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Periodic mesoporous organosilica nanomaterials for rapid capture of VOCs

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1. General Materials and Methods

1,4-Bis(triethoxysilyl)benzene, cetyltrimethylammonium bromide (CTAB), hexanal, butyric acid, sodium hydroxide, ammonium nitrate, and absolute ethanol were purchased from Sigma Aldrich. Hydro Darco 3000 (HD3000); powder activated carbon (PAC) from Norit Inc and FILTRASORB 400 (F400); granular activated carbon (GAC) from Calgon Inc were also used for comparison (more information, see Table S1). All chemicals were used without further purification. Deionized water was used in the synthetic experiment.

Table S1: BET characterization of GAC and PAC materials.

	Carbon	SA_{BET} (m^2/g)	V_T (cm^3/g)	V_T		
				V_{micro} < 2 nm	V_{meso} 2–50 nm	V_{macro} > 50 nm
GAC	F400	849	0.505	0.312	0.071	0.046
PAC	HD3000	642	0.775	0.108	0.449	0.100

2. Synthesis of PMO SiNPs

Periodic mesoporous silica nanoparticles were prepared as previously reported in the literature with minor changes.[1] A mixture of CTAB (250 mg, 0.686 mmol), distilled water (120 mL), and sodium hydroxide (875 μL, 2 M aq. solution) was stirred at 80 ˚C for 30 min at 300 rpm in a 250 mL three-neck round-bottom flask. Thereafter, 1,4-bis(triethoxysilyl)benzene (300 mL, 0.75 mmol) dissolved in 750 μL DMF was added to the solution, and the condensation process was conducted for 2 h. Then, the solution was cooled to room temperature while stirring and fractions were gathered in propylene tubes. The PMO SiNPs were collected by centrifugation (15 min at 15 krpm). The PMO SiNPs were then sonicated twice with an alcoholic solution of ammonium nitrate (6 g/L) at room temperature, and washed sequentially with ethanol, water, and ethanol, respectively. Each wash step was followed by centrifugal collection in propylene tubes for 15 min at 15 krpm. The PMO SiNPs were then dried overnight under vacuum. The PMO SiNPs were prepared in 70 – 80% isolated yield.\

3. Techniques used for characterization of PMO SiNPs

Fourier Transform Infrared (FT-IR) analysis was performed with a Nicolet Magna 500 with NicPlan FT-IR Microscope and Mapping Stage. Thermal gravimetric analysis (TGA) was performed on a TA Instrument Hi-Res TGA 2950 analyzer. Analysis was conducted under nitrogen from 25 to 1000 ˚C using a 10 ˚C min^{-1} gradient. Powder X-ray diffraction (XRD) was used to determine the crystallinity of the PMO SiNPs compared to controls using a Rigaku Ultima IV diffractometer with Cu Kα radiation. Samples were analyzed on a zero background sample holder. Data were collected between 5˚ and 65˚ 2θ at a scan rate of 1 degree per minute in 0.02 degree intervals. Transmission electron microscopy (TEM) images were recorded with a HT7700 microscope (Hitachi, Tokyo, Japan) operated at 100 kV voltage. Nitrogen sorption isotherms were recorded on a V-sorb 2800P analyzer at –196 ˚C. PMO SiNPs were degassed under vacuum at 200 ˚C for 10 h before conducting measurements. Dynamic light scattering (DLS) and zeta-potential analyses were performed by using a Malvern Nano ZS instrument. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using the adsorption data in a relative pressure (p/p0) range from 0.05 to 0.21. The pore size distribution was calculated from the adsorption branch of isotherms applying proper nonlocal density functional theory (NLDFT) methods. The total pore volume was estimated from the adsorbed amount at a relative pressure (p/p0) of 0.99. Figure S1 depicts the nitrogen adsorption-desorption isotherms (right) and the measured pore width (left).

