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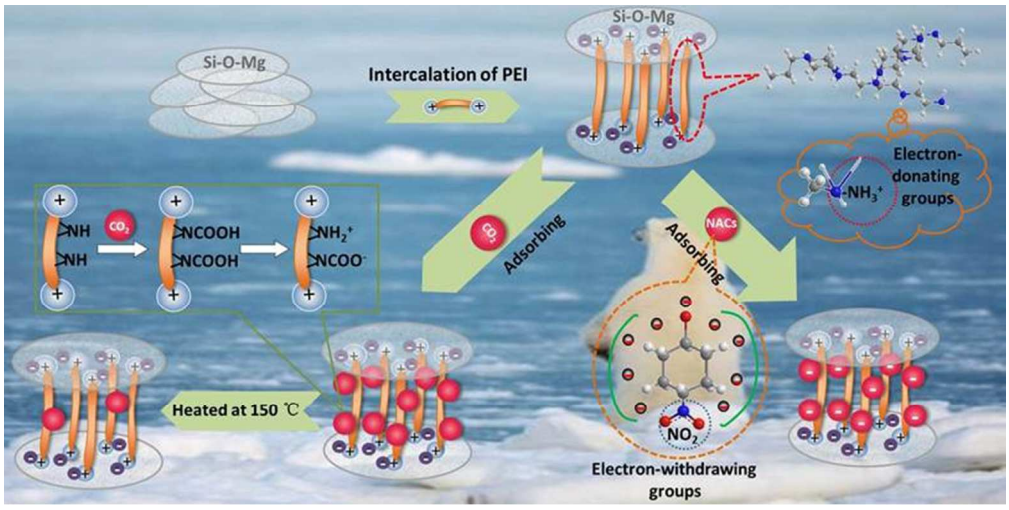

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PEI@Mg_2SiO_4: an efficient carbon dioxide and nitrophenol compounds adsorbing material

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The PEI@Mg_2SiO_4 hybrid composite is readily synthesized for adsorbing carbon dioxide (CO_2) and nitrophenol compounds (NACs), in which more than 11% PEI is embedded. By the removal rate of 4−nitrophenol (10 mg/L) and the capture capacity of CO_2, the Mg^{2+}: PEI: SiO_3^{2-} optimal mole ratio of the PEI@Mg_2SiO_4 is 1: 0.6: 1.5. The composite shows the highest adsorption amounts of 0.94 mmol/g CO_2 at 50 °C. The heat treatment regeneration exhibits a good stability, e.g. CO_2 capture capacity decreasing by only 20% for fourth cycles and the desorption rate of CO_2 remains more than 91%. It also exhibites a fast adsorption and high capacity to 4−nitrophenol (NP), 2,4−dinitrophenol (DNP) and 2,4,6−trinitrophenyl group (TNP). The adsorption capacity of NP, DNP and TNP is 2.40 mmol/g, 2.66 mmol/g and 4.85 mmol/g respectively, which are more than the conventional sorbents. This work presents a new sorbent for CO_2 and nitrophenol coumpouds with the higher capacity and eco−friendly.

Inorganic−organic (IO) materials with hierarchical structures and complex morpholgies assembled through "host−guest" chemistry have attracted much attention for a fundamental interest in environmental science and their potential applications in water treatment and gas remediation.[1] It is necessary to find special properties by intercalating appointed organic material into a stable inorganic matrix. Some entity frameworks in layered architectures have been utilized as an ideal “host” supports in the construction of multifunctional adsorbents such as layered double hydroxides[2], layered transition metal oxides[3], graphite, and other lamellar materials[4-5]. In particular, layered magnesium silicate has been applied in absorbing to pollutants[6] because of their high surface area[7-8], properties of ion exchange, hydrophobic character, adsorbant and molecular sieves[9].

