

## Supporting Information

### Metal-organic frameworks@graphene hybrid aerogel for solid-phase extraction of non-steroidal anti-inflammatory drugs and selective enrichment of proteins

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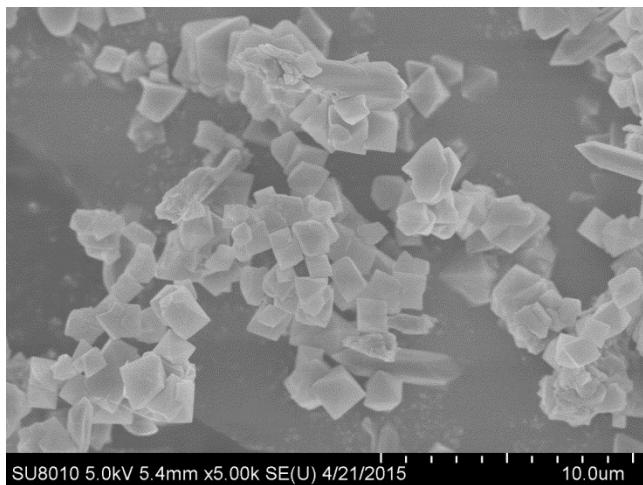
Email: dingmym@mail.tsinghua.edu.cn

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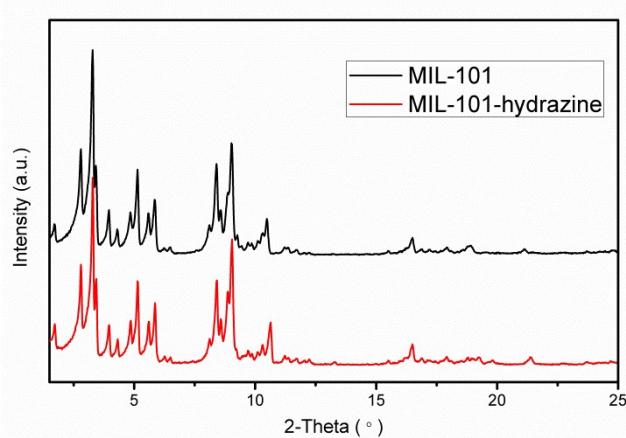
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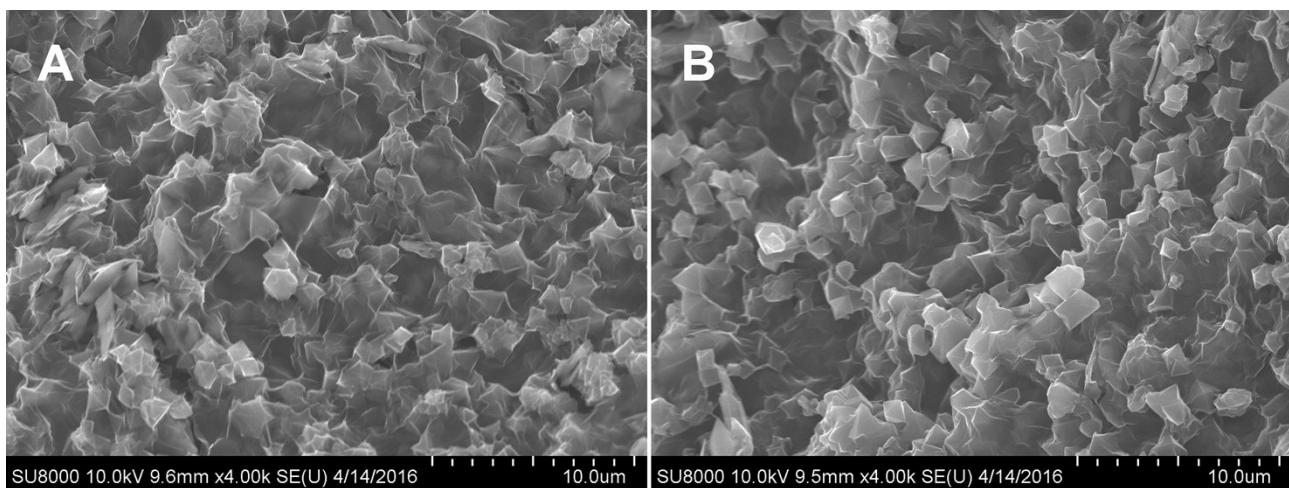
Tel: +86-10-62772263



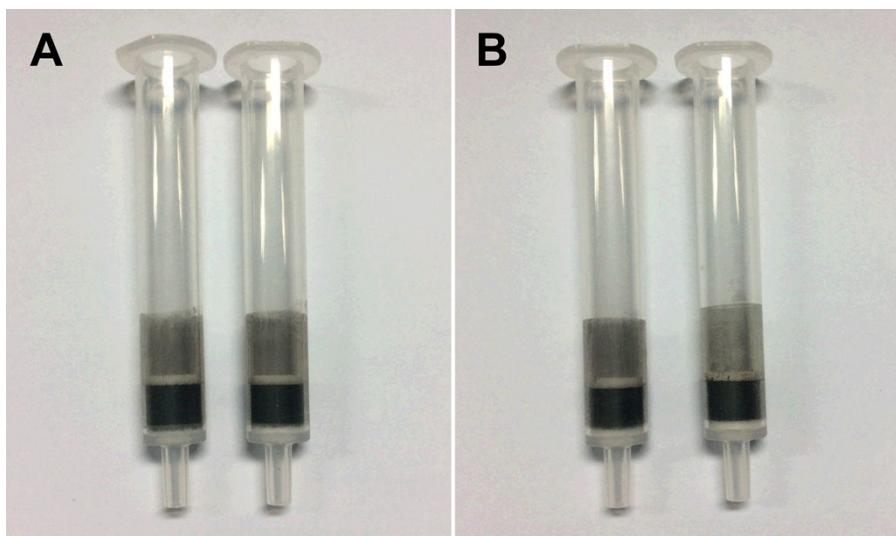
**Fig. S1.** SEM image of MIL-101.



