# Supporting Information

## Emulsion Droplets as A Dynamic Interface for Direct and Large-Scale Synthesis of Ultrathin Free-Standing Mesoporous Silica Films as well as 2D Polymeric and Carbon Nanomaterials

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### *1. Experimental Section*

***Chemicals*:** 1,12-dibromododecane and 1-methylimidazole were received from Isomersyn Chemicals. Tetraethoxysilane (TEOS) was purchased from Acros Organics. N, N-Dimethyl- tetradecylamine and 12-amino lauric acid were received from TCI. Anhydrous ferric chloride, N-methyl morpholine 2, 5-dimethoxy tetrahydrofuran, aqueous ammonia (28 wt%), 1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDCI), hydrofluoric acid (40 wt%), 4-nitrophenol and N-hydroxy benzotrizole (HOBt) were purchased from Alfa Aesar. Petroleum ether, diethyl ether, dichloromethane, methanol, ethyl acetate, acetic acid, anhydrous magnesium sulfate, toluene, N, N-dimethylformamide, acetone, hydrochloric acid and ethanol were purchased from Beijing Chemical Company. Pyrrole, sodium hydride, sodium borohydride, CTAB and chloroauric acid were purchased from Sinopharm chemical reagent Co. Ltd. L-Arginine methyl ester dihydrochloride was purchased from Sichuan shengxin bio-pharmaceutical Co. Ltd. All chemicals were of analytical grade and used as received without any further purification.

***Characterization*:** Typical TEM images were obtained by using H-7650B transmission electronic microscope with an acceleration voltage of 80kV and the high resolution TEM images were obtained using JEM 2010 high-resolution transmission electronic microscope at an acceleration voltage of 120 kV. SEM images were obtained using JSM 7401 high-resolution scanning electronic microscope. XRD measurements were performed on Bruker D8 Advance X-Ray powder diffractometer. $N_2$ adsorption-desorption isotherms were measured with a Micromeritics ASAP2020 surface area and porosity analyzer. Samples were degassed at the temperature of 300℃ for 4 hours. Fourier transform infrared spectra (FTIR) were recorded on AVATAR 360 ESP FTS spectrometer. UV-Vis spectra were collected on

PerkinElmer Lambda 35 spectrometer. Raman spectra were collected on RM2000 microscopic confocal Raman spectrometer. XPS was performed on ESCALAB 250Xi.

## 2. *Synthesis of surfactant*

***Synthesis of $PyC_{12}MIM^{+}Br^{-}$***: The synthesis procedure was followed by the previous literature.[1] Firstly, pyrrole (15 mmol) was added dropwise to a DMF solution (110 mL) containing 1, 12-dibromododecane (43 mmol) and NaH (43 mmol) within the ice bath. The mixture was stirred overnight. The crude product was purified by silica gel column chromatography by using petroleum ether as an eluent to obtain the $PyC_{12}Br$. Subsequently, the resulting $PyC_{12}Br$ (16 mmol) was added to the toluene solution of 1-methylimidazole (18 mmol) and the mixture was refluxed overnight. The crude product was separated by silica gel column chromatography with $CH_2Cl_2/CH_3OH$ (20:1) as an eluent. With desiccated by $Na_2SO_4$, yellow viscous liquid is obtained(yield: 70%). $^1H$ NMR ($CDCl_3$, δ): 10.27 (s, 1H), 7.51 (d, 1H), 7.35 (d, 1H), 6.58 (dd, 2H), 6.04 (d×d, 2H), 4.24 (t, 2H), 4.05 (s, 3H), 3.77 (t, 2H), 1.84 (m, 2H), 1.66 (m, 2H), 1.20 (m, 16H).

