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Nano-functionalized filamentous fungus hyphae with interesting fast macroscopic assembly & disassembly feature

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Electronic Supplementary Information

ESI-1 Materials

Aspergillus niger was purchased from China Center for Type Culture Collection (CCTCC). Aniline, sodium persulfate, hydrochloric acid, Orange G were of analytical grade and used as-received.

ESI-2 Preparation of the fungus hyphae dispersion

The fungus pellets were inoculated into potato-dextrose medium and incubated at 37 ^{o}C with shaking rate of 150 rpm for 72h. Fungus pellets were captured by vacuum filtration and washed by distilled water for 3 times. Then fungus pellets were dispersed in the blender for 3 minutes to prepare the fungus hyphae suspension. The hyphae were reacted with glutaraldehyde (2.5 wt.%) for 24h. Then the hyphae was collected by vacuum filtration and purified by distilled water. Hyphae were finally dispersed in water again as storage solution for further use. The mass concentration of the hyphae suspension is ~8.3 mg mL^{-1}.

ESI-3 Decoration of hyphae by polyaniline

The entire process was conducted below 5 ^{o}C. Glutaraldehyde-treated hyphae were captured by vacuum filtration and pre-cooled to below 5 ^{o}C. Then the collected fungi hyphae were added into the mixture of aniline (various volume) and HCl solution (1 M) with total volume of 100 mL under vigorous stirring. The sodium persulfate was added every half an hour for 5 times. For each time, 1 mL of sodium persulfate solution was added into the mixture solution. The molar ratio of aniline to sodium persulfate is 1:1.25. After 1 h, the polymerization solution was kept standing for overnight.

ESI-4 Characterizations

FTIR. The sample was blended with KBr powder and pressed into a disk, which was then scanned in the range of 1600-1000 cm^{-1} by Nicolet IS10.

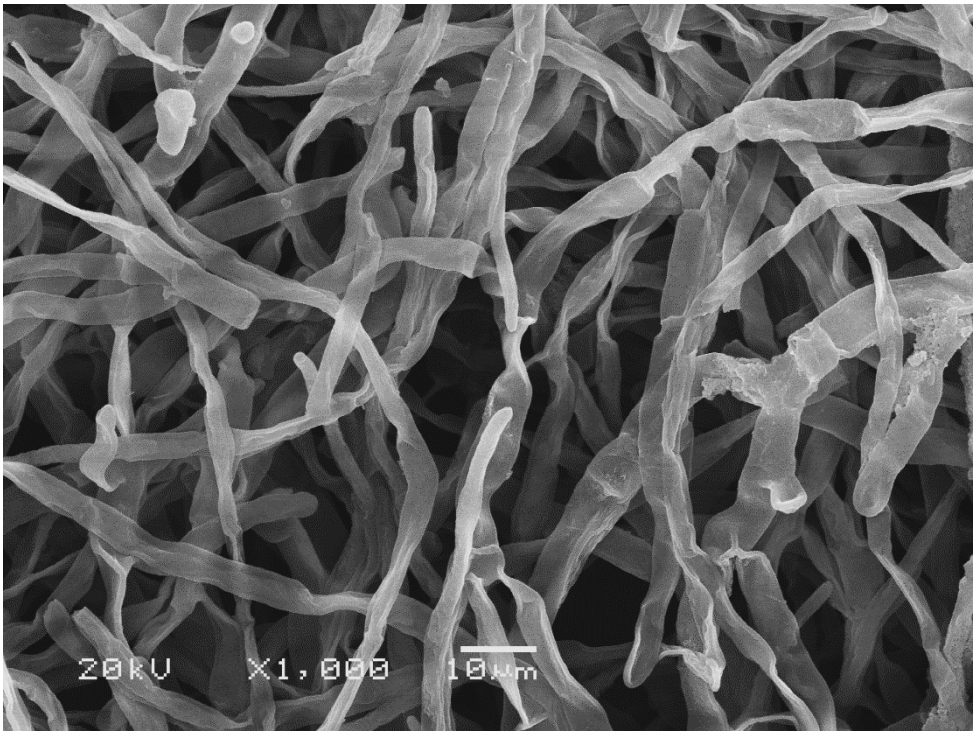
XPS. The sample was examined by ESCALAB 250Xi spectrometer with dual anode (Mg/Al) X-ray source with 400 W power. To compensate for surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6 eV.

