Electronic Supplementary Information (ESI)

Self-assembled graphene oxide microcapsules with adjustable permeability and yolk-shell superstructures derived from atomized droplets

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1. Experimental

1.1. Materials

The natural graphite flakes (500 mesh) were supplied by XFnano chemical Co., Ltd., China., $Cu(NO_3)_2 \cdot 3H_2O$, $KMnO_4$, and $NaNO_3$ in A.R. grade were purchased from Changzheng Chemical Reagent Co., China. Terephthalic acid (TPA, 99%) and other reagents were purchased from Hangzhou Banghua chemical Co., Ltd., China. All the regents were used without further purification. The water used in this study was obtained from a self-made RO-EDI system, in which ion concentration was analyzed by IRIS Intrepid ICP and Metrohm 861 Compact IC and controlled to meet the experimental requirement of $\sigma \leq 0.5$ μS cm^{-1}.

1.2. Synthesis of graphite oxide

Graphite oxide was prepared following a slight modification of the Hummers method. 2 g of natural graphite flakes and 1 g of $NaNO_3$ were dispersed into 46 mL of H_2SO_4 in an ice-bath. 6 g of $KMnO_4$ was added into the suspension slowly under stirring to prevent the temperature from exceeding 293 K. The suspension was kept in ice-bath for 120 min. The temperature was monitored by a thermometer. Then the suspension was heated to 308 K and maintained for 60 min. 92 mL of water was slowly poured into the mixture, and the temperature of suspension was increased to 371 K and maintained for 40 min. Then the mixture was treated by 30% H_2O_2 solution. Finally, the product was rinsed with diluted HCl solution, collected, and dried.

1.3. Synthesis of GO microcapsule and GO-PVP microcapsule

0.2 g of graphite oxide was exfoliated by ultrasonic treatment for 2 h in 100 mL of water. The suspension was centrifuged at 4000 rpm for 10 min, there are almost no precipitate was collected, this indicated that the graphite oxide was exfoliated completely. After the pH was adjusted to 7, the suspension was spray-dried in a mini

spray dryer at a feed rate of 16.5 mL/min. The inlet and outlet temperatures were 553 K and 423 K. The nozzle posses a standard diameter of 1 mm. The drying time was 0.5 s. After the completion of the spray-drying process, the microcapsule was collected. For GO-PVP microcapsule, the difference was that 0.2 g of PVP (K-30, 40,000 Da) was added to the 100 mL of GO suspension.

