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Supporting Information

Hierarchical Superstructures Assembled from pH-Responsive Gold Nanoparticles in Deformable Emulsion Droplets

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EXPERIMENTAL SECTION

Materials. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$, purity: 99.99%) was supplied by Alfa Aesar. Cetyltrimethylammonium bromide (CTAB, purity: 99%), cetyltrimethylammonium chloride (CTAC, purity: 97%), sodium borohydride ($NaBH_4$, purity: 98%), poly (vinyl alcohol) (PVA, M_n = 13K-23K g/mol, 87-89% hydrolyzed), ascorbic acid (AA, 99.99% metal basis), and Nile Red were purchased from Aladdin. Rhodamine 6G (R6G, purity: 99%) was obtained by Sigma-Aldrich. The thiol terminated functional polymers $P4VP_{2.5k}$-SH (the subscript is M_n of the functional polymer, $M_w/M_n = 1.16$) and PS_{2k}-SH ($M_w/M_n = 1.15$) were obtained from Polymer Source. Sulfuric acid was purchased from Beijing Chemical Factory. All the chemicals were used as received without further purification. The glassware used to synthesize AuNPs in the experiment was cleaned by aqua regia for 20 min and rinsed with deionized water prior to experiments.

Synthesis of AuNPs. Monodispersed AuNPs were synthesized according to a modified seed-mediated growth method. In a standard synthesis, the synthesis process of the AuNPs with the diameter of 10.2 nm included the preparation of CTAB-capped Au seeds and the further growth of Au seeds. The seeds were prepared by quickly injecting the freshly prepared $NaBH_4$ ice-cold aqueous solution (0.6 mL, 10 mM) into a mixture aqueous solution containing $HAuCl_4 \cdot 3H_2O$ (10 mL, 0.25 mM) and CTAB (100 mM) in a vial at 27 °C. The resulting solution immediately transformed into the brown solution, indicating the generation of the Au seeds. Then, the brown solution was left undisturbed for at least 3 h to ensure complete reaction. For the growth process, the prepared seeds solution (2 mL), CTAC (40 mL, 200 mM) and AA

(30 mL 100 mM) were mixed in a 250 mL round bottomed flask, followed by one-shot injection of $HAuCl_4 \cdot 3H_2O$ aqueous solution (40 mL, 0.5 mM). The solution turned red within a few seconds, and the reaction was allowed to continue for 15 min at 27 °C under vigorously stirring. Finally, the products were centrifuged (15000 rpm, 30 min) and concentrated for the following ligand exchange process.

Surface modification of AuNPs. A two-step ligand-exchange approach was used to prepare pH-responsive AuNPs building blocks by modifying the surface of AuNPs with thiol terminated functional PS and P4VP polymers. Typically, 2 mL of the concentrated CTAB/CTAC-capped AuNPs aqueous solution (~ 4 mg/mL) was added into the THF solution of PS-SH and P4VP-SH (15 mL, mole ratio Au:PS-SH:P4VP-SH=1:0.3:0.3). The mixture solution was used for ligand-exchange reaction under sonicating for 2 h and incubated for at least 12 h. Then, the products were separated by centrifugation (15000 rpm, 30 min). The secondary ligand exchange was carried out by dispersing the precipitation into THF solution of PS-SH and P4VP-SH (mole ratio Au:PS-SH:P4VP-SH=1:0.15:0.15), followed by sonicating for 2 h and incubating overnight. After ligand exchange was completed, the purified procedure was performed to remove the unbound polymer ligands and residual surfactant. In order to purify the AuNPs, ethanol was added drop by drop into the above THF solution as the poor solvent until the solution became turbid. Subsequently, the turbid solution was left undisturbed at -20 °C for 12 h and centrifugated (15000 rpm, 30 min) to collect the PS and P4VP tethered AuNPs@PS/P4VP building blocks. The same procedure was repeated for 4-5 times to ensure the purity of AuNPs@PS/P4VP building blocks. Finally, the pH-responsive

AuNPs@PS/P4VP building blocks were dispersed in chloroform at a concentration of 10 mg/mL.