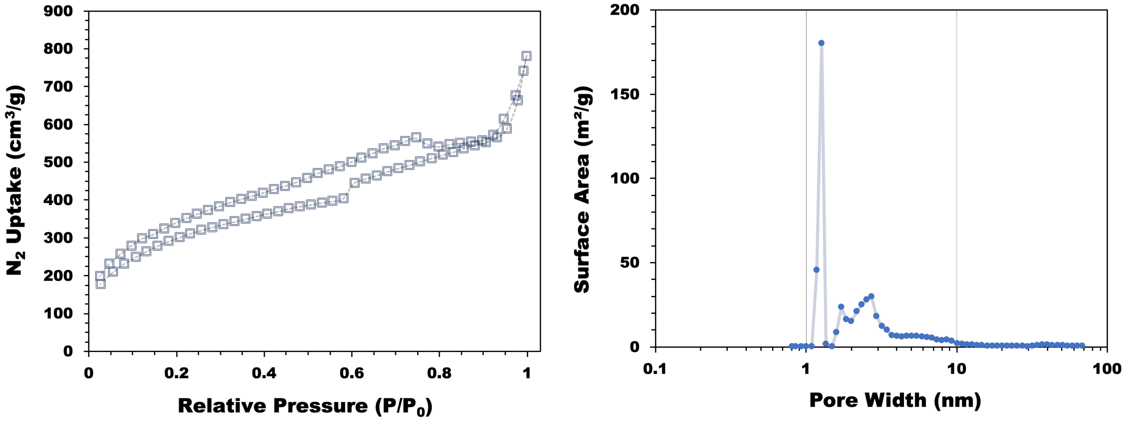

Figure S1: (Left) Nitrogen adsorption–desorption isotherms displaying high textural properties and (right) pore size distributions of PMO SiNPs.

4. DLS and Zeta Potential Data

The size and surface charge of the PMO materials were judged by dynamic light scattering and zeta potenial measurements (Figure S2).

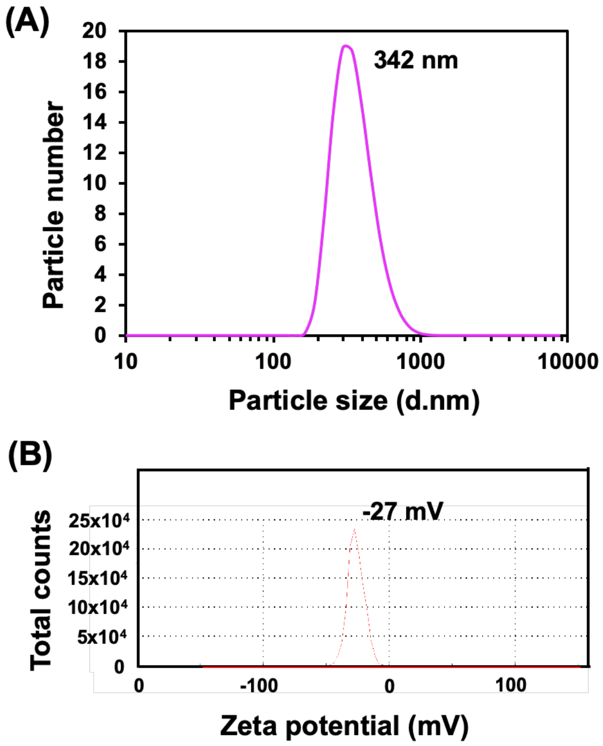

Figure S2. Dynamic laser light scattering microscopy by Zetasizer; (A) hydrodynamic size and (B) zeta potential measurements of PMO SiNPs. All measurements were performed in triplicate.

5. Gas chromatographic (GC) vapor capture assay method

Gas Chromatography (GC) analyses were conducted using a Shimadzu GC-2014 Gas Chromatograph equipped with a Shimadzu AOC-20i Auto-Injector and a Flame Ionization Detector (FID). The GC was equipped with a 30 m x 0.25 mm x 0.25 μm Zebron ZB-WAX Plus capillary GC column. Agilent Technologies Gas Chromatography 1.5 mL volume vials with septum screw-caps were used in the analysis assays. GC analyses were carried out within the following parameters: inlet temperature: 250.0 ˚C; splitless injection at 30.9 mL min^{-1}; injector sampling depth: 10 mm; column flow: 1.33 mL min^{-1}, constant pressure; carrier gas: helium; FID temperature: 225 ˚C; temperature program: 40 ˚C for 5 min, 50 ˚C min^{-1} ramp to 200 ˚C, hold for 5 min.