As a guest, surfactants and block−copolymers often are used extensively in the shape−controlled synthesis of various functional materials, where it palys a soft template or stabilizer role[10-11]. Among the potential “guest” molecules, diverse amine species have prospective absorption of applications in heavy metal[12], organic contamination[13], gaseous pollutants[14] and other fields. Polyethyleneimine (PEI) can effectively adsorb pollutants due to the high amine density, accessible primary amine sites on chain ends and good water−solubility[15]. However, before being used in the absorption for pollutants, the water−soluble PEI must be processed into a solid form. Fortunately, the combination of PEI with inorganic matrix may achieve this goal[16]. For example, Deng[17] and Ting reported that the fungal biomass with PEI−grafting showed high sorption capacity for anionic Cr(VI) and Cr(III); Tailor[18] and co−workers found that the MCM−41−supported modified PEI markedly increased the SO_2 capture capacity than that of traditional adsorbents; Gao *et al*[19] introduced an interesting study for adsorbing phenol perfectly with modified diatomite by PEI impregnating.

Owing to the burning of fossil fuels and various chemical processes, there is huge amounts of emission of CO_2 into the atmosphere, which is greenhouse gases[20]. More and more people believe that the anthropogenic emissions of greenhouse gases allow radiative forcing and contribute to global warming and climate change[21-22]. Meanwhile, the widespread of NACs in water is a main concern that impels researchers to look for remedies[23-26]. These compounds, in particular, nitrobenzene, their transformation products in the environment occur as contaminants worldwide and are known to be hazardous to ecological and human health[27-29]. Amine−layered IO materials has been shown to be successful for the remaval of CO_2 and NACs, such as amine−layered LDHs[30], amine−functionalized mesoporous silica[31] and milli-sized calcium[32]. Currently, there are two main classes of such the amine−based IO materials: (a) amines covalently bound to the support *via* the use of chemical grafting[33-35] and (b) physically impregnated into the support based on a ‘‘wet impregnation’’ method[31, 36-39]. The sorbents mentioned above have some obvious disadvantages, involving lacking of stability, relatively low efficiency, less content of functional compound, and poor regeneration stability[40]. Our previous studies indicate that the layered IO material by coprecipitation technique has a great effect on overcomeing those disadvantages [7, 35, 43-45]. Therefore, there is a significant and untapped opportunity to improve the adsorption characteristics by developing the PEI−layered magnesium silicate material by coprecipitation technique. The objective of this study is (1) to form a hybrid material (PEI@Mg_2SiO_4) by coprecipitation technique (2) to utilize the high amine density and positive charge of the PEI@Mg_2SiO_4 to adsorb NACs and CO_2 and (3) to investigate their resultant adsorptions. The results indicate that the PEI@Mg_2SiO_4 is promising to capture CO_2 and adsorb NACs from wastewater decently.

Experimental section

Apparatus and Materials

The infrared spectra were measured with a Fourier transform infrared spectrometer (Model NICOLET 5700, Thermo Electron Co., USA) to indicate PEI embedded into the hybrid materials and NAC adsorbed into the sorbent. The heat weight change of the materials was performed with a thermal gravimetric analyser (Model NETZSCH TG 209 F1, NETZSCH−Geratebau GmbH, Germany). A scanning electronic microscopy (SEM) (Model Quanta 200 FEG, FEI Co., USA) was used to measure the size and shape of the hybrid sorbents. A transmission electron microscopy (TEM) (Model TECNAI G2, S−TWIN, FEI Co., USA) was used to characterize the morphology of the PEI@Mg_2SiO_4 and Mg_2SiO_4. A ζ−potential instrument (Zetasizer Nano Z, Malvern, UK) was used to determine the surface potential of the sorbents. The surface area of the materials was measured with a surface area and porosimetry analyser (Model ASAP2020, Micromeritics Co., USA). The small−angle X−ray diffraction (SAXRD) (Model D/Max−2550 PC, Japan) was recorded using CuK radiation at a voltage of 30 kV and current of 50 mA and the wide−angle X−ray diffraction (WAXRD) (Model Bruker D8 Advance, Germany) in range of ~10 − 90° 2θ at 40 kV and 40 mA. The elemental analysis device (Model Vario EL Ⅲ, Germany) used to determine C, N and H content of hybrid composite. A photodiode array spectrometer (Model S4100, Scinco, Korea) with the Labpro plus software (Firmware Version 060105) was used to determine the concentration of various NAC solutions.