Preparation of AuNP assemblies. The sheet-like superlattices and hollow capsules self-assembled from pH-responsive AuNPs@PS/P4VP building blocks were prepared through emulsion-solvent evaporation method by precisely tuning the interfacial instability of the emulsion droplets. In brief, the as-prepared pH-responsive AuNPs@PS/P4VP building blocks chloroform solution (100 µL, 10 mg/mL) was emulsified in the PVA aqueous solution (1 mL, 3 mg/mL) with different pH value in a vial by stirring vigorously (3 min, 1500 rpm). The pH value of PVA aqueous solution was mediated by adding the sulfuric acid aqueous solution into the PVA solution. The sheet-like superlattices and capsules were obtained by emulsification of AuNPs@PS/P4VP building blocks chloroform solution in PVA aqueous solution with pH = 1.0 and 3.0, respectively. Then, the cloudy emulsion was left undisturbed for 2 days at 25 °C to allow the complete evaporation of chloroform through the aqueous solution. Subsequently, the assemblies were centrifuged at 10,000 rpm for 30 min to remove PVA surfactant by repeated centrifuged 2-3 times and redispersed in deionized water. Finally, the assemblies were dispersed in deionized water for further characterizations.

Characterization. The surface structures of assemblies were observed by Zeiss Merlin Scanning electron microscopy (SEM). SEM samples were prepared by dropping dilute dispersion of assemblies onto a clean silicon wafer, followed by complete evaporation of the solution at room temperature. Transmission electron microscopy (TEM) measurement was performed on JEOL JEM-1400 at an accelerated voltage of 120 kV. Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) elemental mapping images were recorded by JEOL JEM-F200 at an accelerated voltage of 200 kV. For the preparation of TEM samples, 10 μL of the hierarchical assembly dispersion was deposited onto copper grid covered by carbon film. Then, the sample was allowed to dry under atmosphere condition. The evolution of the emulsion droplets during solvent evaporation was in situ monitored by confocal laser scanning microscopy (CLSM) (Carl Zeiss LSM 700 imaging system). In order to clearly observe the evolution of emulsion droplets, the mixture chloroform solution containing pH-responsive AuNPs@PS/P4VP building blocks and Nile Red was emulsified in PVA aqueous solution. The resulting emulsion droplets containing Nile Red were observed by CLSM. The pH values were measured by depositing 2 μL of aqueous solution onto pH dipstick (Saieise). Interfacial tension values were measured via pendant drop tensiometry using optical contact-angle measuring device (Kruss, DSA 100). To perform the measurement, the syringe was filled with chloroform solution of AuNPs@PS/P4VP building blocks (10 mg/mL), and PVA aqueous solution (3 mg/mL) with different pH value was added in colorimetric dish. Then, syringe extruded a suitable volume of chloroform solution, which was hung on the needle end as a droplet. When the volume of droplets was maximum without deformation, the shape was recorded and the interfacial tension values could be obtained.

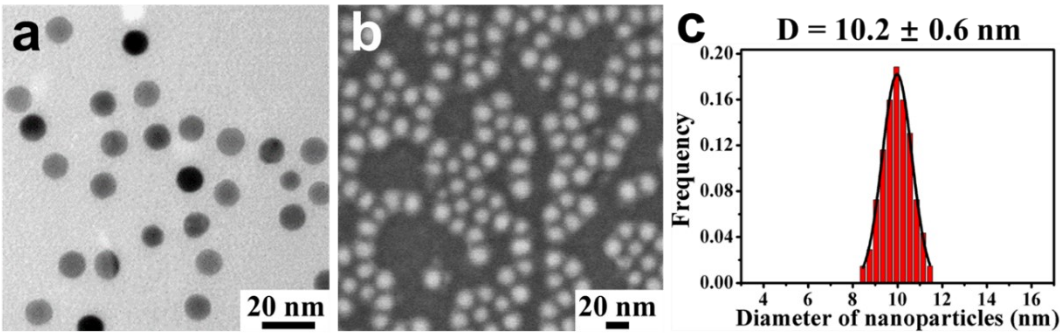

Fig. S1 (a) and (b) are TEM and corresponding SEM images of the monodispersed pH-responsive AuNPs@PS/P4VP building blocks synthesized based on a seed-mediated growth method, followed by surface modification with PS_{2k}-SH and $P4VP_{2.5k}$-SH homopolymers. (c) is the size distribution histogram of corresponding AuNPs@PS/P4VP building blocks.