***Synthesis of $PyC_{11}ArgOMe$:*** Firstly, 2,5-dimethoxy tetrahydrofuran (48 mmol) and 12-amino lauric acid (43 mmol) were dissolved in a mixture solvent of acetic acid (43 mL) and 1,4-dioxane (57 mL), and then refluxed for 4h. After cooled down to the room temperature, ethanol (10 ml × 3) was added and the resulting mixture was evaporated for three times to remove the acetic acid. The crude product was black liquid and purified by chromatography on silica gel with petroleum ether as an eluent. This afforded the pure substance ($PyC_{11}COOH$) as white solid (yield: 71%). $^1H$ NMR ($CDCl_3$, d): 6.65 (d×d, 2H), 6.14 (d×d, 2H), 3.85 (t, 2H), 2.35 (t, 2H), 1.76 (m, 2H), 1.62 (m, 2H), 1.28 (m, 14H).

The precious step products ($PyC_{11}COOH$, 16 mmol) was dissolved in DMF (30 ml), followed by adding EDCI, 17.6 mmol) and N-hydroxy benzotrizole (HOBt, 16 mmol) with vigorous stirring for 20 min. Then L-Arginine methyl ester dihydrochloride (16mmmol) was added to the resulting mixture and N-methyl morpholine (NMM, 2 ml) was added finally to adjust the pH value to 8~9. The reaction was stirring overnight at room temperature. Dicyclohexylurea (DCU) was removed by filtration. After evaporating, ethyl acetate (20 mL) was added and the resulting mixture was washed with 5% sodium bicarbonate solution, then saturated sodium chloride solution, then 5% sodium hydrogen sulfate solution, then saturated sodium chloride solution. The organic phase was dried over anhydrous sodium sulfate overnight and evaporated to afford a yellow liquid. The crude product was purified by chromatography on silica gel with petrol ether/ethyl acetate (5:1) as an eluent, affording the pure product as

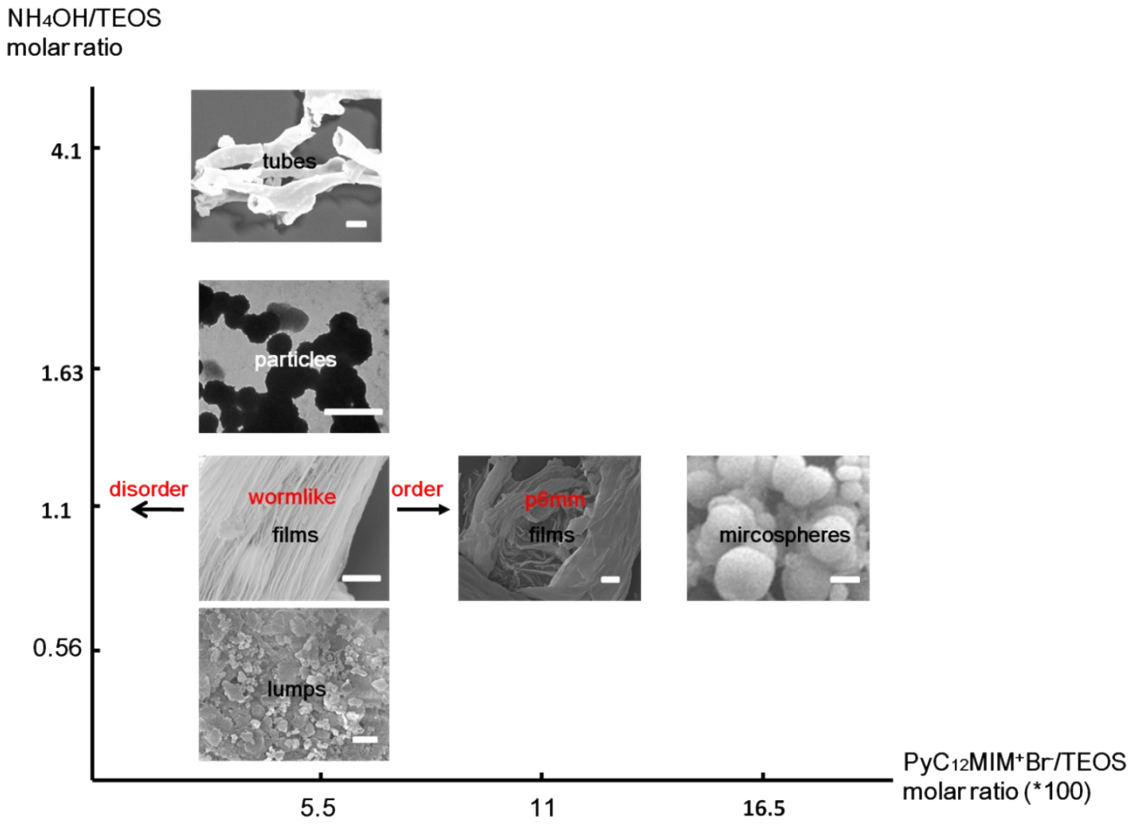
white solid (yield: 53%). $^1$H NMR ($CDCl_3$, d): 8.81 (s, 1H, =NH), 7.71 (t, 1H, -NH-), 7.22 (s, 2H, -$NH_2$), 6.68 (d×d, 2H), 6.22 (d×d, 2H), 4.60 (m, 1H), 3.87 (t, 2H), 3.72 (s, 3H), 3.45 (m, 2H), 3.23 (m, 2H), 2.25 (t, 2H), 1.74 (m, 2H), 1.58 (m, 2H), 1.24 (m, 16H).

