Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Zero-carbon emission chemical method to remove gaseous formaldehyde at room temperature by renewable aminooxy-functionalized graphene composite

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EXPERIMENTAL SECTION

Materials

Reduced graphene (rGO) was purchased from Qingdao Huagao Co., LTD. (BOC-Aminooxy) acetic Acid (98%), N, N'-dicyclohexyl-carbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%) and hydrochloric acid (HCl, 40%) were purchased from Aladdin Co., Ltd. 1-Pyrenemethanol (98%) was purchased from Macklin Co., Ltd. Tetrahydrofuran (THF) (AR, 99.5%), ethyl acetate (AR, 99.5%) and n-hexane (AR, 98%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd.

Synthesis of pyrene-ONH-Boc

A solution of Boc-aminooxy acetic acid (2 g, 10.46 mmol), 1-pyrenemethanol (2.4296 g, 10.46 mmol), DCC (2.59 g, 12.55 mmol), and DMAP (0.1276 g, 1.05 mmol) in THF (20 ml) was prepared. After stirring the reaction at room temperature for 24 h, the precipitate was produced and filtered to afford a yellow filtrate, which was concentrated on an evaporator under reduced pressure at 35 ºC to obtain a yellow residue. Finally, the mixture of n-hexane and ethyl acetate with the ratio of 7 : 3 was used as the eluent

to purify the residue by silica gel column chromatography to afford the desired product, pyrene-ONH-Boc. The production yield of the pyrene-ONH-Boc was 88.4%.

Deprotection of BOC by hydrochloric acid (HCl)

Pyrene-ONH-Boc (2 g) was dissolved in 50 ml of ethyl acetate, then 5 ml of 12 M HCl was added, and stirred for 4 h. The pH of the resulting mixture was adjusted to 7~8 by saturated sodium bicarbonate solution. The solution was separated by a separatory funnel to collect the upper organic phase. After removal of the solvent by an evaporator under reduced pressure at 35 ºC. Finally, the mixture of n-hexane and ethyl acetate with the ratio of 7 : 3 was used as the eluent to purify the residue by silica gel column chromatography to afford the expected product, pyrene-ONH_2. The production yield of the pyrene-ONH_2 was 56.1%.

Preparation of rGO/pyrene-ONH_2

rGO (10 g) was evenly dispersed in the ethyl acetate, Solution A (5 g pyrene-ONH_2 dissolved in ethyl acetate) was slowly dropped into the rGO suspension. After stirring at room temperature for 12 h, the precipitate was then filtered to afford a black solid, which was dried under vacuum to give rGO/pyrene-ONH_2 composite. The filtrate was recovered by evaporation under reduced pressure at 35 °C to reclaim the excess pyrene-ONH_2 for further use.

Reaction of pyrene-ONH_2 with HCHO

In order to obtain the production of the pyrene-ONH_2 reacted with HCHO, we assembled a simple system in the laboratory, as shown in Figure S10. A nitrogen cylinder and a flowmeter (5000 series flow multi-meter, Flowmeter Directory) were

combined to the generator of HCHO to control flow rates (0.5 L/min). In Figure S10b, 100 mg of polyoxymethylene was placed in a water bath (50 ℃) to promote the depolymerization of polyoxymethylene with N_2 flow for the generation of gaseous HCHO at a concentration of around 1-20 ppm which can be controlled. pyrene-ONH_2 was placed at the box for chemical decomposition of HCHO (Figure S10c). The adsorption time was set as 5 h to ensure the full reaction of pyrene-ONH_2 with HCHO. Then the HCHO adsorbed pyrene-ONH_2 was moved into vacuum oven to remove physically adsorbed water and HCHO from its surface, after 8 hours, the sample was taken out for NMR and FTIR tests.

Characterizations

SEM measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. AFM measurements were conducted on Keysight 5500. FTIR spectra were obtained with a Tensor 27 manufactured by Bruker Corporation. The optical transmittance and reflectance spectra were measured in the range of 400 - 4000 nm using a Shimadzu UV3600 spectrophotometer attached to an integrating sphere (ISR-3100). ^{1}H NMR and ^{13}C NMR were measured on a Bruker NMR600.