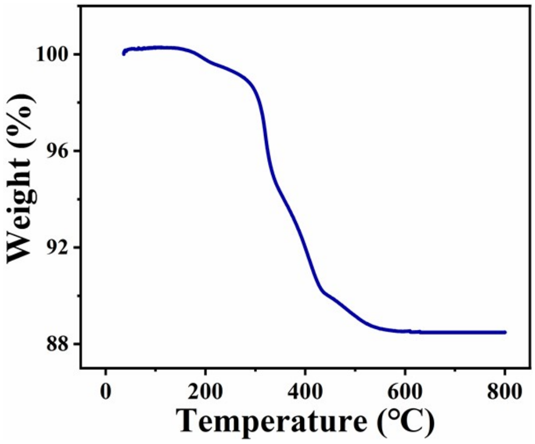

Fig. S2 TGA analysis of the AuNPs@PS/P4VP nanoparticles.

Table. S1 Estimation grafting densities of PS and P4VP on the surface of AuNPs.

$W_{PS+P4VP}$	PS grafting density (chain/nm^2)	P4VP grafting density (chain/nm^2)	F_{PS}	F_{P4VP}
11.6 %	1.15	0.80	0.59	0.41

Note: $W_{PS+P4VP}$ represents the total graft weight fraction. F_{PS} and F_{P4VP} indicate the actual mole fraction of PS and P4VP ligands on Au NPs surface.

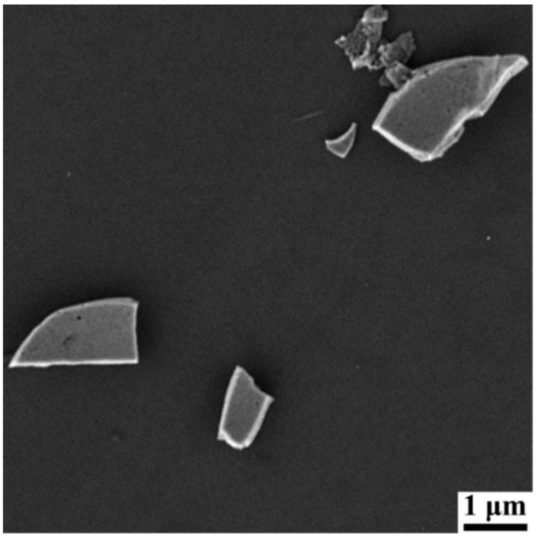

Fig. S3 The SEM image of superlattice at low magnification self-assembled from pH-responsive AuNPs@PS/P4VP building blocks emulsified with PVA aqueous solution at pH = 1.0.