Sodium metasilicate and magnesium nitrate (Aladdin Agents, China), sodium hydroxide (Aladdin Agents, China), PEI (M.W. 600, Aladdin Agents, China), sodium chloride (Aladdin Agents, China), hydrochloric acid (Sinopharm Chemical Reagent Co.,Ltd, China) were used. The adsorptions of five phenolic compounds (Aladdin Agents, China) on the PEI@Mg_2SiO_4 were investigated, which was NP, DNP, TNP, *p*−cresol and *p*−chlorophenol respectively.

Synthesis of the PEI@Mg_2SiO_4 Hybrid Composite and Mg_2SiO_4

2.0 g of magnesium chloride hexahydrate (AR, Aladdin Reagents Co., China) was dispersed into 100 mL of deionized water and mixed with 2.0 g ethylene imine polymer (M.W. 600, 99%, Aladdin Reagents Co., China) for 10 min with an ultrasonic fragmentation device (Model JY92−II, Xinzhi Biotechnol. Co, Ltd, Ningbo, China). 100 mL of 4.3% (w/v) sodium silicate was added rapidly under stirring. After stationarily aging for 24 h, the hybrid composite was washed repeatedly with deionized water to remove the excessive PEI. The PEI@Mg_2SiO_4 suspension liquid was used to dry by freezer dryer. As reference, magniums silicate was prepared according to the same procedure. The PEI@Mg_2SiO_4 and Mg_2SiO_4 powder were used to adsorb CO_2 respectively. The PEI@Mg_2SiO_4 suspension liquid was used to adsorb NACs.

Adsorption of CO_2 to the PEI@Mg_2SiO_4 and Mg_2SiO_4 Material

The amount of adopted CO_2 was determined by using a thermal gravimetric analyzer (Model NETZSCH TG 209 F1, NETZSCH−Geratebau GmbH, Germany). In a typical measurement procedure, the sample was degassed at 150 °C for 30 min in N_2 to remove any physically adsorbed molecules, after the temperature was decreased to 25 °C, the sample was allowed to adsorbed CO_2 by passing CO_2 at a flow rate of 30 mL/min.

The influences of time and temperature on the adsorption of CO_2 were tested by using a thermal gravimetric analyzer (Model NETZSCH TG 209 F1, NETZSCH−Geratebau GmbH, Germany). In a typical measurement procedure, the sample was degassed at 150 °C for 30 min in N_2 to remove any physically adsorbed molecules, after the temperature was decreased to 50 °C, the sample was allowed to adsorbed CO_2 by passing CO_2 at a flow rate of 30 mL/min, the process was continued for 40 min. The temperature of sample was adjusted from 25 °C to 100 °C. The adsorption/desorption cycling was also measured. The sample after adsorption of CO_2 was heated at 150 °C with a ramp rate of 5 °C/min in a nitrogen atmosphere, and then the sample was kept at this temperature for 100 min to remove the adsorbed CO_2. After the temperature was decreased to 50 °C, the sample was allowed to adsorbed CO_2 again by re−passing CO_2 at a flow rate of 30 mL:min, the process was continued for another 80 min, the process was repeated for four times.

Adsorption of NACs and Phenols

The adsorption capacities of the PEI@Mg_2SiO_4 to three kinds of NACs and two kinds of phenols were determined. The 0.02% (w: v) of the PEI@Mg_2SiO_4 was added into the NACs and solutions of phenols e.g. DNP from 15 to 100 mg/L, TNP from 20 to 150 mg/L, *p*−cresol from 20 to 300 mg/L, NP from 50 to 420 mg/L and *p*−chlorophenol from 60 to 600 mg/L. The procedure was followed. The PEI@Mg_2SiO_4−pollutants liquids were mixed for 10 min by ultrasound. After the mixtures were centrifuged, the concentrations of pollutants in the supernatants were determined by spectrophotometry.

In addition, the influences of pH, ionic strength and time on the adsorption of NP (53 mg/L), DNP (19 mg/L) and TNP (20 mg/L) on the PEI@Mg_2SiO_4 were investigated respectively. NaCl (1 M) was used to adjust ionic strength of the liquids from 0 to 0.2 M. The sorption time was carried out from 0 to 30 min. The pH was carried out from 4 to 10. In all the experiments, the pollutants in the supernatents were determined by spectrophotometry.