**Fig. S2.** XRD patterns of MIL-101 and MIL-101 treated by hydrazine vapor at 95 °C for 24 h.



**Fig. S3.** SEM images of hybrid aerogels after (A) replicate extractions and (B) dramatic ultrasonic for 10 min in a mixture solution of EtOH and water.



**Fig. S4.** Photographs of (A) newly prepared hybrid aerogel packed SPE cartridges and (B) SPE cartridges after 20 replicate extractions.

**Table S1**

Analytical figures of merit through MIL-101@graphene hybrid aerogel based SPE-HPLC-UV method.

| Analyte      | pKa  | Regression equation <sup>a</sup> | R <sup>2</sup> | Linear range<br>(ng mL <sup>-1</sup> ) | LOD<br>(ng mL <sup>-1</sup> ) | RSD (%)   |           |                 |
|--------------|------|----------------------------------|----------------|--|-------------------------------|-----------|-----------|-----------------|
|              |      |                                  |                |  |                               | Run-to-   | Day-to-   | Cartridge-to-   |
|              |      |                                  |                |  |                               | run (n=6) | day (n=3) | cartridge (n=4) |
| Naproxen     | 4.39 | y = 0.21478x + 0.05264           | 0.9996         | 0.2 – 50                               | 0.01                          | 6.1       | 4.3       | 5.5             |
| Felbinac     | 4.30 | y = 0.03735x + 0.00176           | 1.0000         | 0.2 – 50                               | 0.08                          | 4.4       | 4.6       | 4.8             |
| Carprofen    | 4.42 | y = 0.08628x – 0.00782           | 0.9997         | 0.2 – 50                               | 0.03                          | 5.6       | 5.3       | 9.1             |
| Flurbiprofen | 4.42 | y = 0.03066x + 0.02130           | 0.9984         | 0.2 – 50                               | 0.04                          | 8.5       | 9.0       | 6.0             |
| Ibuprofen    | 4.38 | y = 0.03806x + 0.02115           | 0.9973         | 0.2 – 50                               | 0.10                          | 3.7       | 3.4       | 5.0             |

<sup>a</sup>y=peak area in mAU min and x= concentration in ng mL<sup>-1</sup>.

**Table S2**

Comparison of different methods for the determination of non-steroidal anti-inflammatory drugs.

| Method  | Detection  | Sample volume<br>(mL) | LOD<br>(ng mL <sup>-1</sup> ) | Refs.     |
|---|------------|-----------------------|-------------------------------|-----------|
|   |            |                       |                               |           |
| Hollow fiber liquid-phase microextraction           | UPLC-MS/MS | 5                     | 0.5-1.25                      | [38]      |
| C18 sorbent based microextraction                   | HPLC-PDA   | 0.1                   | 0.03                          | [39]      |
| Electromembrane extraction                          | HPLC-DAD   | 10                    | 0.08-3.36                     | [40]      |
| Magnetic matrix solid phase dispersion              | HPLC-UV    | 1000                  | 1-2                           | [41]      |
| Immobilized carboxylated carbon nanotubes based SPE | CE-MS      | 5                     | 1.6-2.6                       | [42]      |
| MIL-101@graphene hybrid aerogel based SPE           | HPLC-UV    | 100                   | 0.01-0.10                     | This work |

**Table S3**

Recoveries of environmental water samples spiked with five NSAIDs (n=3).

| Analyte      | Concentration<br>added (ng mL <sup>-1</sup> ) | Tap water samples |         | River water samples |         |
|--------------|---|-------------------|---------|---------------------|---------|
|              |   | Recovery (%)      | RSD (%) | Recovery (%)        | RSD (%) |
| Naproxen     | 0.5   | 97.6              | 3.8     | 92.6                | 3.6     |
|              | 2.0   | 105.0             | 5.7     | 80.8                | 3.4     |
| Felbinac     | 0.5   | 105.5             | 3.3     | 99.4                | 8.7     |
|              | 2.0   | 106.9             | 3.6     | 89.7                | 2.3     |
| Carprofen    | 0.5   | 106.5             | 2.5     | 87.7                | 7.3     |
|              | 2.0   | 99.1              | 3.7     | 83.2                | 4.1     |
| Flurbiprofen | 0.5   | 82.6              | 2.6     | 96.2                | 5.3     |
|              | 2.0   | 93.8              | 5.5     | 96.3                | 6.0     |
| Ibuprofen    | 0.5   | 96.2              | 4.2     | 102.6               | 4.6     |
|              | 2.0   | 92.0              | 3.4     | 105.8               | 4.0     |