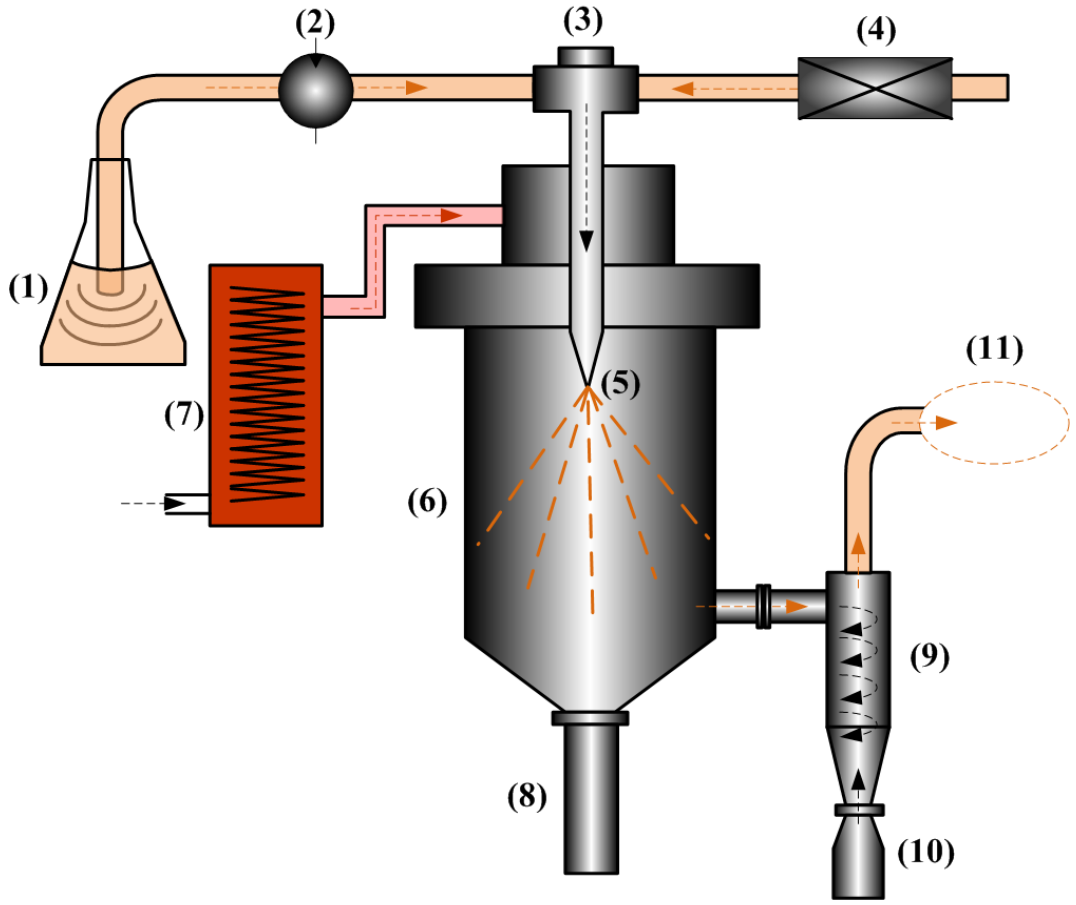

Figure S1. Schematic illustration of the mini spray dryer**.** (1) Feed suspension; (2) Peristaltic pump; (3) Hot air distributor; (4) Air compressor; (5) Sprayer; (6) Drying tower; (7) Heater; (8) Collector 1; (9) Cyclone separator; (10) Collector 2; (11) Bag filter.

1.4. Loading and releasing of small molecular substances

The dye molecules- reactive red X-3B were selected as target small molecular substance and loaded at the synthetic process of GO microcapsule of GO-PVP

microcapsule. The dye was added into the suspension. And then after spray-drying, the dye molecules will be adsorbed on the microcapsule wall or fixed inside the microcapsule. After preparation, to release the dye molecules, the loaded microcapsule was immersed into water and stirring. The concentration of the dye in surrounding solvent was measured by UV spectrophotometer (UV 1102). Ultrasound was used to detect the total contents of the dye in microcapsule.

1.5. Synthesis of MOF-GO yolk-shell superstructure

CuTPA crystals were synthesized by solvothermal method. 0.93 g of $Cu(NO_3)_2 \cdot 3H_2O$, and 0.66 g of TPA were dissolved in DMF. The solution was transferred into a Teflon-lined autoclave for heated treatment. The condition was at 383 K for 24 h. After crystallization, the crystals was obtained and isolated by centrifugation. For MOF-GO yolk-shell superstructures, 0.2 g of graphite oxide was exfoliated by ultrasonic treatment in water. After the pH was adjusted to 7, 0.2 g of PVP, and 0.2 g of MOF crystals were added into the GO suspension. The additives were dispersed completely by shaking table, the suspension was used to fabricate MOF-GO yolk-shell superstructures by spray-drying as like the GO microcapsule.

1.6. Characterization

PNAlytical X' Pert PRO X-ray diffractometer was used to collect the X-ray diffraction (PXRD) patterns in the reflection mode with CuKα radiation (40kV, 40mA, λ=0.154056 nm). The morphology was observed by scanning electron microscopy (SIRION-100, FEI, USA). In order to minimize charging, the ion sputter coater (E-1045, Hitachi, Japan) was used to coat a thin layer gold on the samples. TEM images were taken on a transmission electron microscopy (Hitachi JEM-1200EX, Tokyo, Japan), operating with an accelerating voltage of 80 kV.