A GC vapor capture assay was designed in order to assess the effectiveness of the PMO SiNPs by determining the standard vapor areas for each substrate of interest followed by their percent reduction upon interaction with the NP material. All vapor capture experiments were conducted in 1.5 mL glass GC screw-top vials. Briefly, the vial was first charged with a prescribed amount of the PMO SiNP material. Then the opening of the vial was covered with a 5 x 5 cm piece of Kimwipe tissue paper. A small well was created by gently applying pressure to the Kimwipe with the tip of a glass stir rod. The vial cap was then secured and a 1 μL injection of the analyte of interest was introduced into the system via microliter syringe. This was accomplished by piercing the septum with the syringe needle and depositing the analyte onto the Kimwipe, taking care not to rupture the Kimwipe barrier between the analyte and solid sample at the bottom of the GC vial. The analyte was then allowed to vaporize at RT for the allotted amount of time prior to GC analysis. Control and experimental analyses were conducted in triplicate.

6. PMO SiNP Material Loading Experiment

To determine the effect of PMO SiNPs loading on VOC capture efficiency, a series of GC vials were prepared containing 1, 5, 10, 15, and 20 mg of the PMO SiNP material. Samples were prepared following the above-described procedure for the GC vapor capture assay. Once the Kimwipe well was prepared and the vials were capped, a 1 μL injection of hexanal or butyric acid was added to the system onto the Kimwipe barrier. These samples were allowed to vaporize at RT for 30 min and subsequently react with the PMO SiNPs sorbent. Upon completion of the prescribed reaction time, the vial was subjected to GC analysis. A series of control experiments were also conducted, in parallel, to determine the vapor areas of untreated samples. These samples were prepared in same manner as described by the GC vapor capture assay without the addition of the solid NP material.

7. Adsorption kinetic study

A similar assay was also conducted to probe the VOC removal efficiency of the PMO SiNPs over time. Screw-top GC vials were prepared containing 10 mg of the sorbent material followed by a 1 μL injection of hexanal or butyric acid and allowed to vaporize at RT for various times followed by GC analysis. Experiments were conducted in triplicate for analysis at 10 min, 20 min, 30 min, 1 h, and 2 h time points. Hexanal and butyric acid analyte standards were also prepared in the same manner, *i.e.* pre-prepared vials were charged with 1 μL of analyte and no sorbent material. The standards were allowed to vaporize for the same amount of time as their respective treated counterparts *i.e.* 10 min, 20 min, 30 min, *etc.* All experiments were conducted in triplicate.

8. PMO SiNPs Reuse Experiments

Pre-prepared GC vials containing 10 mg of the PMO SiNP material were charged with 1 μL of hexanal or butyric acid. These samples were allowed to vaporize for 30 min at RT and then subjected to GC analysis. Concomitantly, pre-prepared GC vials containing no sorbent material, were also charged with 1 μL of hexanal or butyric acid and allowed to vaporize at RT for 30 min to serve as controls. In order to assess the possibility of reusing the NP material, previously treated samples were immediately charged with an additional 1 μL or hexanal or butyric acid following GC analysis. The analyte was once again allowed to vaporize for 30 min prior to GC analysis. This was repeated for a total of 5 reuse cycles. All experiments were conducted in triplicate.

The recyclability of a 10 mg sample of PMO SiNPs was evaluated against hexanal and butyric acid vapors (Figure S3).