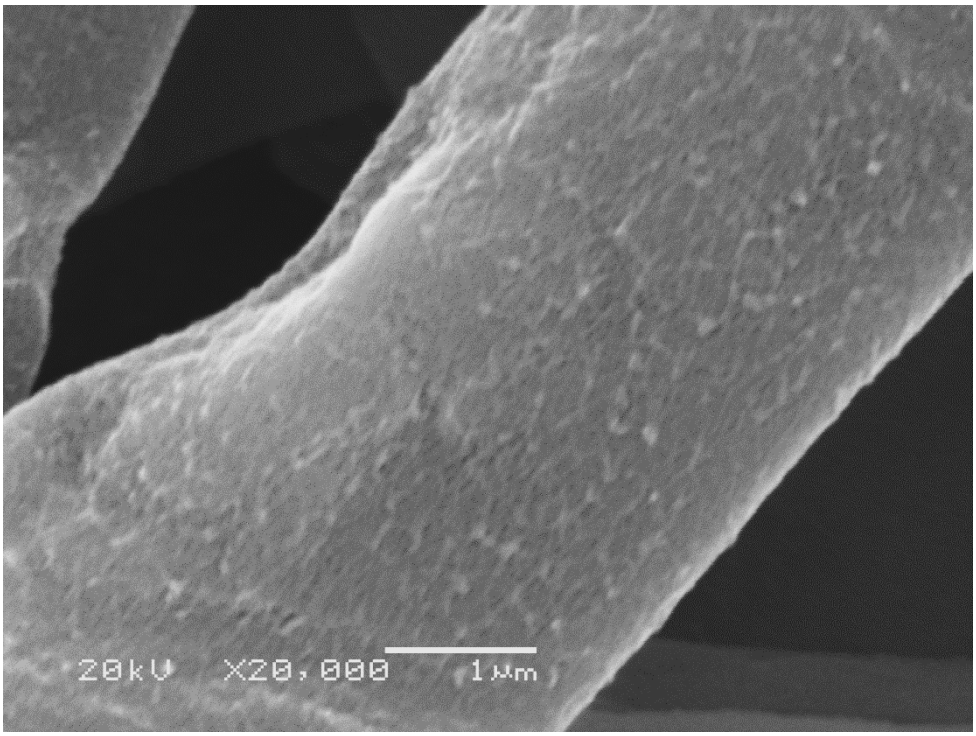
Raman. LABRAM-HR 800 Raman spectrometer was employed in the range of 4000-500 cm^{-1} with a He-Le laser excitation at 513 nm and an acquisition time of 10 s.

SEM. The sample was freeze dried and then adhered onto a conducting tape. JSM-6360 scanning electron microscope was adopted to analyse the morphology.

ESI-5 SEM images

Aniline volumetric concentration (mL/L)





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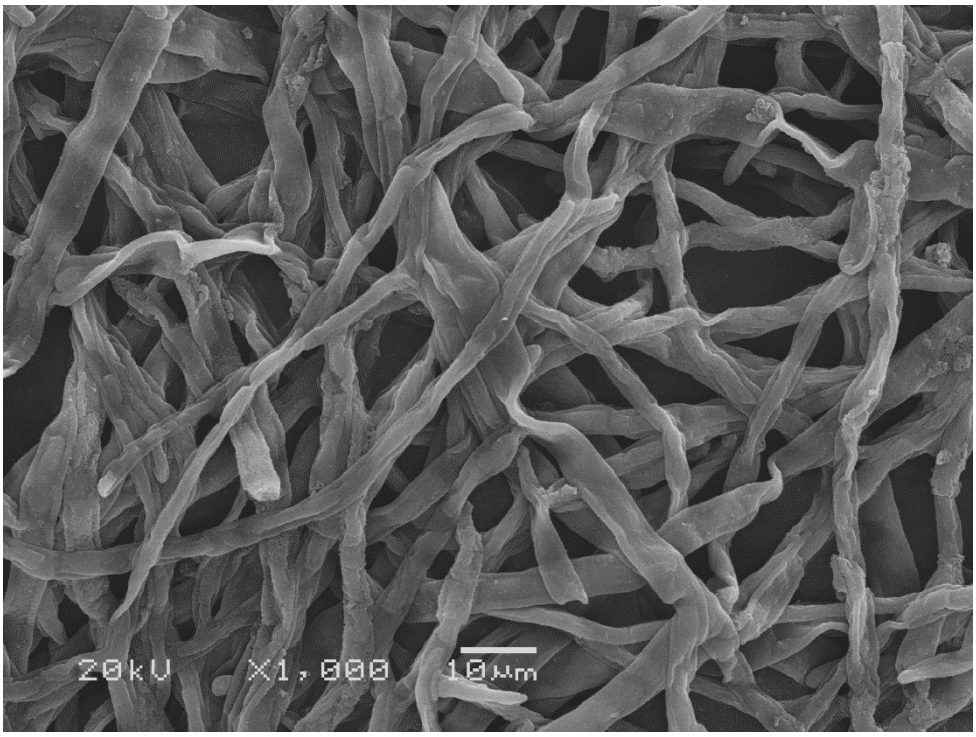