Results and discussion

Interaction of PEI with Magnesium Silicate

Our previous study indicates that the initial optimal mole ratio of Mg^{2+} : SiO_3^{2-} is 1 : 1.5 for preparing the organics−layered magnesium silicate.[6] From the interaction of PEI with *in-situ* formed magnesium silicate, embedded amount of PEI increases with increase of SiO_3^{2-} and then the embedded amount of PEI approaches equilibrium.[6] The hybridization obeys the Langmuir isotherm model (Fig. 1A, 1B), e.g. $1/q_e = 1/(K_a c_e q_\infty) + 1/q_\infty$[41-44], where c_e is the equilibrium molarity of PEI in g/L, q_e the amount of PEI binding to magnesium silicate in mg/g, q_∞ the saturation amount of PEI in mg/g and K_a the binding constant. The q_∞ of PEI is calculated 0.41 g per gram of magnesium silicate, i.e. the

content maximum of embedded PEI in the PEI@Mg_2SiO_4 approaches 29.4%, which is more than other results of previous similar studies.[19, 45-46] During the growing of Mg−O−Si particles, the positively charged amino group of PEI can bind to the negatively charged Mg−O−Si ones *via* the electrical attraction. The ζ−potential of the magnesium silicate−only is determined to be -45.5 mV in aqueous media, which may be attributed to the fact that lots of OH− in basic media are adsorbed *via* the interaction with Mg^{2+} and O−Si.[47]

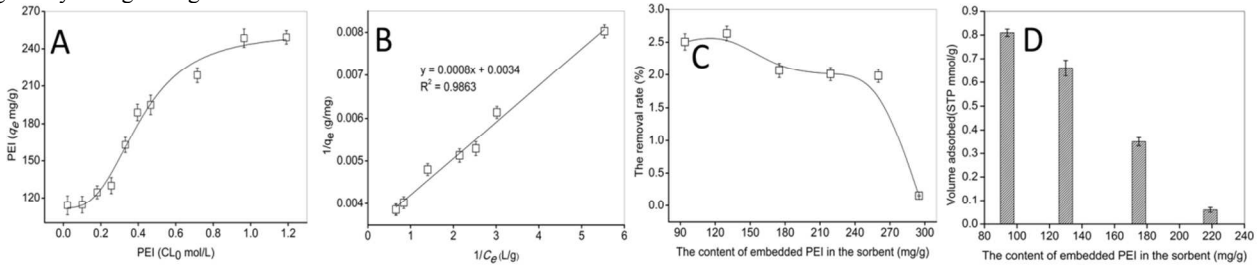

Fig. 1 Effect of PEI on the hybridization. A: plots q_e vs c_0, B: Plots c_e/q_e vs c_e. C: the removal rate of NP with the different content of embedded PEI in the sorbent. D: the adsorption of CO_2 with the different content of embedded PEI in the sorbent.

However, the results of previous studies show that there is a substantial decrease in the adsorption capacity of IO−sorbent with the increasing of the content of embedded PEI, due to partial blockage of pores by the grafted amine molecules.[46, 48-49] In order to optimize the ratio of PEI in the PEI@Mg_2SiO_4, CO_2 and NP (10 mg/L) is selected as a representative to measure the optimal pollutant adsorption capacity of the different content of embedded PEI in the PEI@Mg_2SiO_4, e.g. 94 mg/g, 130 mg/g, 175 mg/g, 219 mg/g, 260 mg/g and 295 mg/g, respectively. As a result, the removal rates of NP are 2.50 %, 2.63 %, 2.07 %, 2.01 %, 1.98 % and 0.16%, which is got by using the above corresponding PEI@Mg_2SiO_4 (Fig. 1C). The adsorptions of CO_2 are 0.81 mmol/g, 0.66 mmol/g, 0.35 mmol/g, 0.06 mmol, 0 mmol and 0 mmol/g respectively (Fig. 1D). Thus the adsorption of NP and CO_2 are maximal on the adsorbents with the Mg^{2+}: PEI: SiO_3^{2-} ratio of 1: 0.6: 1.5. The PEI@Mg_2SiO_4 is formed and used. The molar ratio of Mg to PEI and Si in the PEI@Mg_2SiO_4 is calculated 1: 0.13: 1.3 determined with element analysis and ICP.