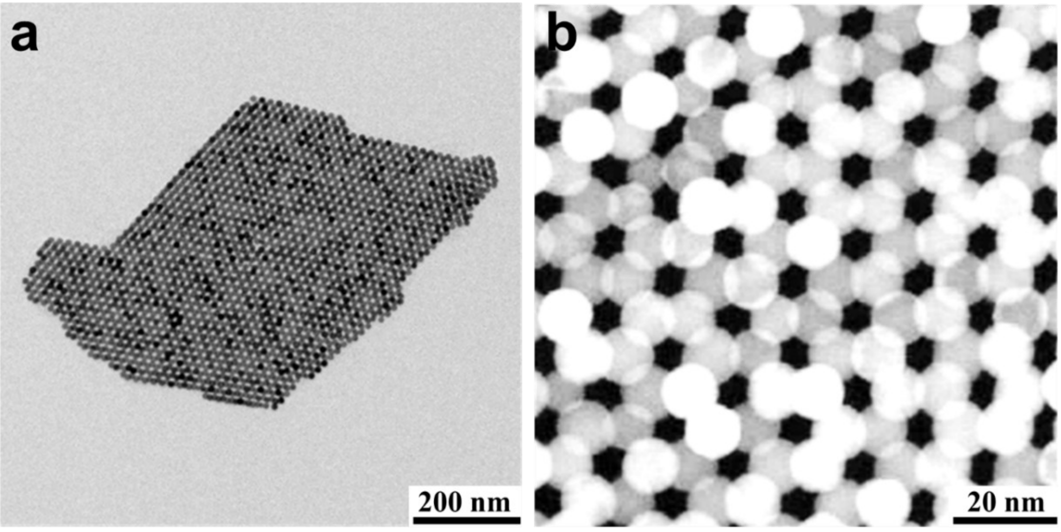

Fig. S4 (a) TEM image of superlattice at low magnification self-assembled from pH-responsive AuNPs@PS/P4VP building blocks emulsified with PVA aqueous solution at pH = 1.0. (b) Magnified STEM image of the superlattice showing the ordered arrangement of the AuNPs@PS/P4VP building blocks in the superlattice nanostructure.

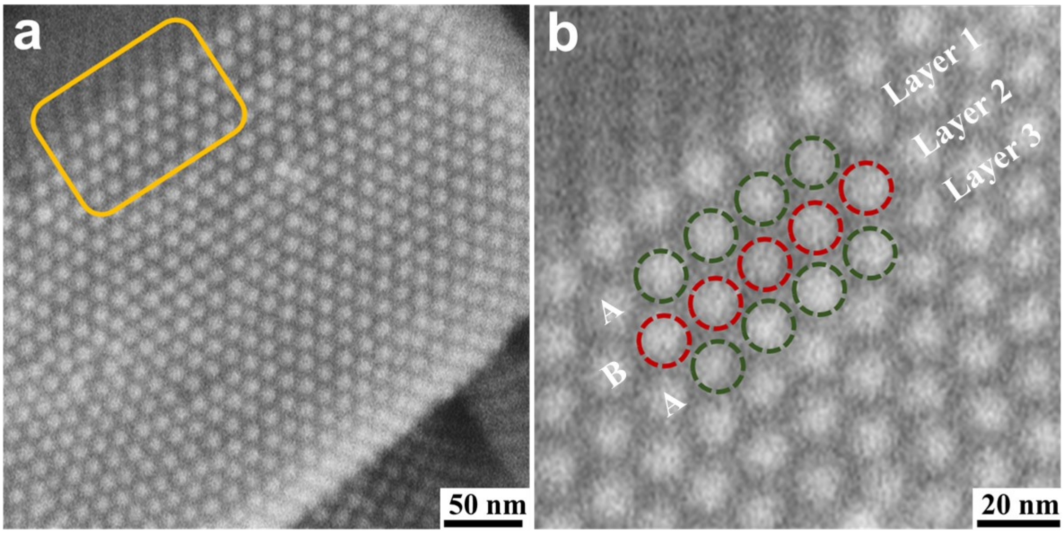

Fig. S5 (a) SEM image of the edge of superlattice structure. (b) Magnified SEM image of superlattice edge showing that AuNPs@PS/P4VP building blocks are arranged in the format of “ABA”.

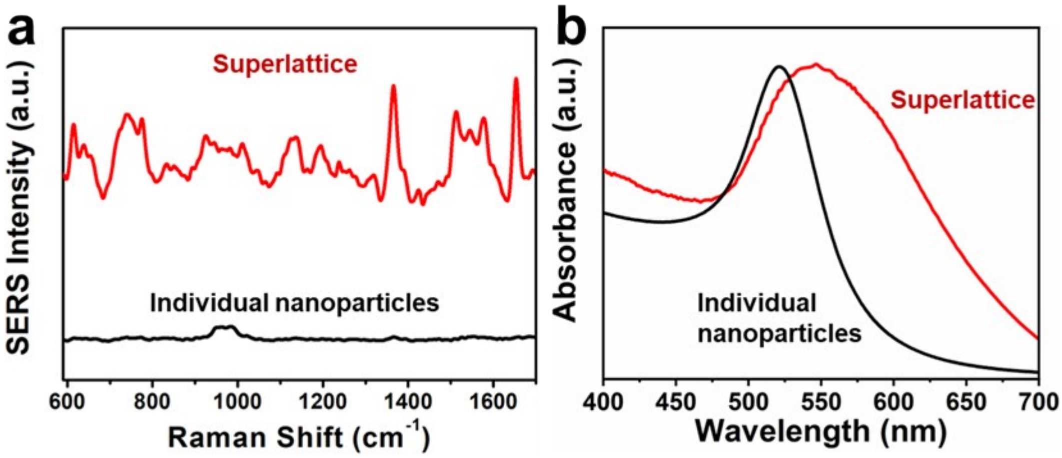

Fig. S6 (a) Raman scattering spectra of Rhodamine 6G on individual nanoparticles (black line) and the superlattices (red line) substrates, respectively. (b) UV-vis spectrums of the nanoparticles (black line) and the superlattices (red line), respectively.