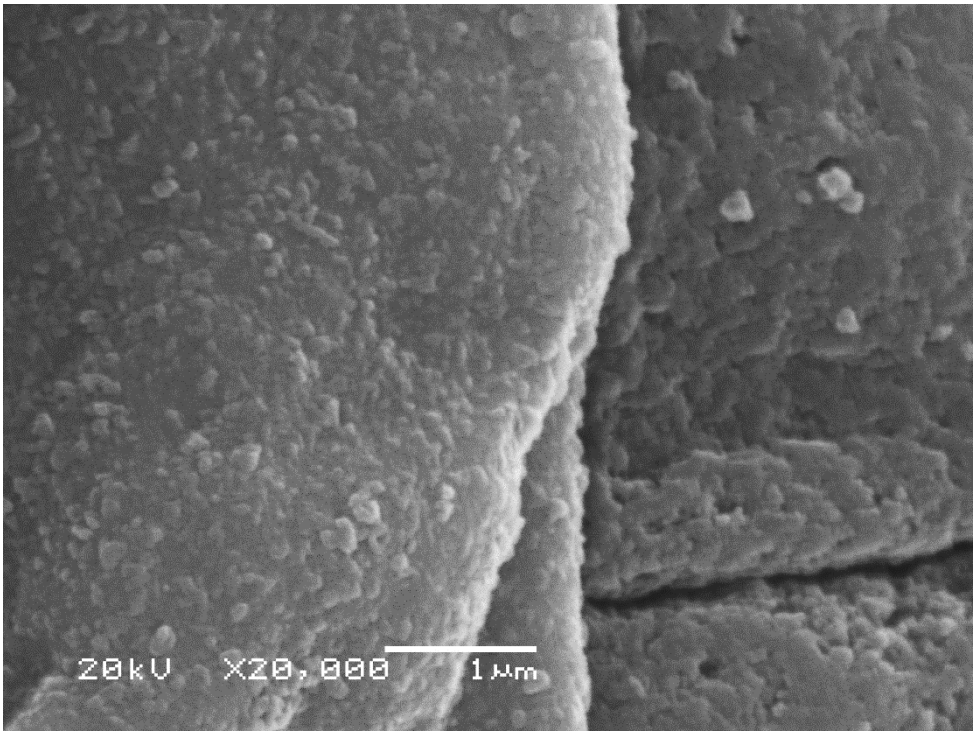

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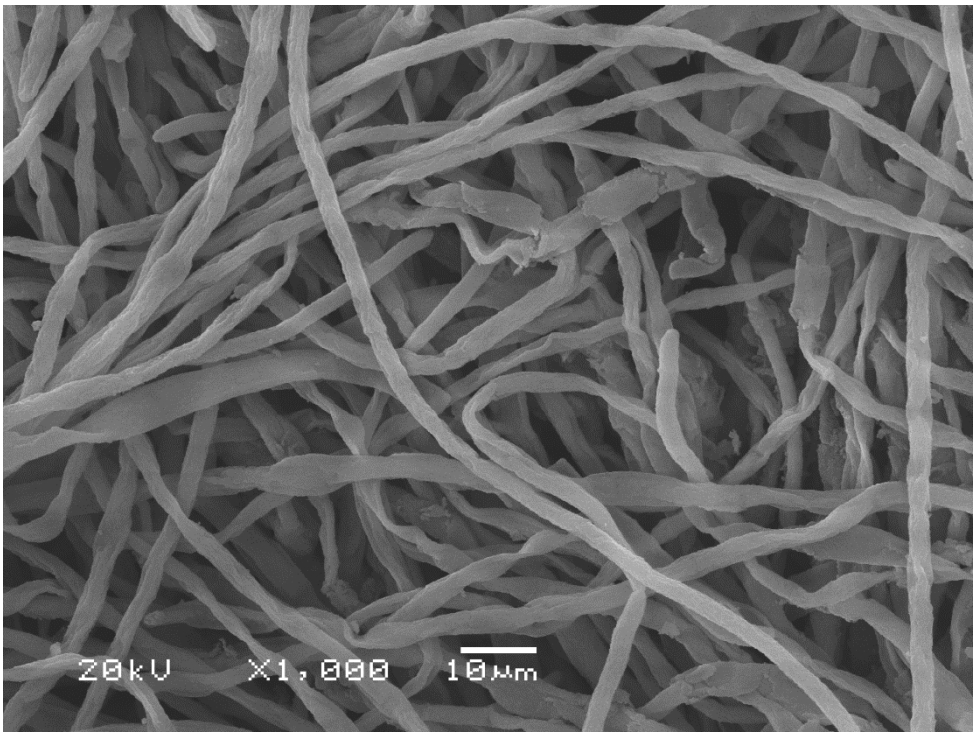

