Supporting Information

Janus droplet microreactors for preparing polyaniline/AgCl nanocomposites

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A. Material and Characterizations

Magnetic ionic liquid 1-butyl-3-methylimidazolium tetrachloroferrate ([bmin]$FeCl_4$) was purchased from Dibo Chemical Technology Co., Ltd. (Shanghai, China). Soybean oil (Aladdin Co., Ltd) was used as the ambient phase for the generation of [bmin]$FeCl_4$-water Janus droplets. Silver nitrate ($AgNO_3$) and polyvinylpyrrolidone (PVP) were purchased from Lanyi Chemical Product Co., Ltd. (Beijing, China). Aniline (Shanghai Macklin Biochemical Technology Co., Ltd.) was doubly distilled at room pressure before use. Aqueous solutions were prepared using de-ionic water.

The synthesized products were analyzed via scanning electron microscope (SEM, JSM7401, JEOL), transmission electron microscope (TEM, JEM-2010, JEOL), X-ray diffraction (XRD, D8 Advance, Bruker) and fourier transform infrared spectrometer (FTIR, Nexus 670, Nicolet).

B. Synthesis of Polyaniline/AgCl nanocomposites in Batch

6 mL 0.5%, 4% or 8% PVP aqueous solution mixed with $AgNO_3$ (0.02 M) and aniline (0.02 M) were carefully added to a beaker that contains equal-volume [bmin]$FeCl_4$ to form an

interface for reaction. After 10 min, white precipitates were observed at the interface between the aqueous and MIL layers, and the color of the aqueous phase became orange. Reactions were carried out at a maintained temperature of 40 ℃ for 24 h, till the aqueous phase color finally turned emeraldine. On completion, the upper aqueous phase was collected for centrifuging and washing several times with both ethanol and de-ionic water. After that, the dark green precipitate was transferred to a grass dish to dry under vacuum at 40 ℃ for 24 h.

The TEM images of PANI/AgCl nanocomposites synthesized in the batch method during the reaction time are shown in Figure S2. It can be seen that, at the early stage of the reaction, the dark spots, AgCl particles with diameters in several nanometers, are aggregated, and owing to the amphiphilic property of the anchor agent PVP, the inorganic particles are coated by thin PANI layers. After 24 h continued reaction, there was an observable increase in the AgCl particle size and the PANI layer thickness, indicative of the aggregation phenomena. Figure S3 further displays that the PVP concentration has positive effects on the degree of particle dispersion and reduces the aggregation of PANI fibers.

C. Synthesis of Polyaniline/AgCl nanocomposites in Janus Droplet Microreactors

In the droplet microflow systems, soybean oil was employed as the continuous fluid. $AgNO_3$ (0.02 M) and aniline (0.02 M) were pre-mixed with 4% PVP aqueous solution, serving as one of the dispersed phases and stored in the dark at low temperature prior to use. And MIL [bmin]$FeCl_4$, the oxidant, was used as the other dispersed phase. The aforementioned fluids were pumped into a coaxially assembled 3D-printed microchannel, separately by syringe pumps (Baoding Longer Precision Pump Co., Ltd, Beijing, China). The 3D-printed droplet