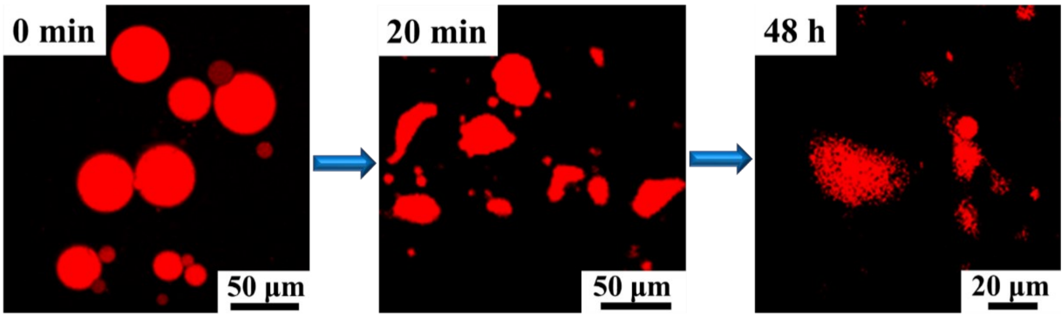

Fig. S7 CLSM images of the evolution of emulsion droplets at different evaporation stages. The emulsion droplets containing pH-responsive AuNPs@PS/P4VP building blocks are marked by Nile Red. The initial time (*i.e.*, 0 min) is defined as the moment of capturing the images of the freshly prepared emulsion droplets. With the evaporation of chloroform, the spherical droplets collapse into non-spherical droplets (*i.e.*, 20 min). After the complete evaporation of the chloroform phase, the flat 3D free-standing organic/inorganic AuNP superlattice sheets are constructed.

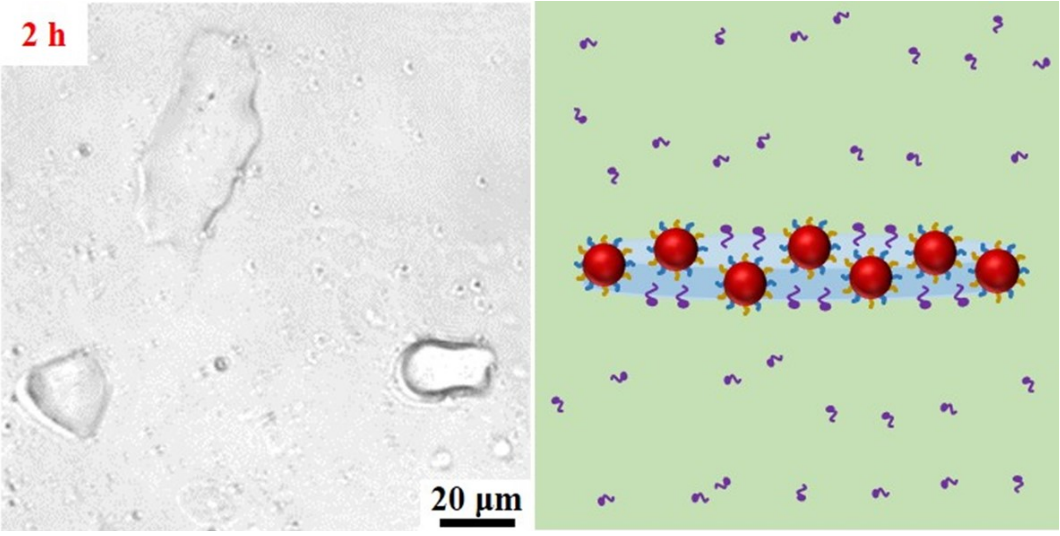

Fig. S8 OM image (left) and the corresponding schematic illustration (right) of the thin flat emulsion droplets after evaporation for 2 h.