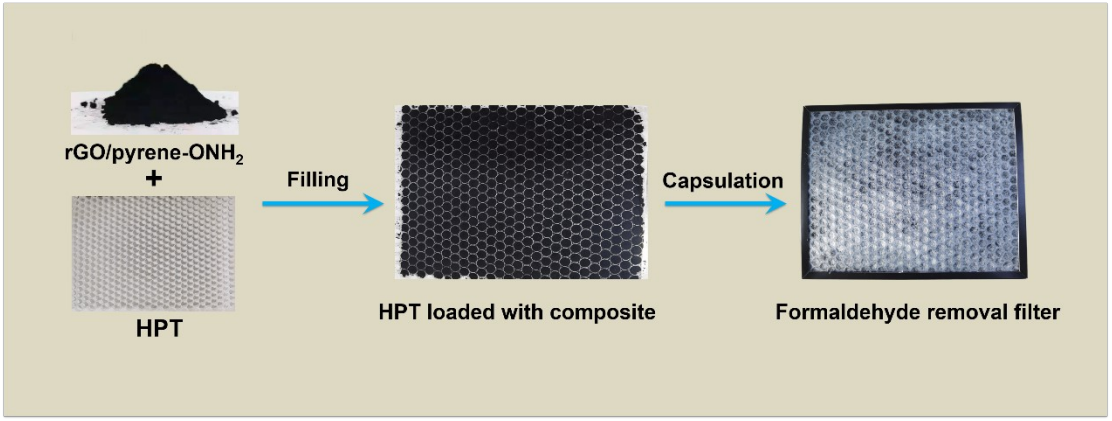

Figure S1. The assembly of the formaldehyde removal filter using the rGO/pyrene-ONH_2 composite for chemical removal of gas HCHO molecules.

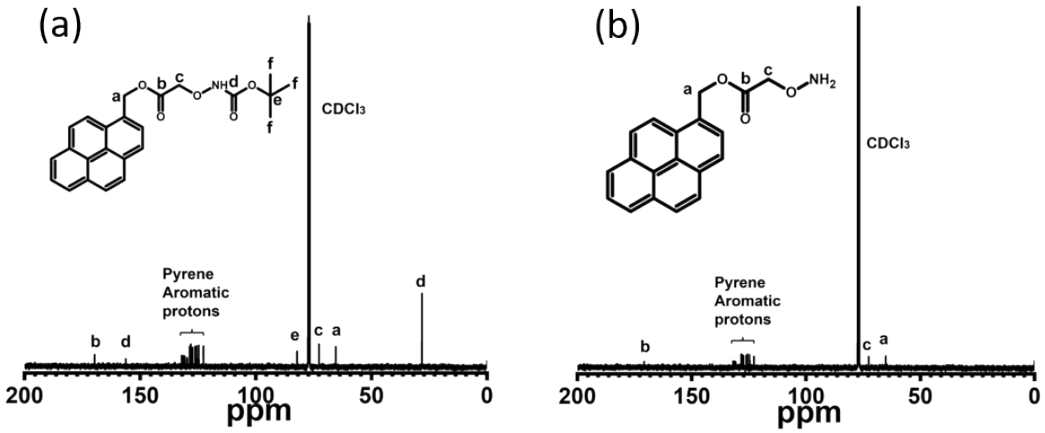

Figure S2. ^{13}C NMR spectra of (a) pyrene-ONH-Boc and (b) pyrene-ONH_2.