2. Results and discussions

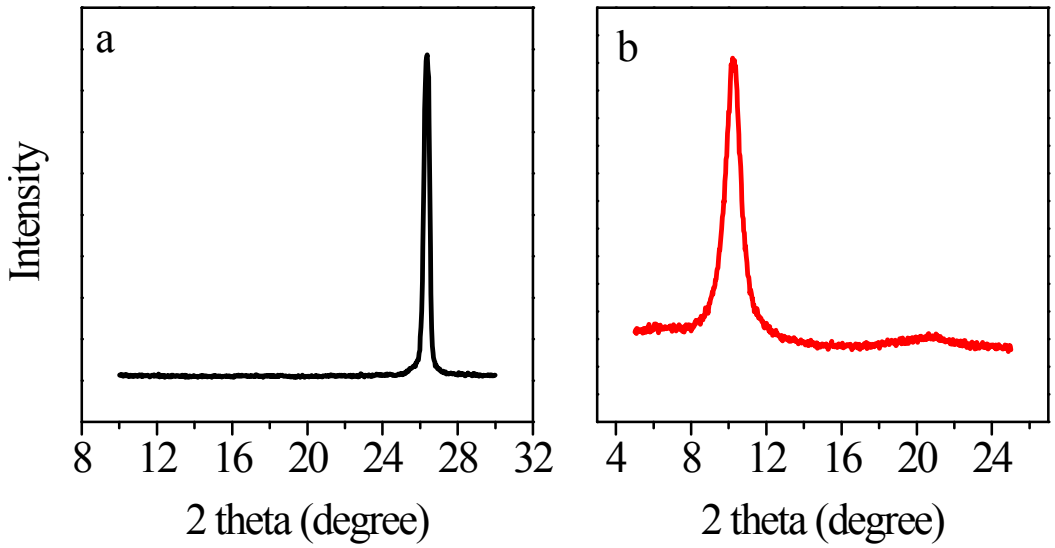

Figure S2. XRD patterns of (a) natural graphite flake and (b) graphite oxide. It shows that the interlayer distance of natural graphite flakes is around 0.330 nm. After oxidation of graphite, the interlayer distance of graphite oxide extends to 0.863 nm. It is larger than most of graphite oxide in previous studies,[1] which indicates the high degree of oxidation.

(S1) S. You, B. Sundqvist, A. V. Talyzin, *ACS Nano*, 2013, **7**, 1395.