Characterization of the PEI@Mg_2SiO_4

An initial estimate of PEI bilayer content in the PEI@Mg_2SiO_4 is obtained from infrared spectra (IR). As shown in Fig. 2A, the Si−O absorption peak is at 1059 cm^{-1}. The absorption peaks at 2935 (C−H stretching), 2819 (C−H stretching), 1756 (−NH_2 and −NH− deformation), 1472 (−NH_2 and −NH− deformation) and 1290 (−NH_2 and −NH− deformation) cm^{-1} indicate that PEI is embedded into the PEI@Mg_2SiO_4. From the element analysis of the PEI@Mg_2SiO_4, both 7.1% C and 3.8% N indicate that 11.4% PEI is embedded into the PEI@Mg_2SiO_4 (Table S1, ESI†). From the small−angle XRD (SAXRD) (curve 2 in Fig. 2B), the PEI@Mg_2SiO_4 composite possesses the layered structure. During the synthesis, the positively charged amino group of PEI (structured in Fig. 2B) can bind to the negatively charged Mg−O−Si particles *via* the electrical attraction. The ζ−potential of Mg_2SiO_4−only is determined to be -45.5 mV in aqueous media, which may be attributed to the fact that lots of OH^- in basic media are adsorbed *via* the interaction with Mg^{2+} and O−Si[47]. After the intercalation of PEI, the ζ−potential of the PEI@Mg_2SiO_4 changes to +15.9 mV. The electrostatic interaction occurs between PEI^+ and magnesium silicate. In addition, the alkyl chain (−[CH_2−CH_2−NH]−$_n$) of PEI in length of 3.4 nm may be embedded into two Mg_2SiO_4−sheets. PEI is fixed between Mg_2SiO_4 particles in the interval of 3.9 nm (Fig. 2B).

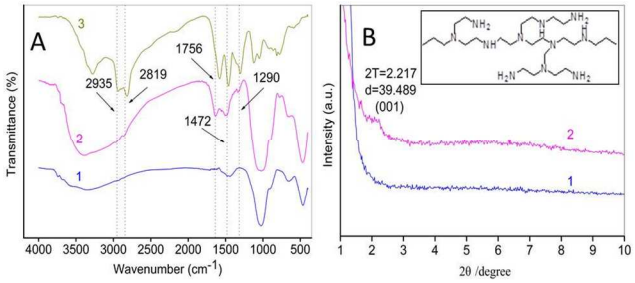

Fig. 2 IR spectra (A) of Mg_2SiO_4 (1), the PEI@Mg_2SiO_4 (2) and PEI (3) and SAXRD (B) of Mg_2SiO_4 (1) and the PEI@Mg_2SiO_4 (2).

As shown in Fig. 3, the PEI@Mg_2SiO_4 shows the sheet morphology with an average diameter of 40 to 60 nm (Fig. 3B), which is similar to that of Mg_2SiO_4 (Fig. 3D). However, the PEI@Mg_2SiO_4 also shows the layer structure (Fig. 3A) because two sheets of Mg_2SiO_4 are aged into the layer−by−layer material by electric attraction. Meanwhile, the width of silt is about 4 nm (Fig. 3A,C), which is consistent with the SAXRD. As shown in the SEM images (Fig. 3E,F), the PEI@Mg_2SiO_4 has flaky structure with an average diameter of 60 to 100 nm while Mg_2SiO_4 has the granule structure with the average diameter of 60 to 80 nm (Fig. 3G). The presence of PEI affects the stacking of lamellar Mg_2SiO_4, which is just stringed by the intermolecular action with PEI[6]. The PEI in interior of the hybrid is also confirmed by the EDX (Fig. S1, ESI†).