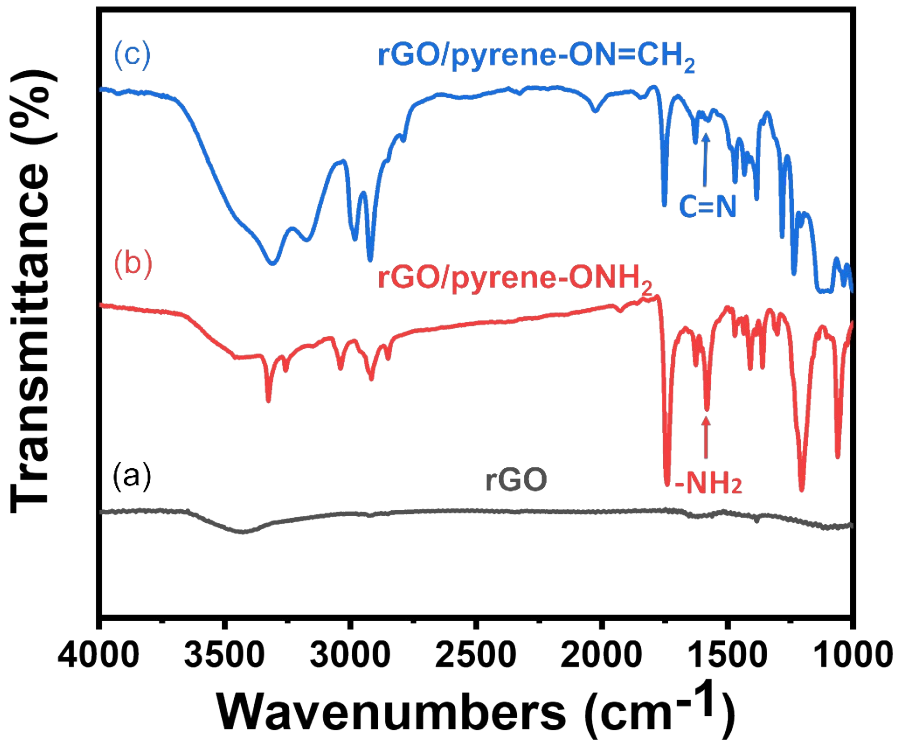

Figure S3. FTIR spectra of a) rGO, b) rGO/pyrene-ONH_2 and c) rGO/pyrene-$ON=CH_2$.

The product of rGO/pyrene-$ON=CH_2$ reacted with formaldehyde was characterized by FTIR. It can be seen from Figure S3 that the stretching vibration peak of N-H at 1560 disappears after rGO/pyrene-$ON=CH_2$ reacts with formaldehyde, which means that -ONH_2 can react with formaldehyde.

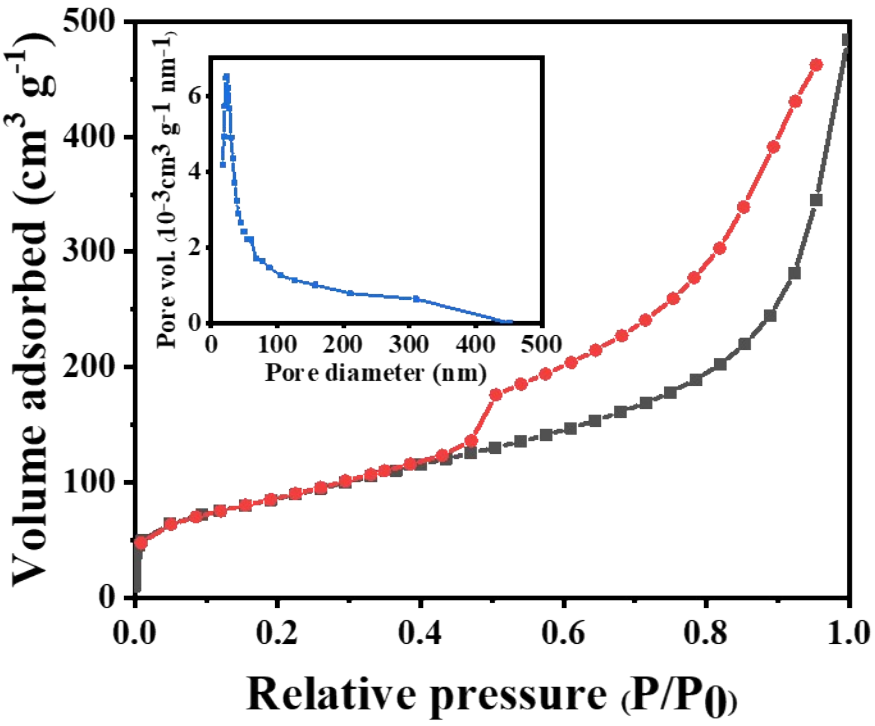

Figure S4. The N_2 adsorption-desorption isotherm and the pore-size distribution of the rGO.

The N_2 adsorption-desorption isotherm is displayed in Figure S7 and the specific surface area of the rGO was measured to be 309.7 m^2/g by the BET and the pore-size distribution of the rGO is displayed as the inset of Figure S7. The average aperture was characterized to be 108.71 nm and the pore volume was 0.748 cm^3/g.

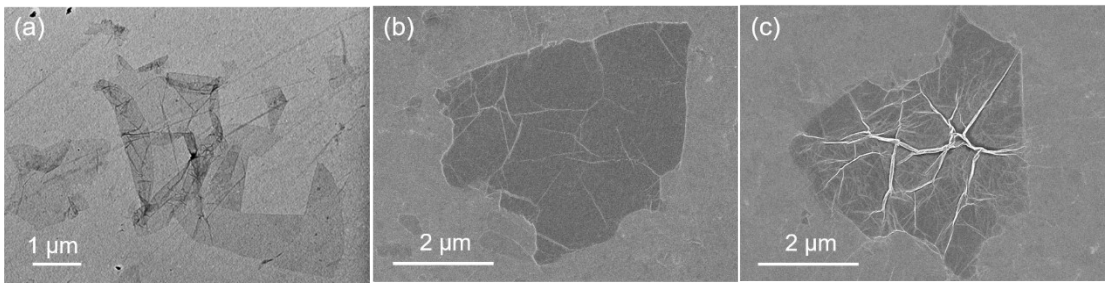

Figure S5. (a) TEM images of rGO. SEM images of (b) rGO and (c) rGO/pyrene-ONH_2.