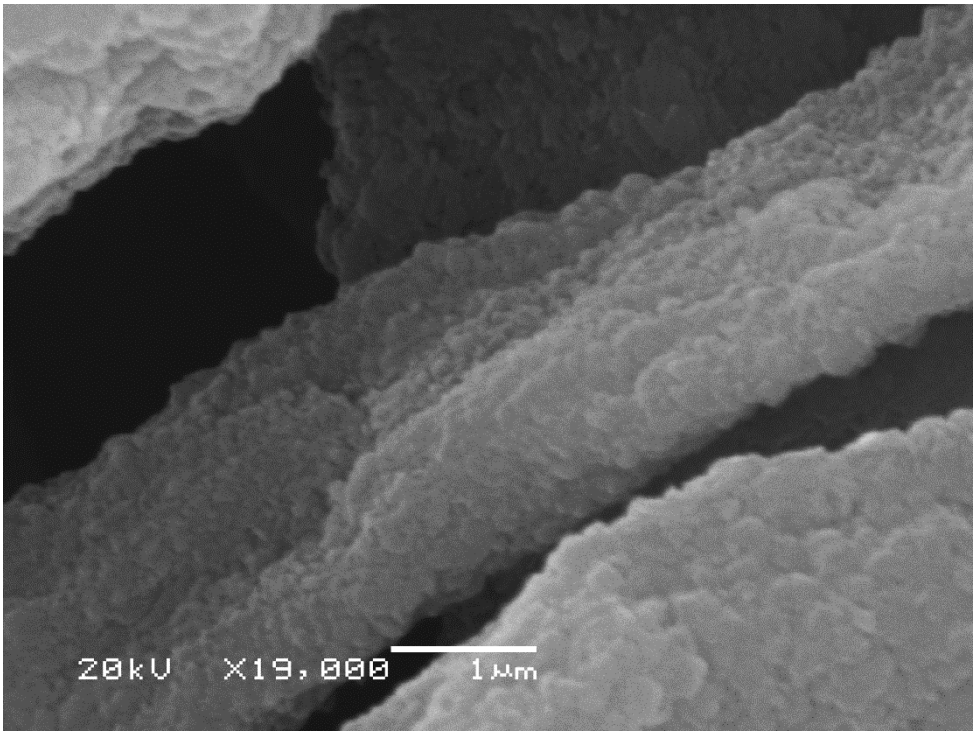

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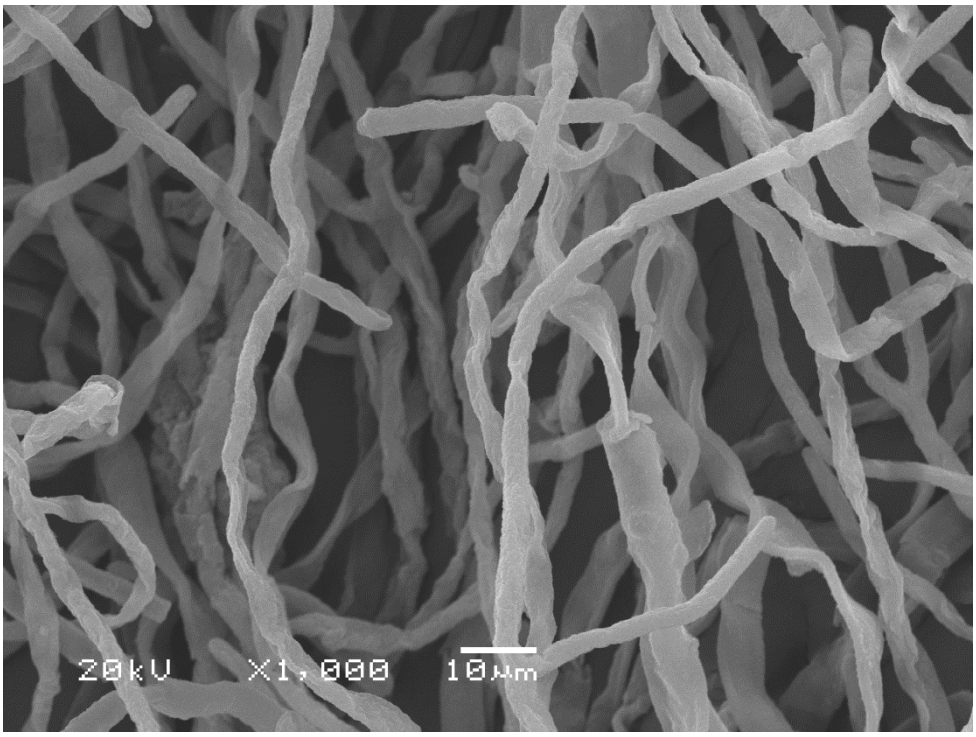