generator, measuring 30 mm × 20 mm × 5 mm, was fabricated by a Stratasys Polyjet™ printer (EDEN 260VS™) using transparent photopolymer material known as VeroClear™, where the two vertical channels with the diameters of 0.8 mm were for the injection of the continuous phase, and a theta capillary possessing bi-nozzles each with approximately 50 μm inner diameter was inserted in the cross channel of the 3D-printed fitting for injecting two dispersed flows.[1] To prevent products clogging the orifices of dispersed phases, the droplet makers were immersed in an ice bath to suppress the reaction process. To stably generate aqueous-[bmin]$FeCl_4$ Janus droplets with sizes comparable to the hydraulic diameter of the microchannel and maintain an appropriate droplet spacing preventing droplet fusion, the flow rate of the continuous phase Q_c is maintained at 50 μL/min, and the flow rates of two dispersed phases are set at 20 μL/min each.[1] Once the aqueous-[bmin]$FeCl_4$ Janus droplets are generated, the reaction initiates at the inner interface of Janus droplets promptly. Subsequently, the generated Janus droplets flow through a spiral PTFE tubing with a 0.8 mm inner diameter at a water bath temperature of 40 °C for proceeding the reaction. The total tubing length was preliminarily chosen to be 2.28 m, at which point the aqueous compartments of the Janus droplets at the end of the microchannel turned completely emerald green and the color ceased to deepen, indicating the formation of a specific amount of polyaniline. Under the stated operating conditions, the residence time of the Janus microreactors is about 13 min.

The formation of Janus droplet microreactors was recorded by the high-speed color CCD camera (edge 5.5, PCO GmbH, German) connected to the microscope (Nikon, MM400/L) at a frequency of 200~500 fps (frames per second). The droplets that flowed out of the spiral microchannel were collected in a separatory funnel filled with ethanol for reaction quenching.

After allowing the effluent to stand for 30 min, the bottom layer of the dark brown liquid is separated for the recovery of the expensive MIL. The emeraldine layer was centrifuged and washed multiple times with both ethanol and deionized water, then the precipitate was collected to a glass dish and dried in a vacuum oven at 40°C for 24 h. The effluent obtained within the initial 10 minutes was discarded.

Table S1. Characteristic peaks of pure PANI and AgCl/PANI nanocomposites synthesized in batch or Janus droplets (JDs)

Peak regions (cm^{-1})	Assignment	pure PANI	AgCl/PANI (batch)	AgCl/PANI (JDs)
~1650	C=O[2]	absent	present	present
~1570	the C－C stretching of quinoid[2, 3]	present	present	present
~1480	the C－C stretching of benzenoid[2, 3]	present	present	present
1370~1400	O-CH_2 groups in glycerol moiety of monoglycerides, diglycerides, and triglycerides[4]	absent	present	present
1301~1285	C–N stretching[2, 3]	present	present	present
1245~1230	C=N stretching[2, 3]	present	present	present
1140~1124	the in-plane bending of C–H[2, 3]	present	present	present
790~805	the out-of-plane bending of C–H[2, 3]	present	present	present