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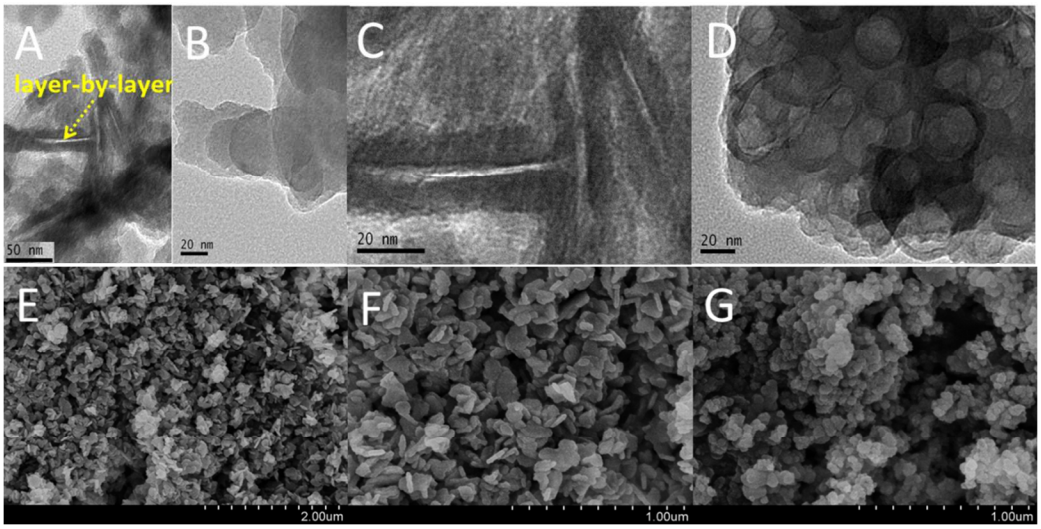

Fig. 3 TEM images of the PEI@Mg_2SiO_4 (A, B, C) and Mg_2SiO_4 (D). SEM of the PEI@Mg_2SiO_4 (E, F) and Mg_2SiO_4 (G).

Fig. 4 illustrates the N_2 sorption isotherm and the pore−size distribution with Barrett−Joyner−Halenda method of Mg_2SiO_4 and the PEI@Mg_2SiO_4. All of the isotherms are classical type IV, which refers to the mesoporous materials. Furthermore, the isotherms have two hysteresis loops, indicating a bimodal pore size distribution in the mesoporous regions. The shapes of the two hysteresis loops are different from each other[50]. At the high relative pressure between 0.8 and 0.9, the hysteresis loops are type H1, suggesting the presence of cylindrical mesopores[51]. The above bimodal pore−size distribution is further confirmed by the pore−size distribution in Fig. 4a,b. From the pore plots, no peak appeared in the pore, indicating the presence of irregular mesopores. The mesopores may be formed by the stacking of lamellar Mg_2SiO_4. The BET analysis of the materials indicate that the specific surface area of Mg_2SiO_4 and PEI@Mg_2SiO_4 is determined to be 51.61 and 89.51 m^2/g. The increased area should be contributed to the partial impregnation of PEI into Mg_2SiO_4.

As seen in the thermal gravimetric analysis (TGA) differential thermal gravity of the PEI@Mg_2SiO_4 (Fig. S2, ESI†), the first step in the range of 40 to 200 °C is attributed to the removal of the physisorbed water and interlayer water, the second step in the range of 200 to 400 °C due to the removal of layer silicate and the third step in the range of 400 to 600 °C due to the removal of interlayer PEI. At 700 °C, the weight loss of the PEI@Mg_2SiO_4 is 33.2%, where the physisorbed water, layer silicate and interlayer PEI distributed 15.0, 7.9 and 10.3% respectively, approaching that obtained from the element analysis.

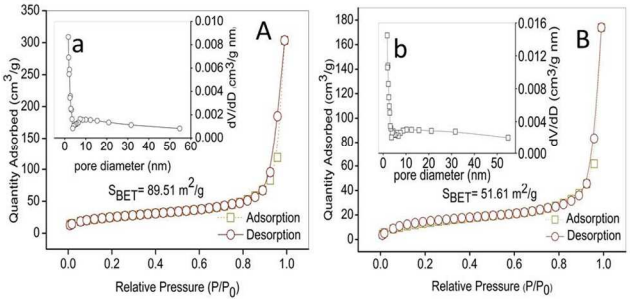

Fig.4 N_2 absorption−desorption isotherm and pore−size distribution (inset) for Mg_2SiO_4 (A, a) and the PEI@Mg_2SiO_4 (B, b).

