µL deionized water as the water droplet and 5 µL 1, 2-dichloroethane as the oil droplet).

The TiO_2 nanocluster-based mesh is flexible, and TiO_2 nanoclusters can retain adhesion on the copper mesh when it is bended (Fig. S15).

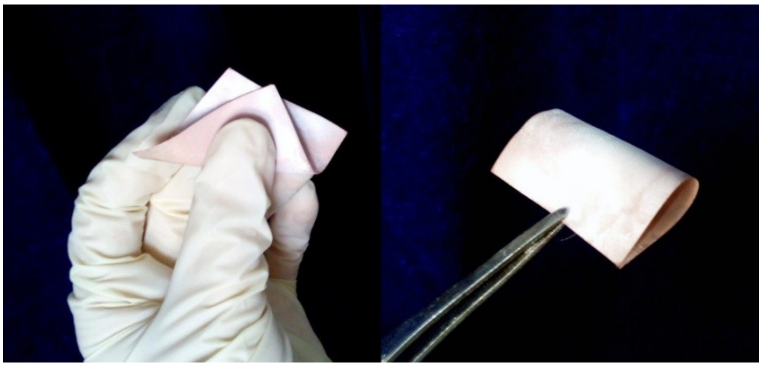

Fig. S15 The flexibility of the TiO_2 nanocluster-based mesh.