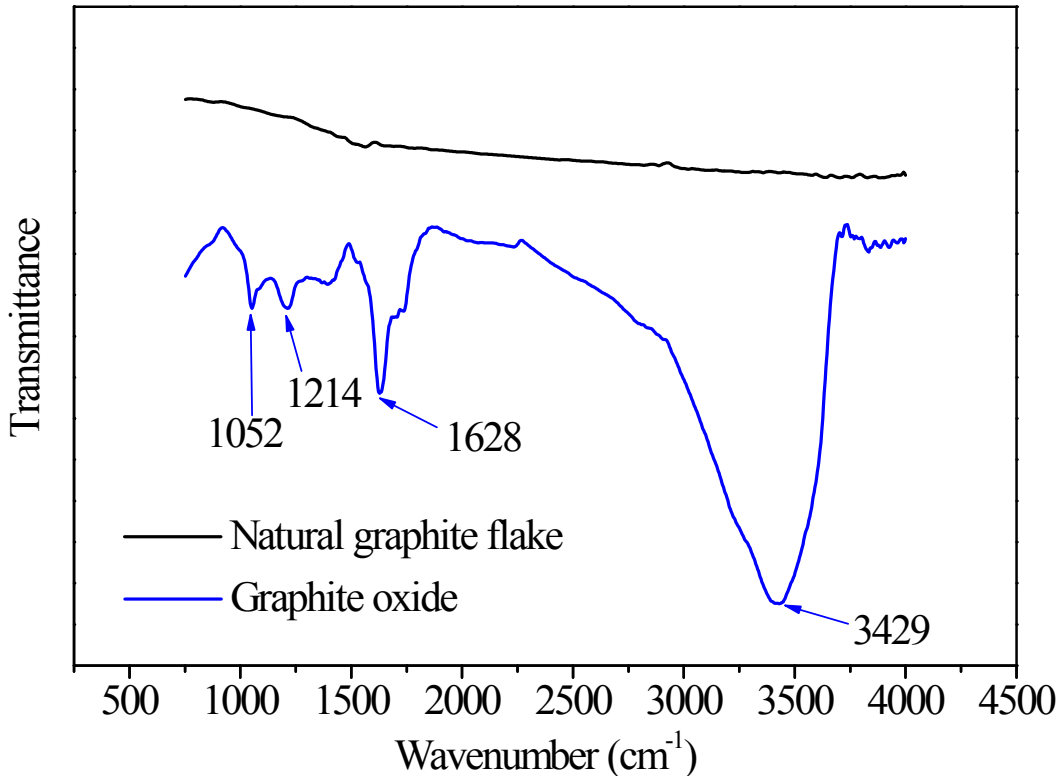

Figure S3. FTIR spectrums of natural graphite flake and graphite oxide. This results also show the graphite oxide is obtained.

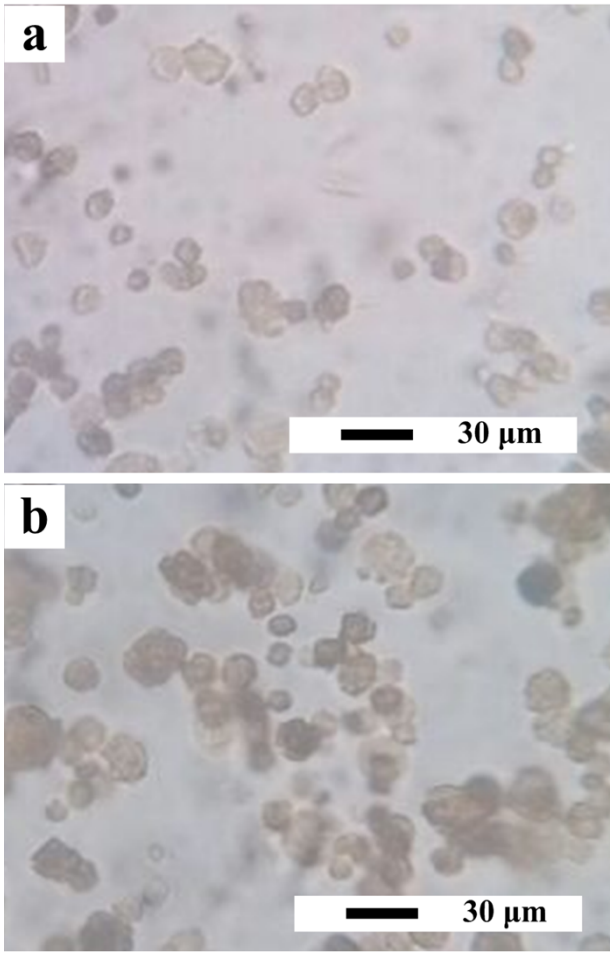

Figure S4. (a) (b) Optical microscopy images of GO microcapsule and GO-PVP microcapsule, respectively.