***Synthesis of PyDDTAB:*** $PyC_{12}Br$ and N,N-Dimethyltetradecylamine were dissolved in the toluene. Then, the mixture was refluxed for 16 h. After the removal of solvent, the crude product was purified by the silica gel column chromatography with dichloromethane/methanol (20:1) as an eluent. The final product is the faint yellow viscous liquid (yield: 90%). $^1$H NMR ($CDCl_3$, d): 6.62(d×d, 2H), 6.12(d×d, 2H), 3.85(t, 2H), 3.52(t, 4H), 3.38(s, 6H), 0.87(t, 3H), 1.74 (m, 2H), 1.53 (m, 4H), 1.24(m,38H).

### *3. Preparation of FSMSFs*

***Synthesis of PyDDTAB-FSMSFs:*** PyDDTAB (2.2 mg) was dissolved in deionized water (20 ml). Then TEOS (122 μL) and aqueous ammonia (28 wt%, 10 μL) were added to the solution and the resulting solution was stirring in an ice bath for 12 h. After aging at 80℃ for 12 h, the mixture was filtrated by the membrane with a pore diameter of 1.6 μm. Then the residue was washed with Millipore water, and dried in air.

***Synthesis of CTAB-FSMSFs*****:** CTAB (7 mg) was dissolved in deionized water (10 ml). TEOS (122 μL) was added to the solution. After stirring for 10 min, the aqueous ammonia (28 wt%, 40 μL) was added in the solution. And the resulting solution was stirring in an ice bath for 12 h. Due to the similar size between CTAB-FSMSFs and by-products which were agglomerated by small nanoparticles, it is difficult to separate the CTAB-FSMSFs completely.




**Scheme S1.** The morphology and mesostructure of the as-prepared samples at different $PyC_{12}MIM^{+}Br^{-}$/TEOS ratio and $NH_4OH$/TEOS ratio (the scale bar =1μm).

**Table S1.** Nitrogen adsorption-desorption isotherm data and the d-spacing calculated from the (100) X-ray diffraction peak of FSMSFs-$PyC_{12}MIM^{+}Br^{-}$

| Samples | $S_{BET}$/$m^2$ $g^{-1}$ | $V_t$/$cm^3$ $g^{-1}$ | $D_{BJH}$/nm | d(10) /nm |
|---|---|---|---|---|
| FSMSFs-$PyC_{12}MIM^{+}Br^{-}$-0.055 | 1017 | 0.73 | 2.17 | 3.400 |
| FSMSFs-$PyC_{12}MIM^{+}Br^{-}$-0.11 | 1107 | 0.67 | 2.02 | 3.273 |
| FSMSFs-$PyC_{11}$ArgOMe-0.12 | 221 | 0.89 | 2.72 | - |
| FSMSFs-PyDDTAB-0.0072 | 544 | 1.01 | 2.61 | - |