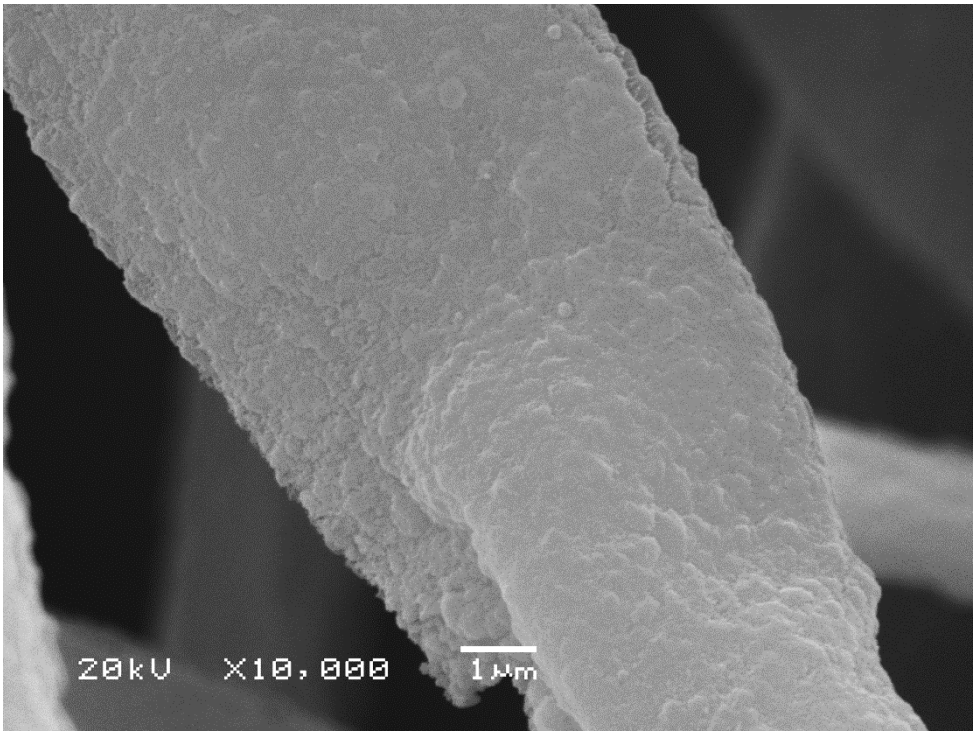

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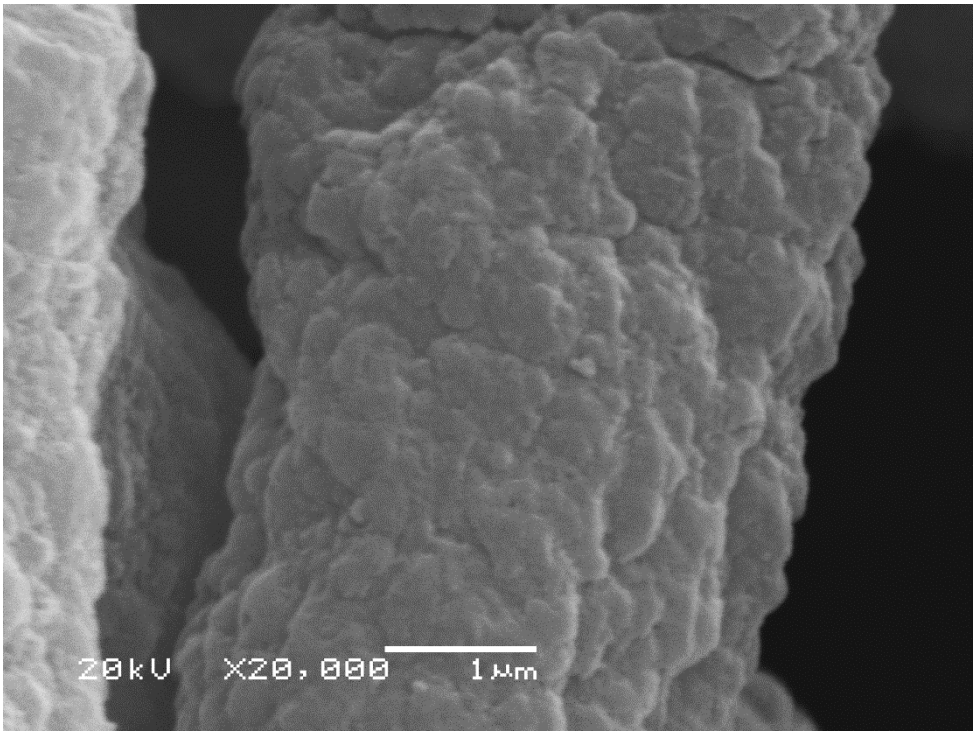

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