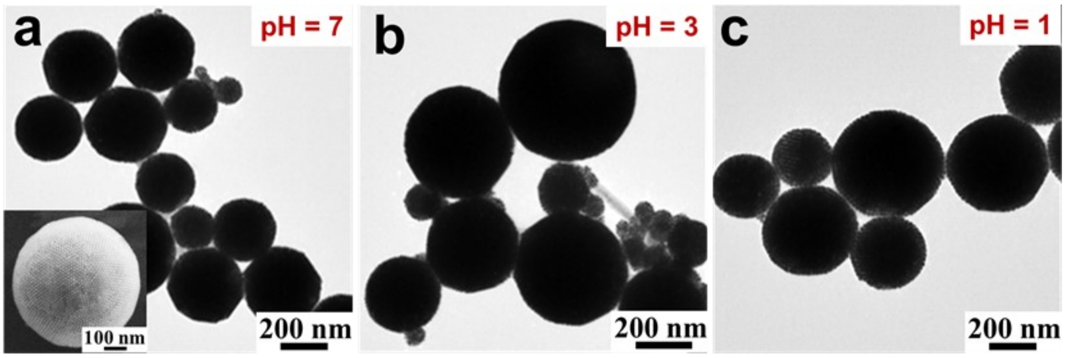

Fig. S9 TEM images of the spherical particles assembled from the PS tethered AuNPs at different pH values. (a) pH = 7; (b) pH = 3; and (c) pH = 1. The inset of (a) is the corresponding SEM image of the spherical particles.