**Table S2** Properties of FSMSFs prepared by different surfactants

| Surfactants[a)] | Yields% [b)] | Thickness /nm[c)] | Mesostructure |
|---|---|---|---|
| $PyC_{12}MIM^{+}Br^{-}$ | 65~85 | 30~60 | Wormlike/p6mm |
| $PyC_{11}ArgOMe$ | 90~95 | 20~24,90~95 | Wormlike |
| PyDDTAB | 70~80 | 35~60 | Disordered |
| CTAB | <30 | 30 | Disordered |

[a)] the chemical structural formula of the surfactant were shown in Scheme S1; [b)] data calculated by mass ratio of FSMSFs to total products for multiple measurements; [c)] data measured by scanning electron microscope.

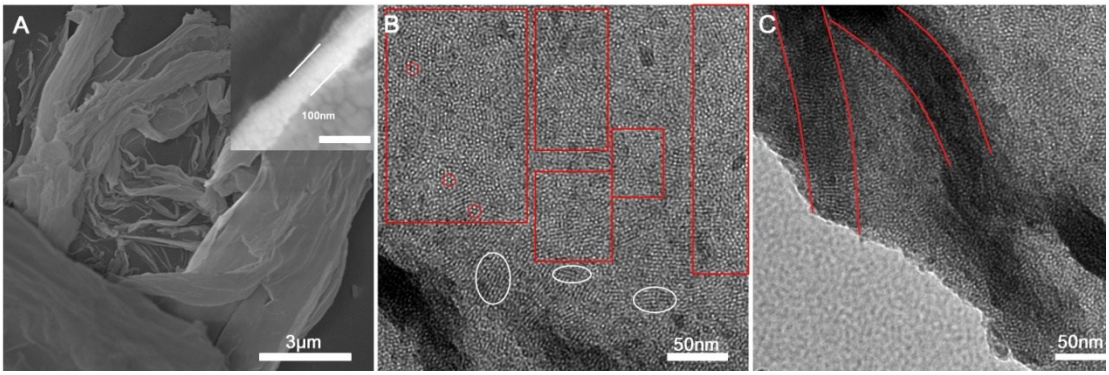



**Fig. S1** A) SEM image of $PyC_{12}MIM^{+}Br^{-}$-FSMSFs-0.11 (molar ratio of surfactant/ TEOS=0.11); B) top-view of the $PyC_{12}MIM^{+}Br^{-}$-FSMSFs-0.11 (red region: channels aligned perpendicular to the surface; white region: channels aligned parallel to the surface) and C) cross-section TEM image of the tilted edge of the $PyC_{12}MIM^{+}Br^{-}$-FSMSFs-0.11(red region). Inset in A) is the cross-section SEM image.