Supplementary figures

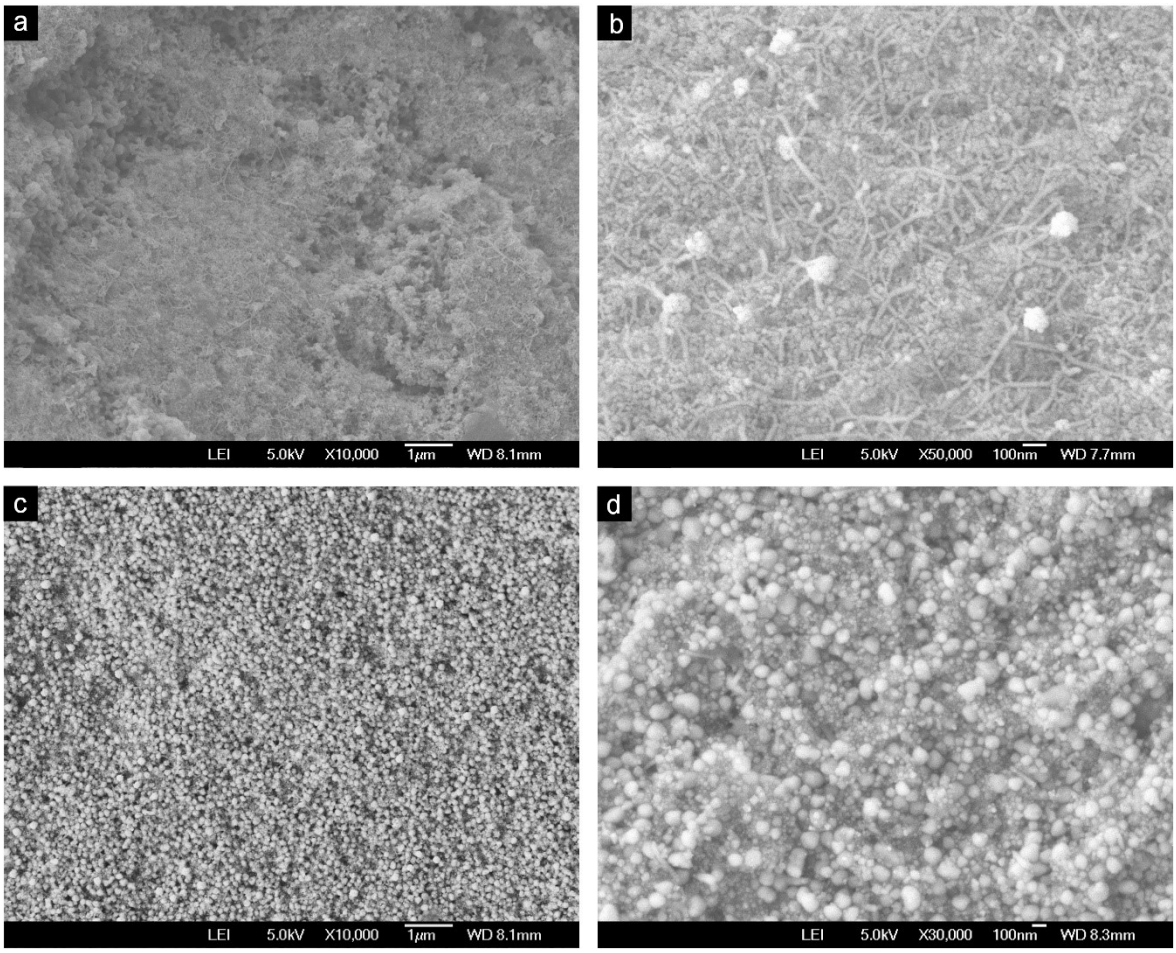

Fig. S1. SEM images of PANI/AgCl nanocomposites prepared (a-b) in batch (with soybean oil as the ambient phase in a breaker), (c-d) in Janus droplet microreactors.