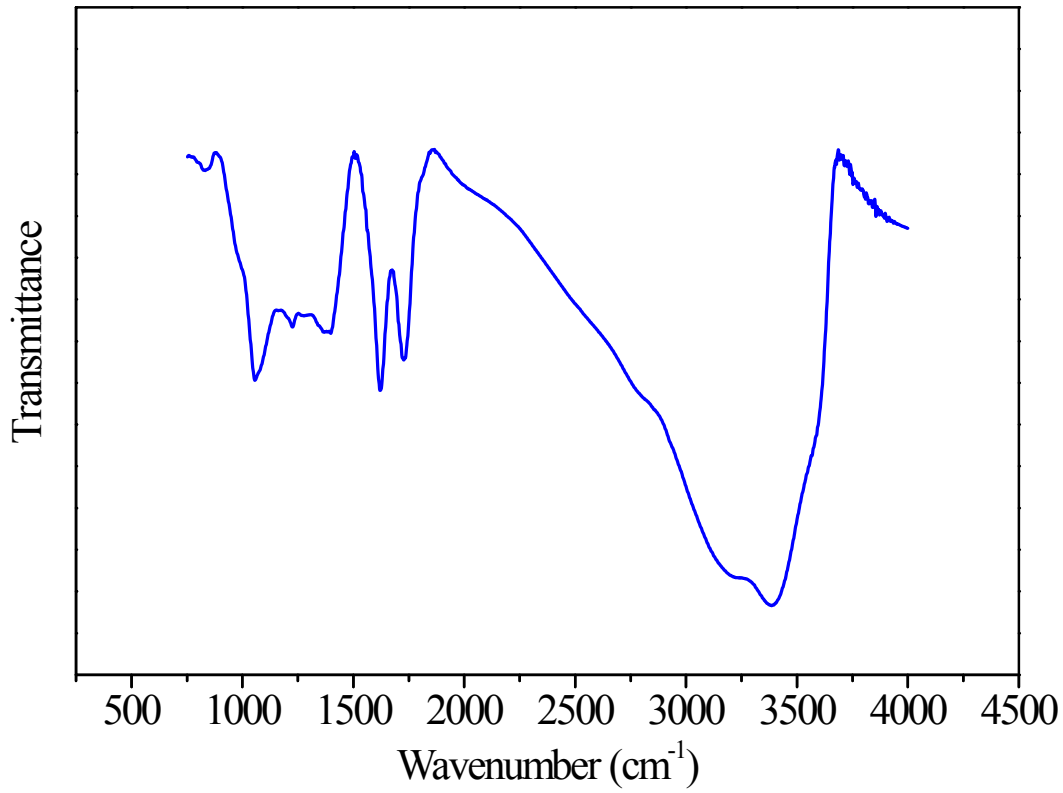

Figure S5. FTIR spectrum of GO capsule.

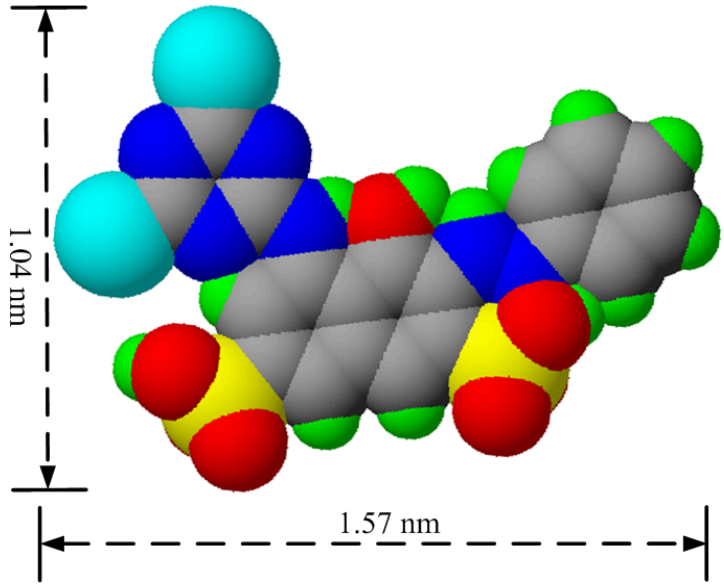

Fig. S6 Chemical structure of the dye molecules. Molecule weight: 615 Da. Green: hydrogen. Blue: nitrogen. Red: oxygen. Light green: chlorine. Gray: carbon.