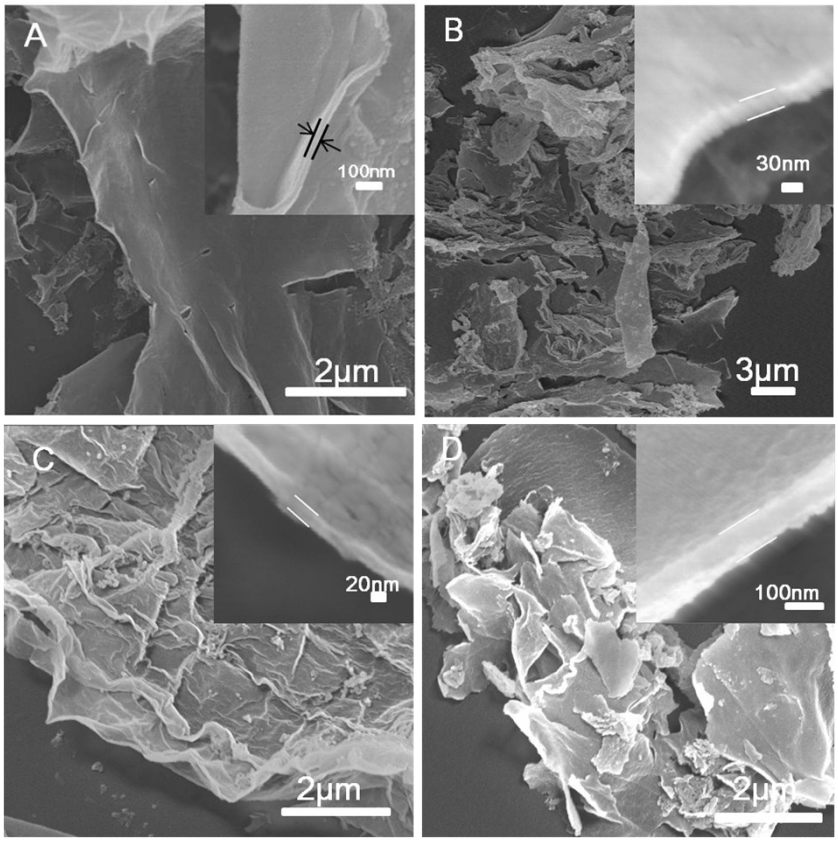



**Fig.S2** SEM images of the resultants: A) PyDDTAB-FSMSFs-0.0072 and B) CTAB-FSMSFs-0.035; C) $PyC_{11}ArgOMe$-FSMSFs-0.12 (surfactant/TEOS =0.08 , $NH_4OH$/TEOS =0.29); D) $PyC_{11}ArgOMe$-FSMSFs-0.195 (surfactant/TEOS=0.13, $NH_4OH$/TEOS=0.44.) Insert: cross-section SEM images.

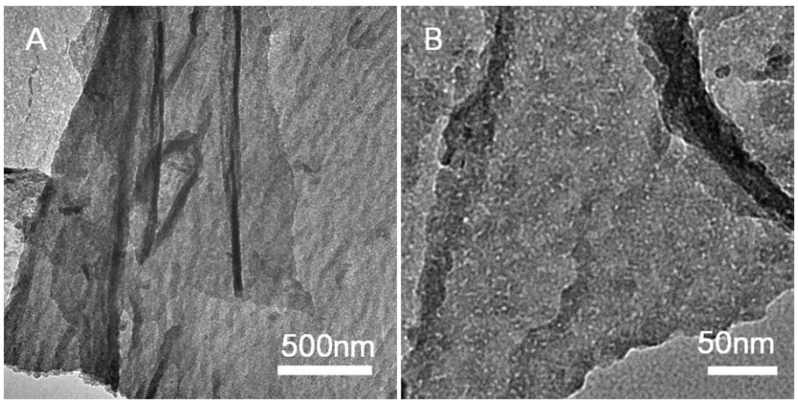



**Fig. S3** Representative A) TEM and B) HRTEM images of $PyC_{11}ArgOMe$-FSMSFs-0.195(surfactant/TEOS=0.13, $NH_4OH$/ TEOS=0.44).