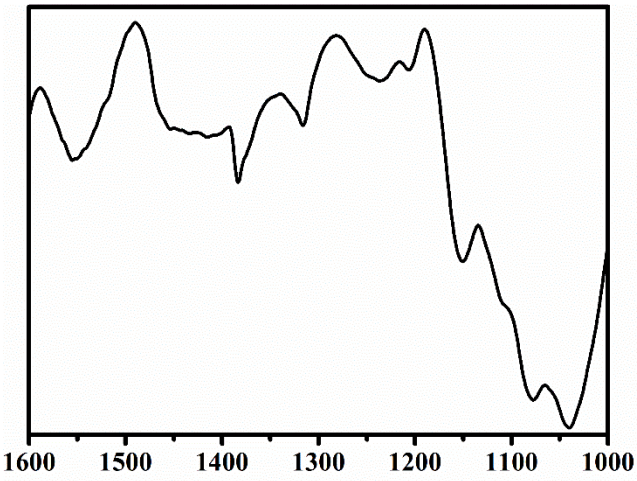
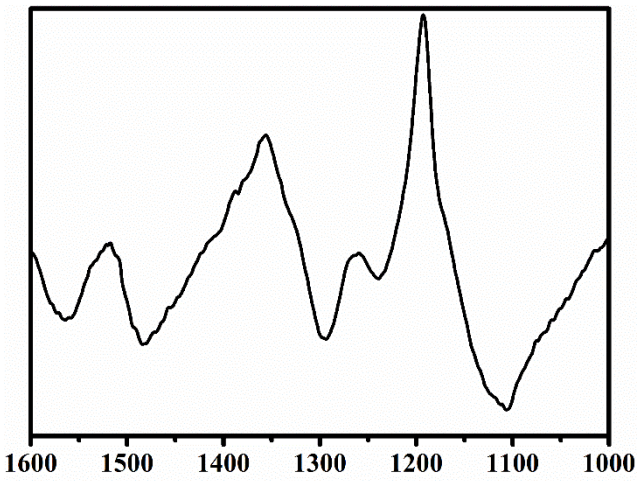
ESI-6 FTIR spectra of fungus and PANI (y axis: Transmittance %)