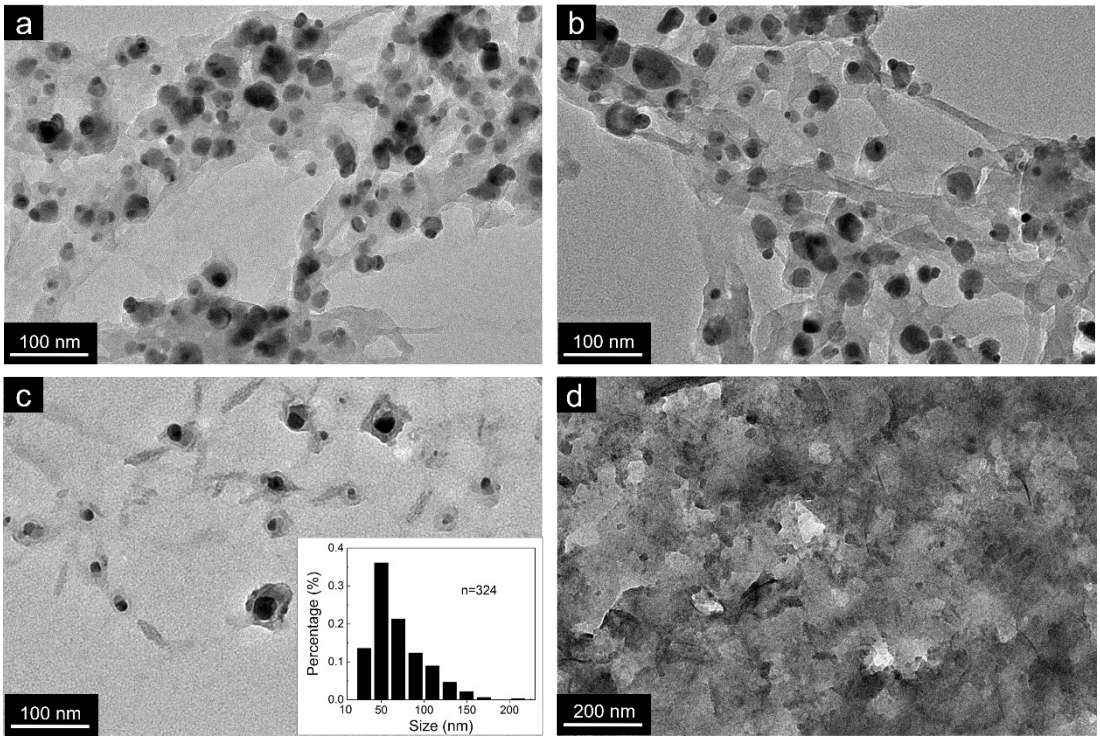

Fig. S2. TEM images of PANI/AgCl nanocomposites synthesized (a) in batch, (b) with soybean oil as ambient phase in the beaker, (c-d) in Janus droplet microreactors. The size distribution diagram of the nanoparticles produced in the Janus droplets is shown in the inset of (c).

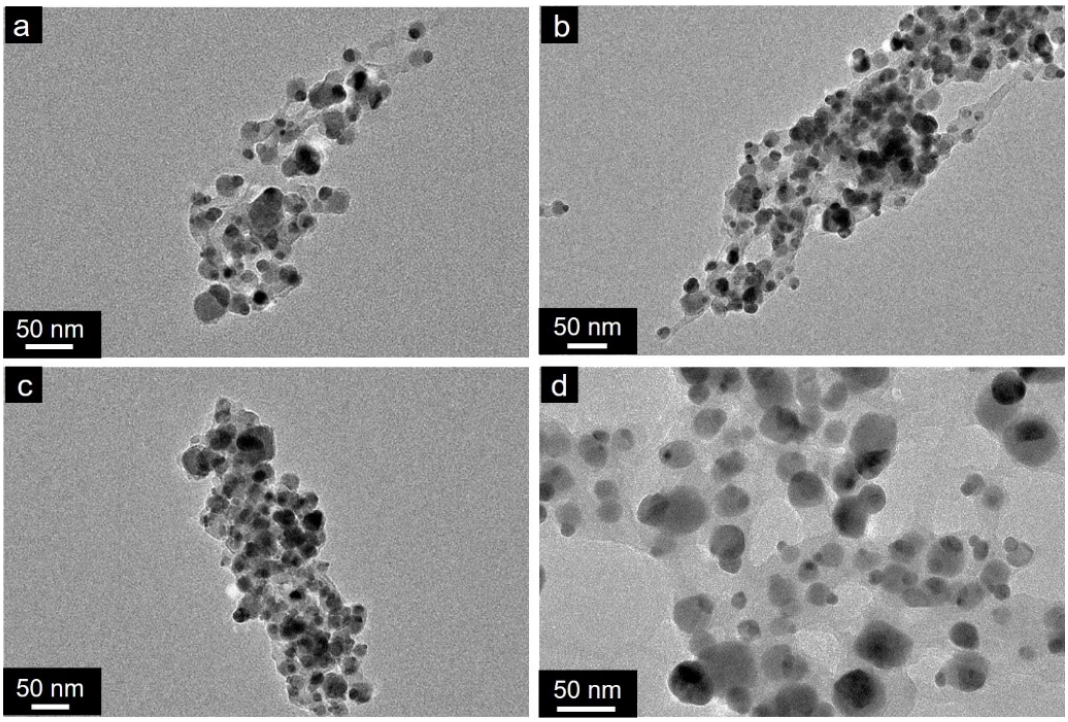

Fig. S3. TEM images of PANI/AgCl nanocomposites prepared in batch under different reaction times when the PVP concentration is 4%. (a) 2 h; (b) 3 h; (c) 5 h; (d) 24 h.