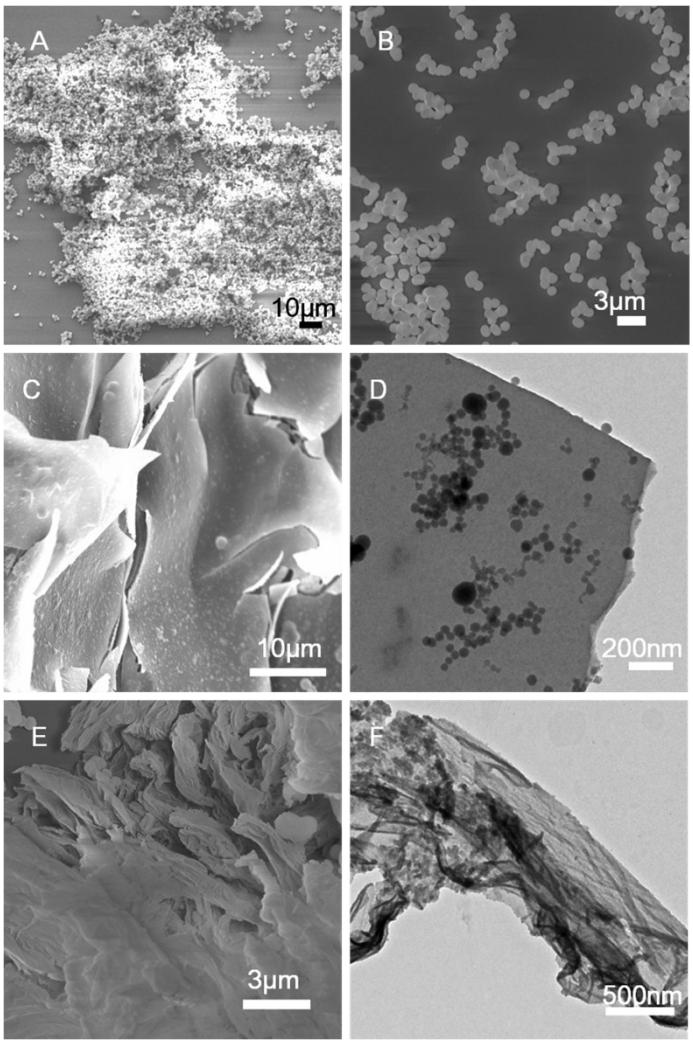



**Fig. S4** SEM and TEM images of the controlled samples prepared A-B) under static condition in an ice bath and C-D) 80°C; E-F) controlled sample prepared by using Teflon bottles.