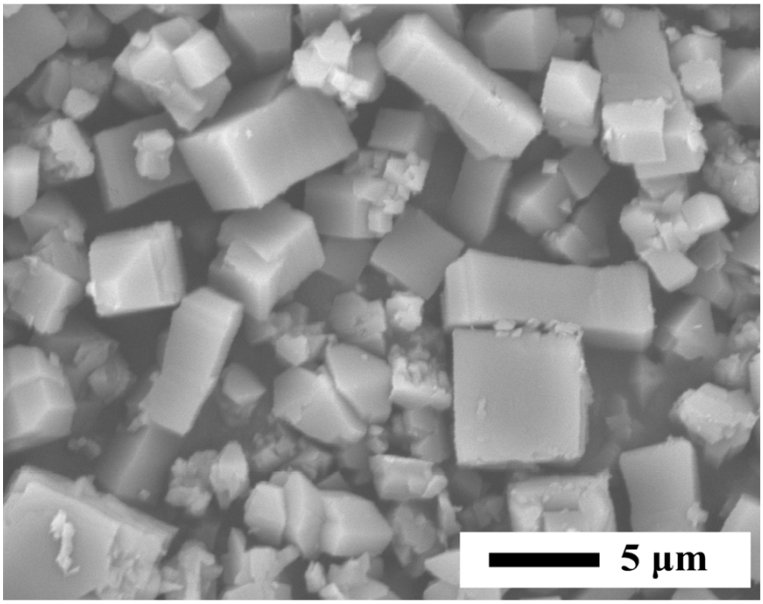

Figure S7. SEM image of CuTPA. SEM image shows that the sizes of CuTPA is 3-5 µm.