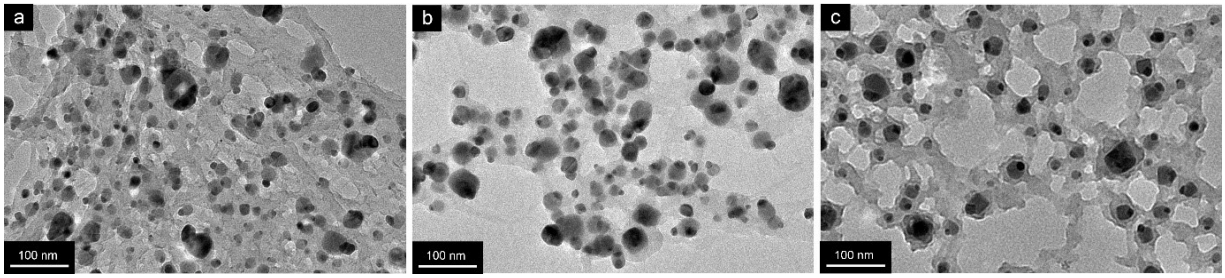

Fig. S4. TEM images of PANI/AgCl nanocomposites prepared in batch under different concentrations of PVP, (a) 0.5%; (b) 4%; (c) 8%.

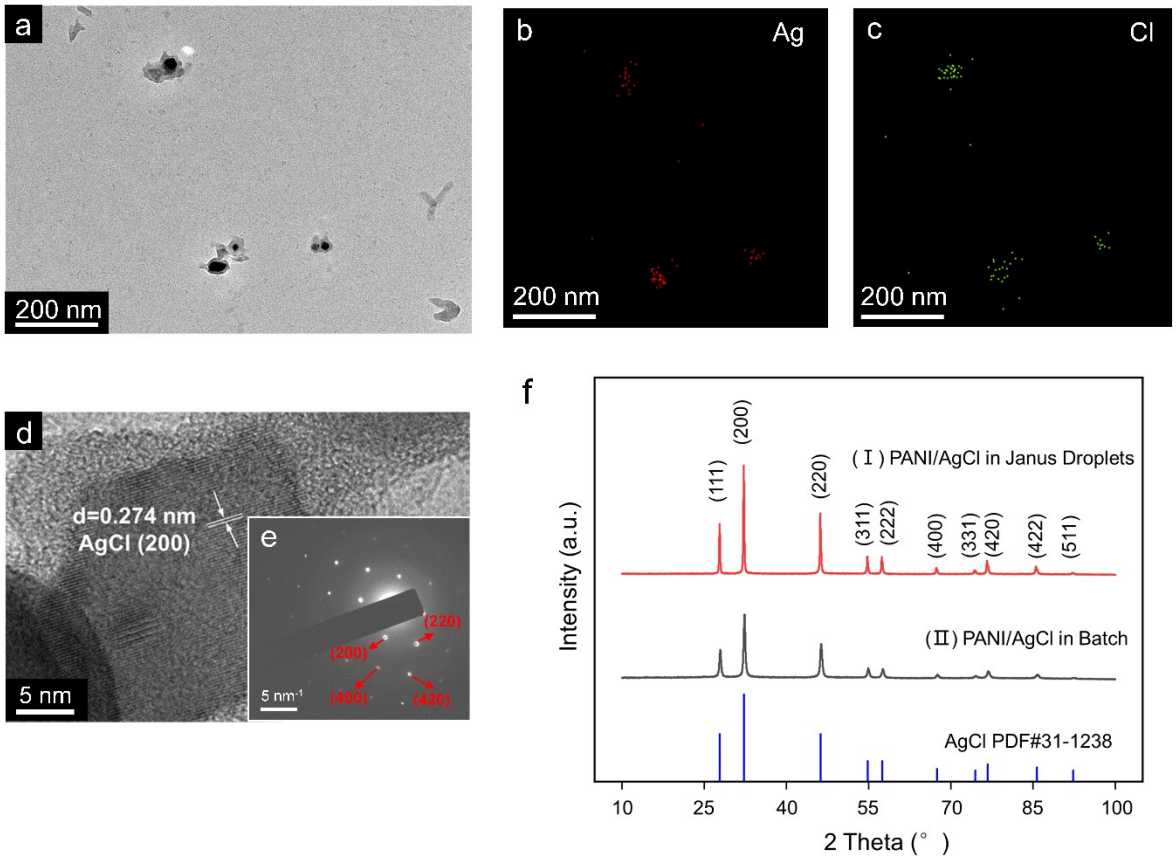

Fig. S5. (a) TEM image of PANI/AgCl nanoparticles synthesized in Janus droplet microreactors. (b-c) EDX element maps. (d) High-resolution TEM images of AgCl/PANI nanoparticles, whose lattices spacing value d of 0.274 nm was resolved, corresponding to AgCl (200) plane.