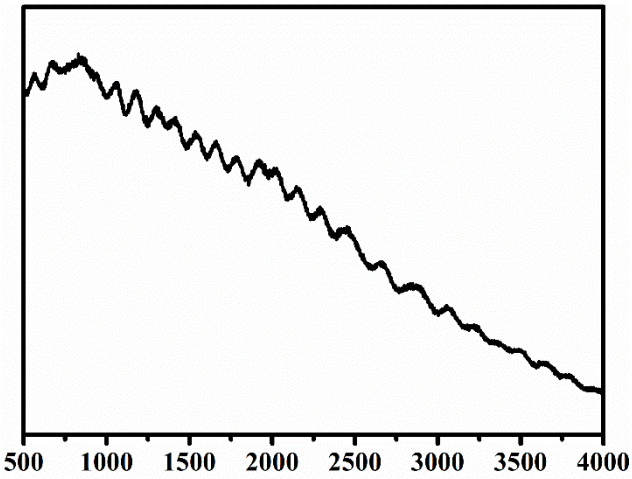


Fungus:



PANI:

ESI-7 Raman spectra of fungus and PANI



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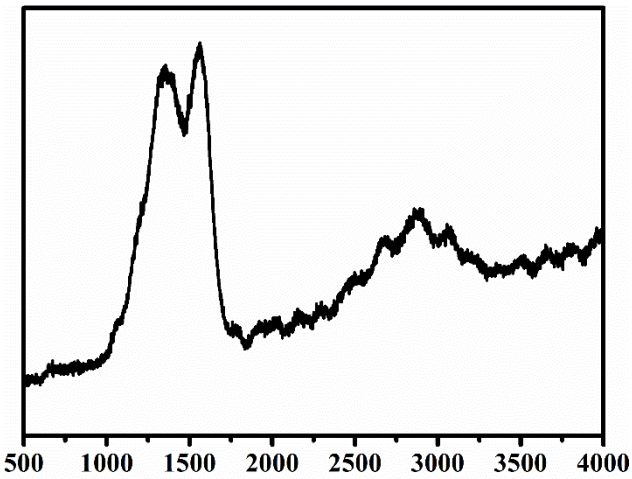
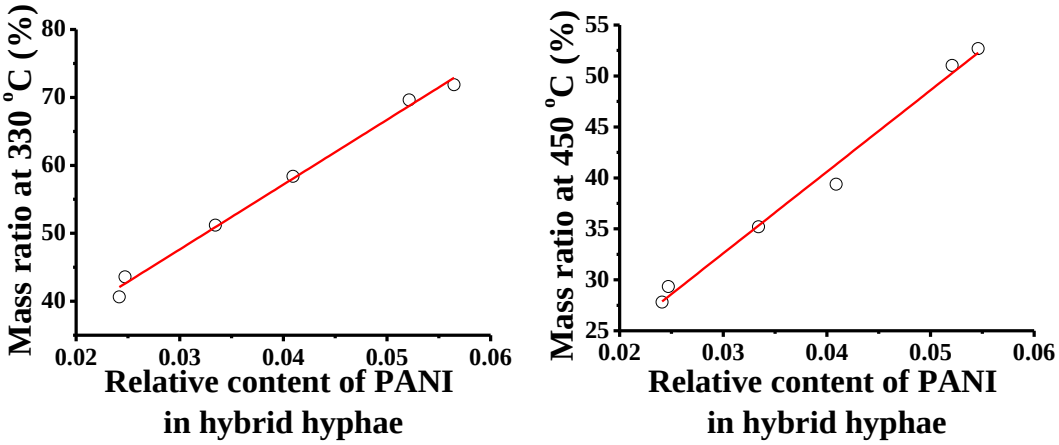


PANI:

ESI-8 The fitting of the mass ratio data at 330 (left) and 450 ºC (right) with the relative content of PANI in the hybrid hyphae measured by a digital balance.



ESI-9 Adsorption method and results

Adsorption:

PANI-decorated hyphae were captured by vacuum filtration and dispersed in 20 mL of acidic Orange G solution (pH ~1) with a certain concentration. The whole solution was put into an incubator shaker controller at constant 30 °C with shaking rate 150 rpm for 3h.