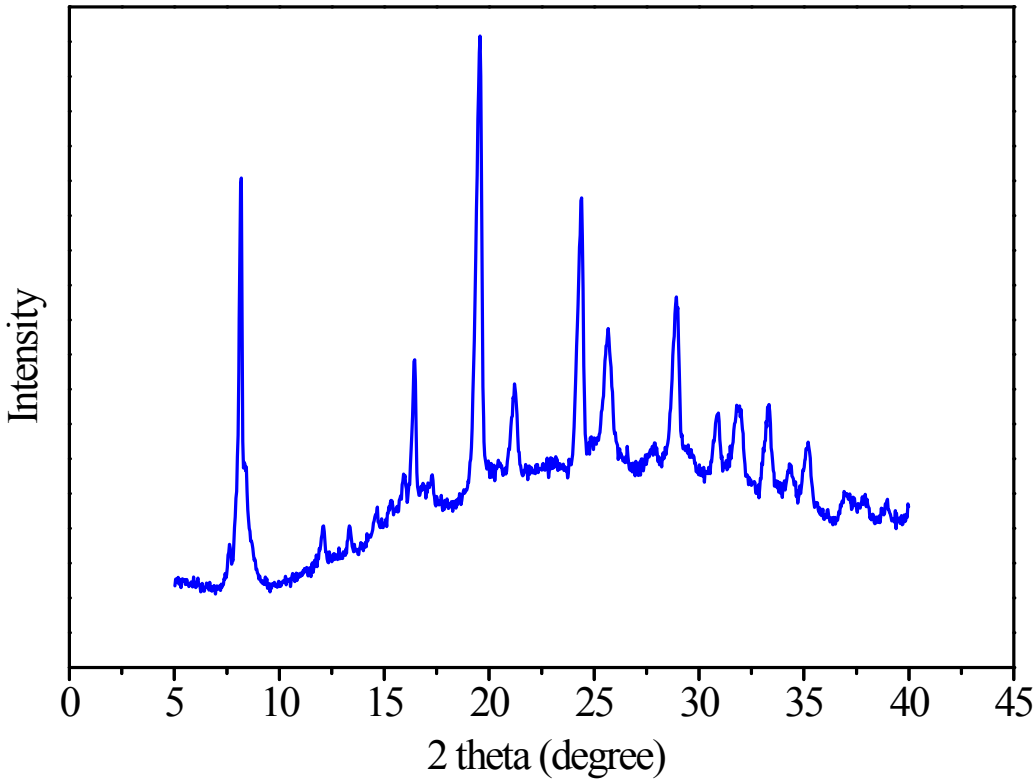

Figure S8. XRD pattern of MOF-GO yolk-shell superstructures. The XRD pattern indicate that the CuTPA is encapsulated into the GO-PVP microcapsules

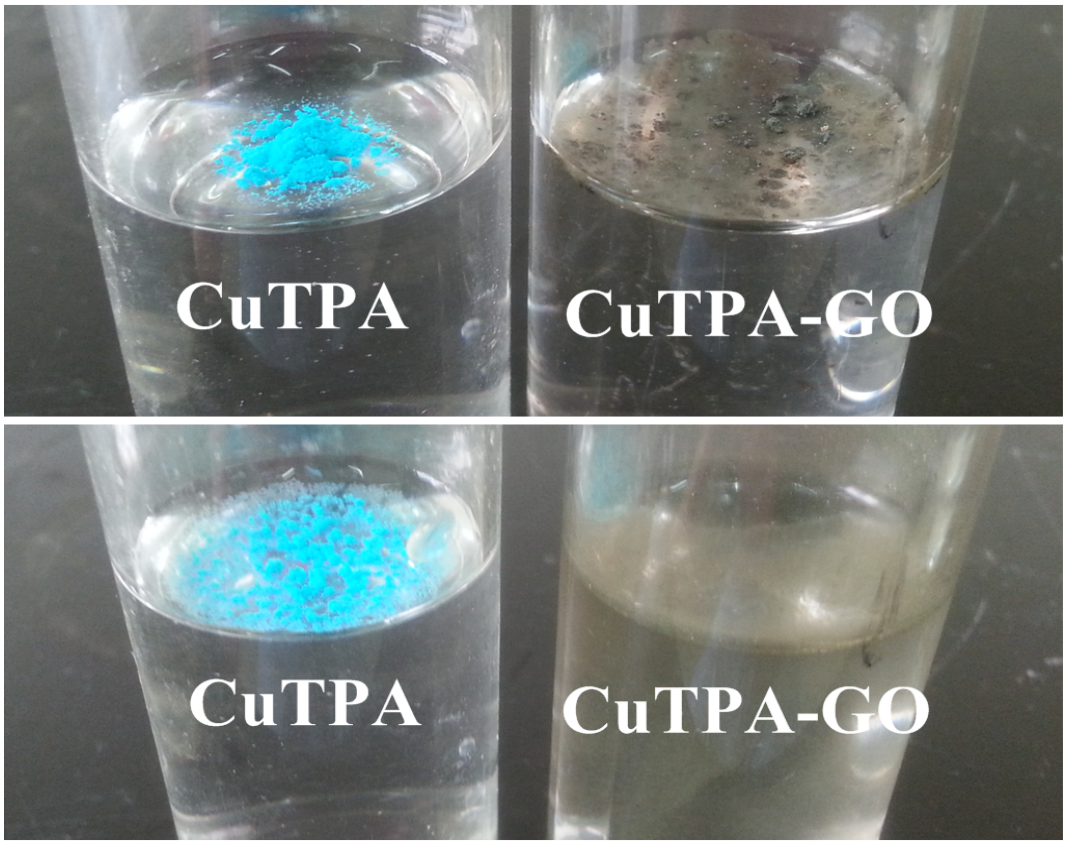

Figure S9. Photographs of CuTPA and CuTPA-GO yolk-shell superstructures dispersing in water at the beginning and after gentle shaking for 3 seconds.