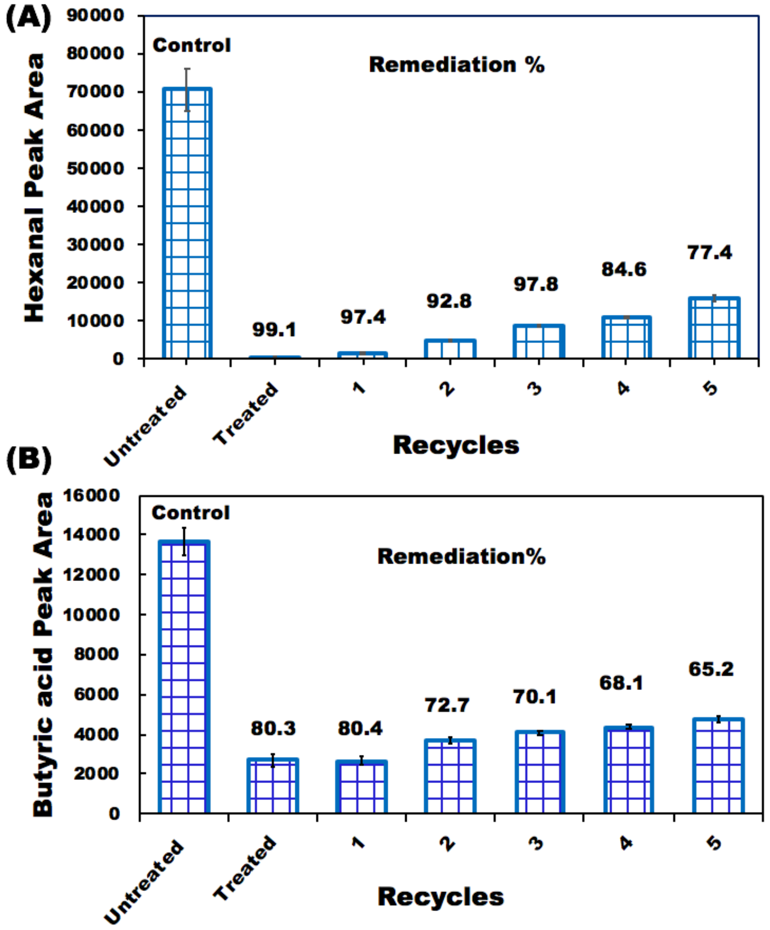

Figure S3. Recycle studies of PMO SiNPs for adsorption of hexanal (A) and butyric acid (B) vapors. Experiments were carried out at 10 mg adsorbent / 1 μL analyte. Measurements were performed in triplicate.

9. Comparison Experiments of PMO SiNPs to other adsorbents.

The performance of the PMO materials prepared in this study was compared against previously reported materials from our group (CNC-PEI and Kao-PEI) as well as two commercially available activated carbon materials (PAC and GAC) (Figure S4).

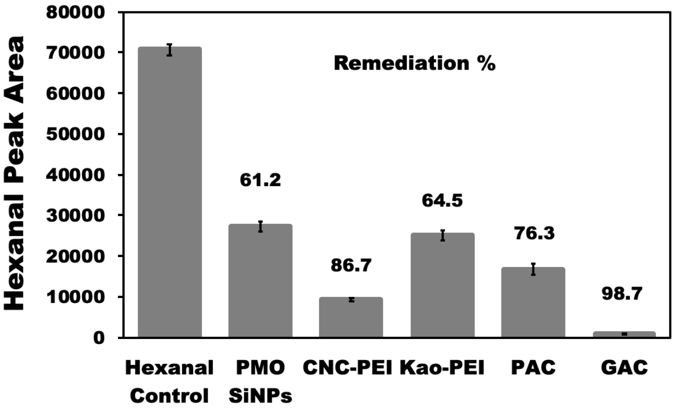

Figure S4. Comparison study for evaluation of adsorption efficiency of hexanal vapors by five materials (PMO SiNPs, CNC-PEI, Kao-PEI, PAC, and GAC (See text for acronym definitions)). Experiments were conducted at a loading of 2 mg adsorbent/1 µL analyte. Experiments were conducted in triplicate.

10. References

1 J. G. Croissant, Y. Fatieiev, H. Omar, D. H. Anjum, A. Gurinov, J. Lu, F. Tamanoi, J. I. Zink and N. M. Khashab, *Chem. Eur. J*, 2016, **22**, 9607.