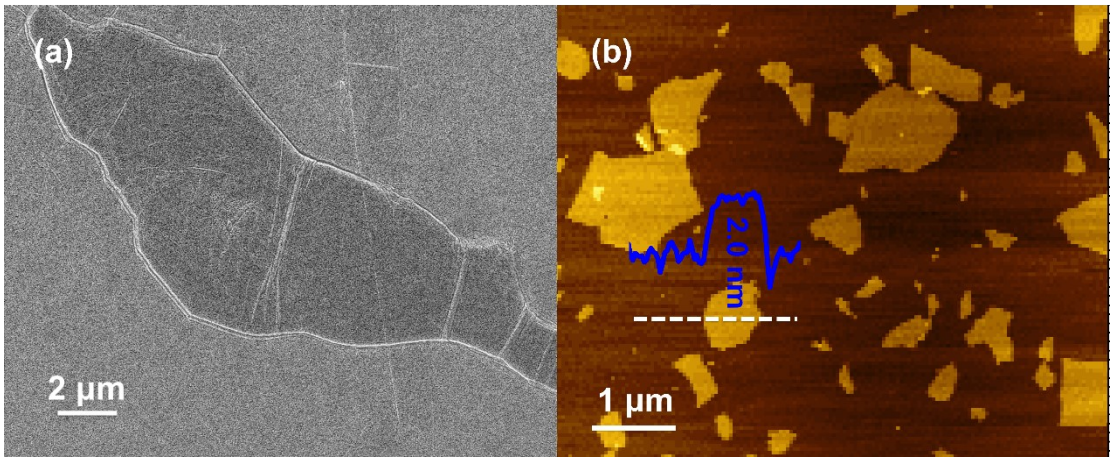

Figure S6. The (a) SEM and (b) AFM images of rGO/pyrene-ONH_2 after acid treatment.

The SEM and AFM images of the composites after acid treatment are shown in Figure S6. Figure S6 (a) showed the SEM image of graphene after acid treatment, from which it can be seen, and that the thickness of the composites is about 2.0 nm, indicating that the acid treatment has no significant effect on the materials.

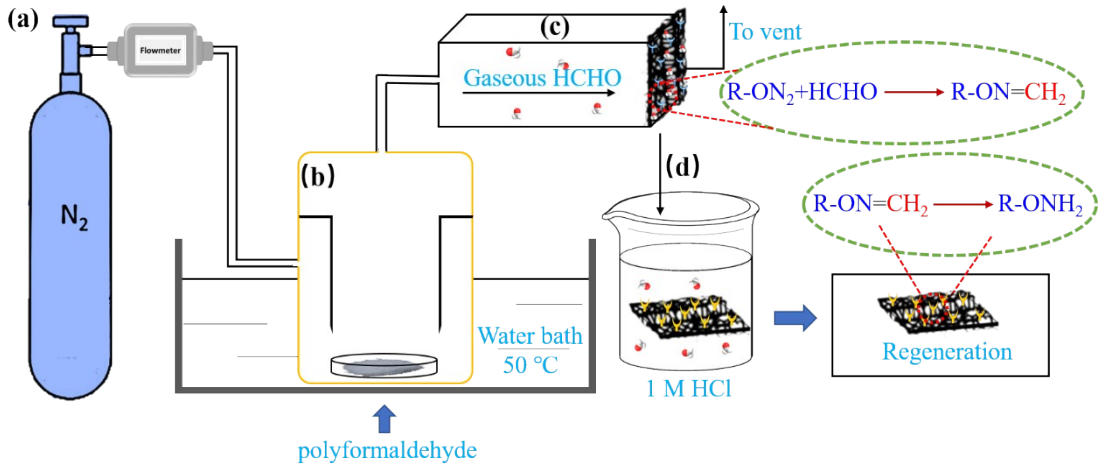

Figure S7. Schematic illustration for chemical removal of HCHO using rGO/ONH_2 as adsorbent at different conditions and the subsequent regeneration.

Figure S8. The apartment with an air purifier inside for chemical removal of HCHO.