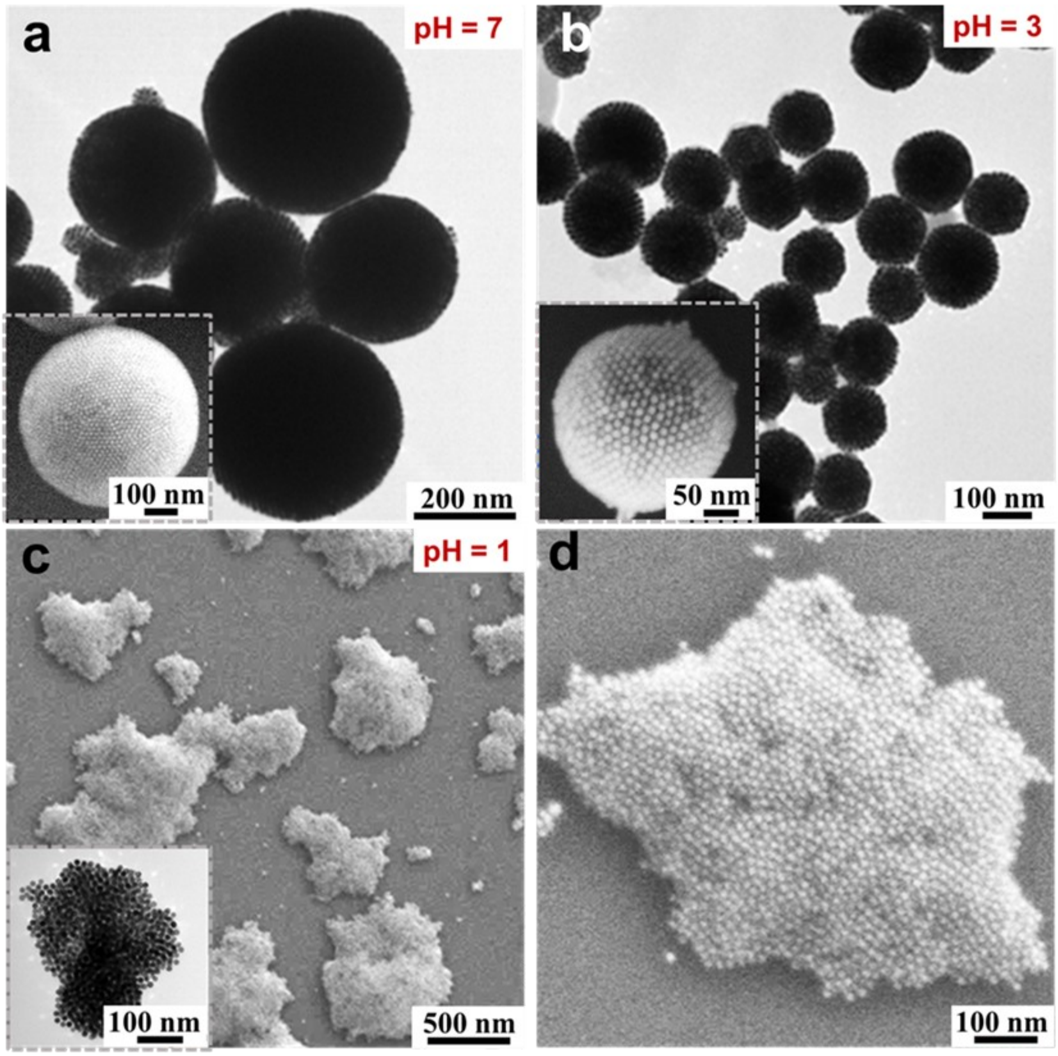

Fig. S10 TEM and SEM images of the hierarchical superstructures assembled from the P4VP tethered AuNPs at different pH values. (a) pH = 7; (b) pH = 3; and (c) pH = 1. The insets of (a-c) are the corresponding SEM and TEM images of the superstructures. (d) is the magnified SEM image of the irregular structure.

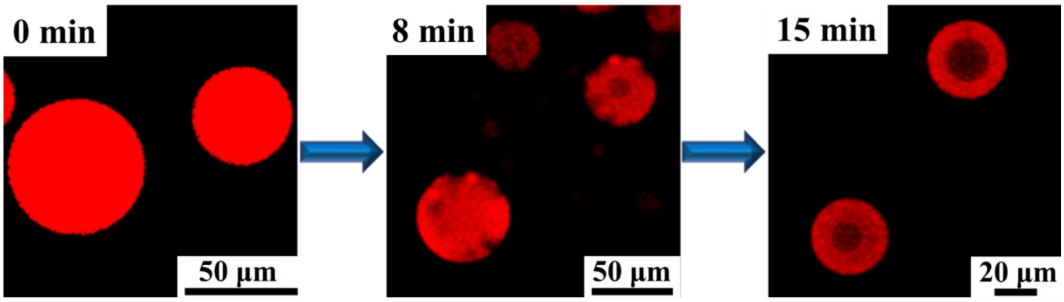

Fig. S11 CLSM images of the evolution of emulsion droplets emulsified with PVA aqueous solution at the pH = 3.0. The emulsion droplets are marked by Nile Red. The initial time (*i.e.*, 0 min) is defined as the moment of emulsifying chloroform solution containing pH-responsive AuNPs@PS/P4VP building blocks in PVA aqueous solution at pH = 3.0. At the beginning, the emulsion droplets are spherical and homogeneous. With the evaporation of chloroform, aqueous solution gradually infiltrates into emulsion droplets through the surface of droplets (*i.e.*, 8 min). As the emulsion droplets further evaporate, the aqueous solution converges into an individual droplet located at the center of emulsion droplets (*i.e.*, 15 min).

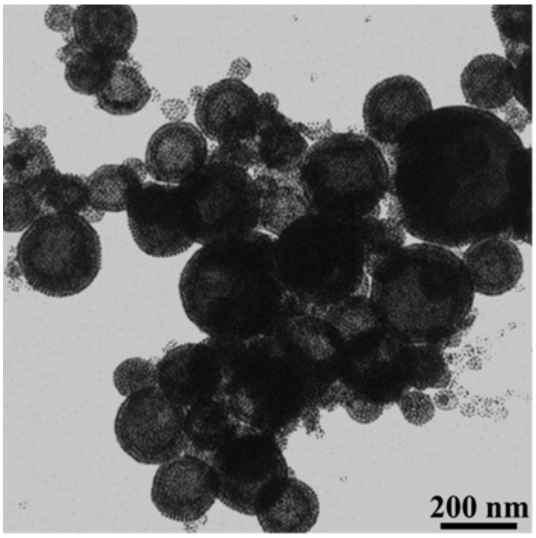

Fig. S12 TEM image of the hollow capsule self-assembled from pH-responsive AuNPs@PS/P4VP building blocks emulsified with PVA aqueous solution at the pH = 3.0.