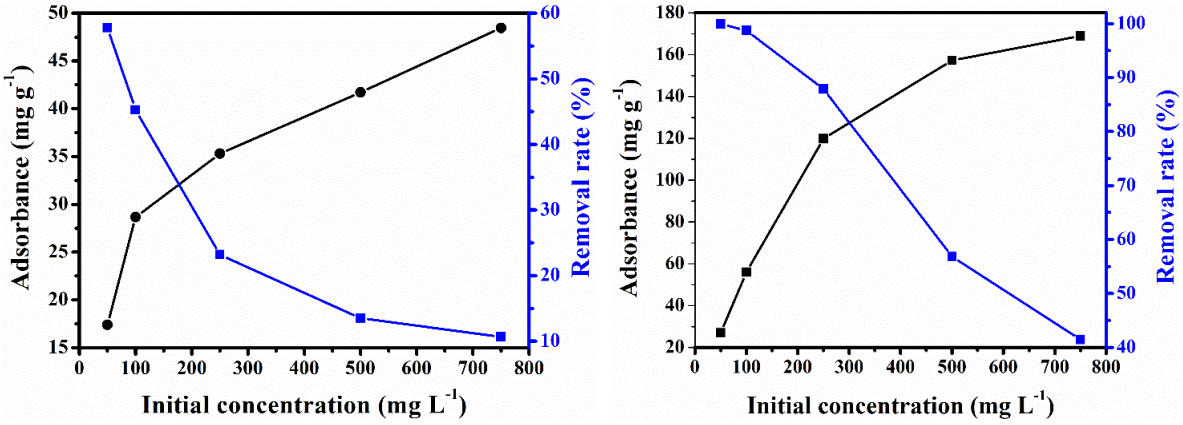
For each adsorption, 5 mL of the PANI-decorated hyphae suspension was used. The total mass of the adsorbent is 0.03 g. The amount (gram) of PANI on the hyphae was calculated by subtracting the hyphae mass from the total mass and the result is 0.009 g. The hyphae mass is 0.021 g.

Calculation method on the dye adsorbance (mg g^{-1}) of PANI:

$$M_{PANI} = (0.03 \times M_{\text{Hybrid}} - 0.021 \times M_{Fungus}) / 0.009$$

where M_{PANI}, M_{Hybrid} and M_{Fungus} represent the adsorbance of PANI, PANI-decorated hyphae (hybrid) and fungus at specific dye concentration.

Dye adsorption by purely fungus hyphae (left) and the PANI-decorated fungus hyphae (right)



Adsorption-desorption cycles:

First, PANI-decorated hyphae was added into 100 mL of Orange G solution (10 mg L^{-1}). The dosage of the adsorbent and adsorption conditions is the same to the "**Adsorption**" above. After adsorption the PANI-decorated hyphae were assembled by vacuum filtration (10 s only). This filtrate from adsorption experiment was measured by UV-vis spectrometer to calculate the dye concentration (C_a).

Then the hybrid hyphae were disassembled in 30 mL of distilled water, to which 58μL of NaOH (1 M) was added and stirred at 30 °C for 10 min for desorption (final pH is ~8). The disassembly

process needed less than 10 s. After desorption, the hybrid hyphae were assembled again by vacuum filtration for another turn of adsorption. This filtrate from desorption experiment by UV-vis spectrometer to calculate the dye concentration (***C_d***).

Desorption rate (***D***) was calculated by equation:

$$D = \frac{C_d \times 30}{(10 - C_a) \times 100} \times 100\%$$

Adsorption rate (***A***) was calculated by equation:

$$A = \frac{C_a}{10} \times 100\%$$

Dye adsorption by the assembled PANI-decorated hyphae:

To verify the importance of mass transfer efficiency, we directly used the assembled PANI-decorated hyphae as adsorbent that is the hyphae film. To avoid the disassembly in solution, the hyphae film was dried at 60 ^{o}C in vacuum. 20 mL of Orange G (750 mg L^{-1}) was added into the hyphae film. Other adsorption conditions were the same to the "**Adsorption**".

ESI-10 Comparison of the adsorption performance of common materials

Materials	Adsorbance (mg g^{-1})	References
Magnetic silica	65.89	1
Activated carbon	9.129	2
Bagasse fly ash	18.796	3
Aggregated poly(m-phenylenediamine)	165	4
Poly(m-phenylenediamine) nanoparticles	387.6	4

References

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ESI-Media1 Display of reversible assembly & disassembly

This multimedia file was uploaded to the submission system.

We also uploaded this file in rayfile:

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The Chinese words mean download.