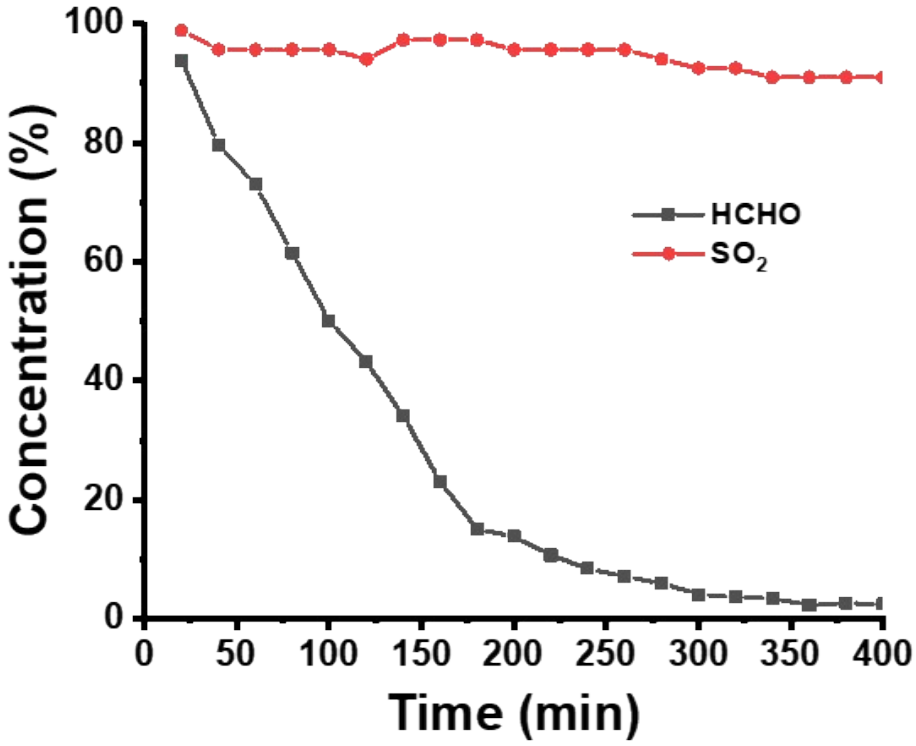

Figure S9 The actual test of HCHO removal in a 3 m^3 confined space with a HCHO concentration of 10 mg/m^3 and SO_2 concentration of 10 mg/m^3.

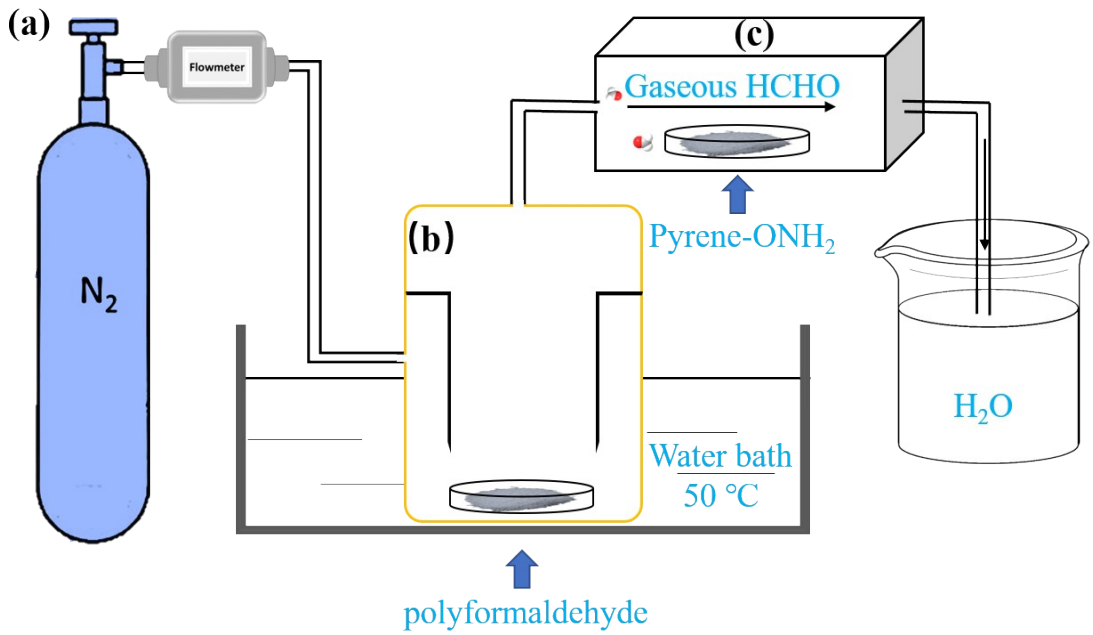

Figure S10. A schematic illustration for the pyrene-ONH_2 reacted with HCHO for testing, (a) N_2 source and flow controller; (b) gaseous HCHO generator and (c) pyrene-ONH_2 reacted with HCHO.