[33] (e) SAED pattern of AgCl/PANI nanoparticles. (f) XRD patterns of PANI/AgCl nanocomposites prepared in batch (with soybean oil as the ambient phase in a breaker) and in Janus droplet microreactors.

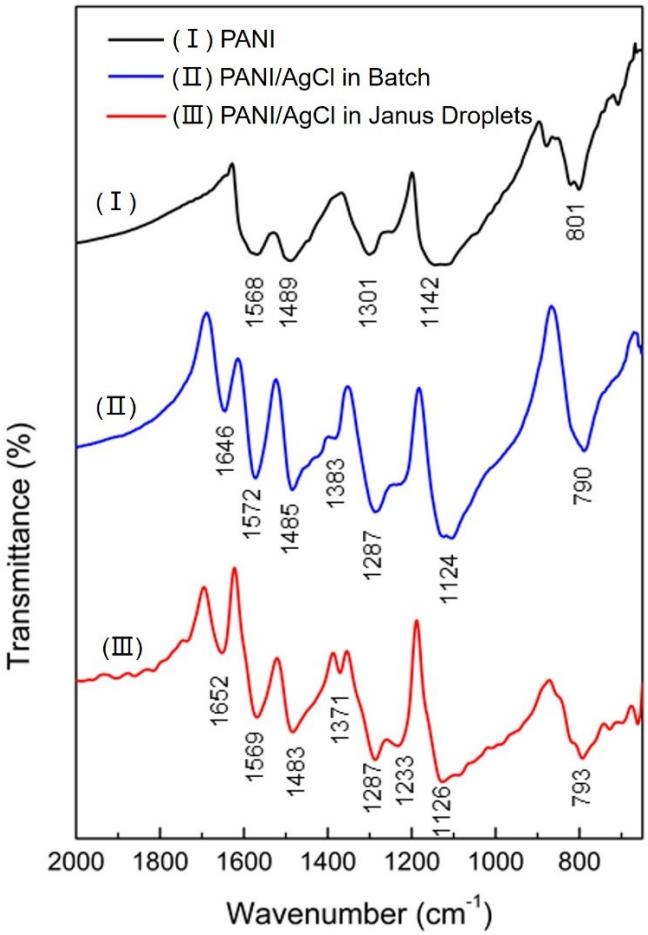

Fig. S6. FTIR spectrum of pure PANI (the black line I), AgCl/PANI nanocomposites prepared in batch (the blue line II) and AgCl/PANI nanocomposites synthesized via Janus droplet microreactors (the red line III).

References

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