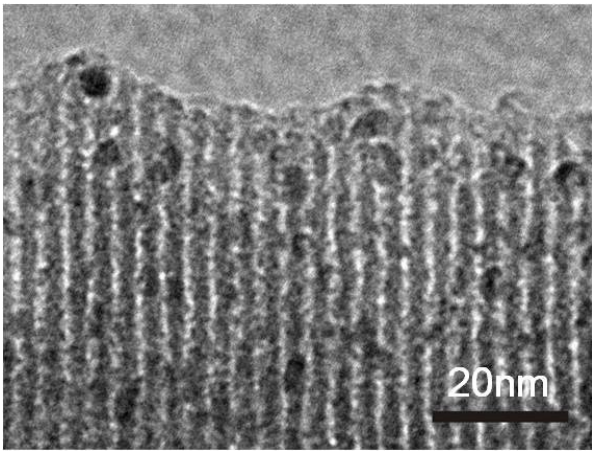



**Fig. S5** HRTEM image of the tilted edge of sample, indicating Au NPs indeed are located within the mesochannels.

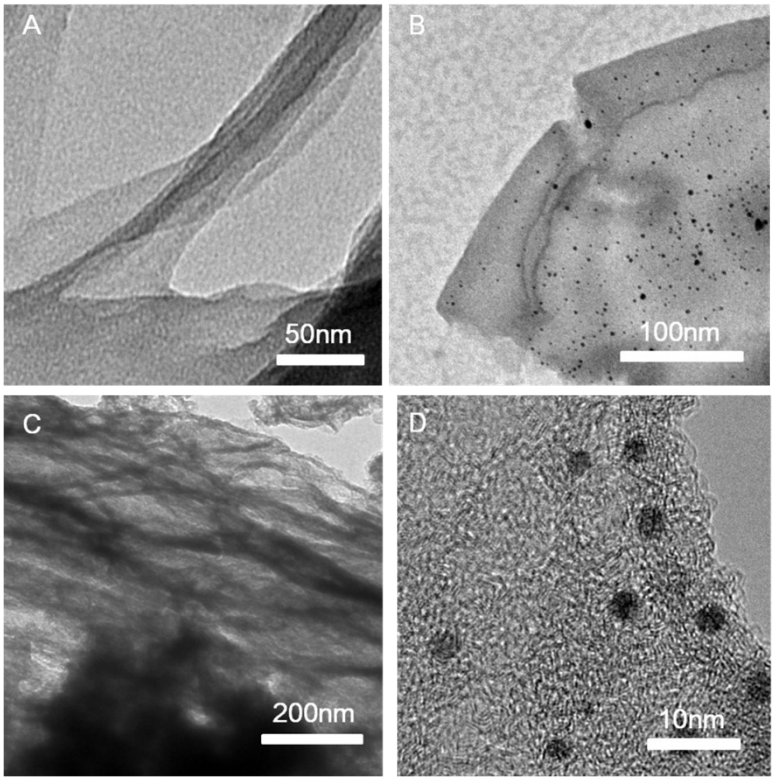



**Fig. S6** HRTEM images of A) the synthesized PpyF and D)Au-GF; TEM images of B) the Au-PPyF and C) GF.

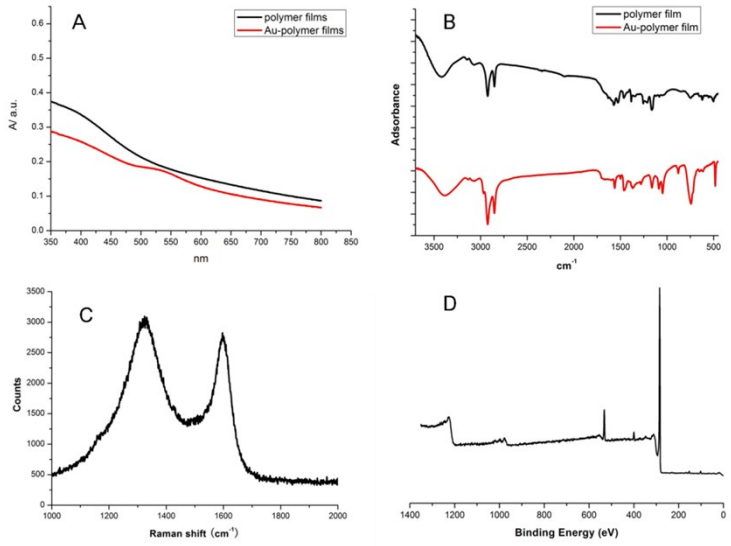



**Fig. S7** A) UV spectrum and B) IR spectrum of the PFs and Au-PFs; C) Raman spectrum and D) XPS spectrum of the GFs.

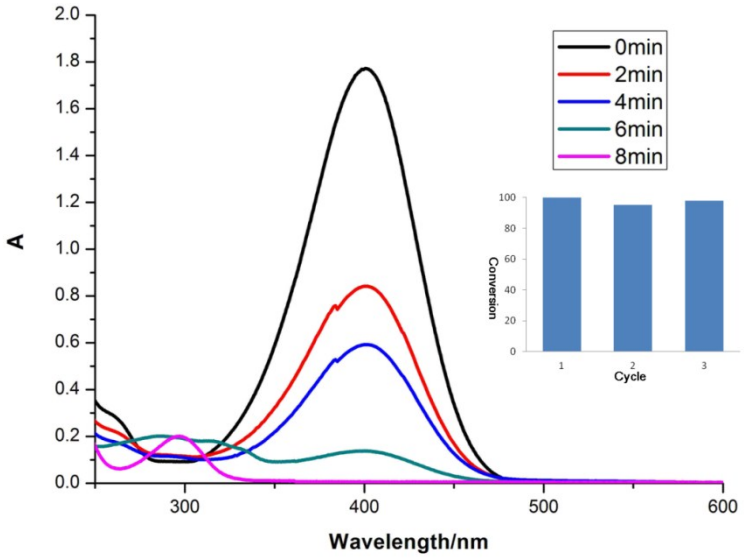



**Fig. S8** UV/Vis spectra of 4-nitrophenol reduction. Black curve correspond to the spectra without the addition of the Au-GFs and red curve/blue curve/green curve/pink curve correspond to the spectra of 2min/4min/6min/8min after the addition of the Au-GFs, respectively. Inset: a graph of the conversion of 4-nitrophenol within 10min versus the number of catalyst recycles.

**Reference:**

[1] W. Zhang, J. Cui, C. Tao, C. Lin, Y. Wu and G. Li, *Langmuir*, 2009, **25**, 8235-8239.