Prediction of CO_2 Adsorption Uptakes in the PEI@Mg_2SiO_4

The CO_2 capture capacity of Mg_2SiO_4 and the PEI@Mg_2SiO_4 materials is measured at 25 °C by using a thermal gravimetric analyzer. The chemisorption of CO_2 may occur through the formation of carbamate by the reaction of the secondary amine group (R_2NH) and primary amine (RNH_3) of PEI with CO_2, as shown in Eq. (1) and (2) below.

$$CO_2 + 2RNH_2 \rightleftharpoons R\overset{+}{N}H_3\ O\overset{O}{\overset{\|}{C}}NHR \quad (1)$$

$$CO_2 + 2R_2NH \rightleftharpoons R_2\overset{+}{N}H_2\ \overset{-}{O}\overset{O}{\overset{\|}{C}}NR_2 \quad (2)$$

It suggests that CO_2 would form a weak chemical bond with the secondary amine group, and subsequently lead to the formation of carbamate zwitterions[52]. The CO_2 capture capacity on Mg_2SiO_4 is around 0.69 mmol/g, which is higher than that of the results reported[30, 53-54]. The interlayer anions in Mg_2SiO_4[47] is favourable to CO_2 capture[31, 55]. The CO_2 capture capacity increases up to 0.75 mmol/g with the PEI@Mg_2SiO_4. This competing kinetic (diffusion) and thermodynamic (adsorption) effects has been observed and reported previously[45, 53]. The nanopores of the PEI@Mg_2SiO_4 provide CO_2 with a diffusion path, where PEI

located on the nanopore wall offers the active adsorption sites.

For CO_2 capture, any adsorbent should have not only a high sorption capacity but also a fast adsorption to be energy−efficient[56]. A recent study demonstrated the high loading of amine may hamper the adsorption kinetics but increase the capacity[57]. A double−exponential model (DEM) is applied to describe the CO_2 adsorption kinetics on the PEI@Mg_2SiO_4, expressed by the relation:

$$q_t = q_e - D_1\exp(-K_1t) - D_2\exp(-K_2t) \qquad (3)$$

where D_1 (mg/g) and K_1 (min^{-1}) are the adsorption rate and diffusion parameter for the fast step, and D_2 and K_2 those for the slow step. The model is suitable for adsorbent with two different types of adsorption sites, and the adsorption contains fast and slow adsorption steps[56, 58]. The experimental data are fitted by the DEM model at 25, 50, 75 and 100 °C (Fig. 5A). Both D_1 and D_2 first increase and then decrease with increase of temperature from 25 to 100 °C and the highest value appeared at 50 °C (Table S1, ESI†). At 100 and 75 °C, the CO_2 adsorption equilibrium reached within 5 min. With decrease of temperature, the adsorption of CO_2 goes slow on the PEI@Mg_2SiO_4. The slow adsorption is much more obvious at 25 and 50 °C and the equilibrium have not reached at 15 min. This demonstrates a strong diffusion of CO_2 is hindered by PEI phase at low temperature[57], proved from the diffusion parameter (K_1, K_2) (Table S2, ESI†). Evidently, the PEI@Mg_2SiO_4 exhibits the highest adsorption for CO_2 at 50 °C. The kinetic results are also consistent with previous reports[56]. It may provide a valuable application to collect CO_2 from flue gas. In addition, the CO_2 adsorption equilibrium on the PEI@Mg_2SiO_4 is completed in 18 min while that on Mg_2SiO_4 in 35 min (Fig. S3, ESI†). The adsorption time is close to other types of adsorbent[10, 56, 59-60]

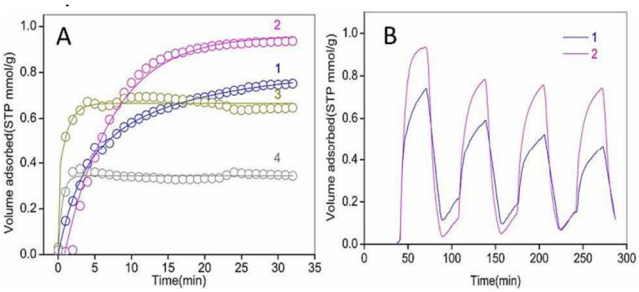

Fig.5 A: The CO_2 adsorption kinetics of the PEI@Mg_2SiO_4 at 25 °C (1), 50 °C (2), 75 °C (3) and 100 °C (4) fitting by DEM. B: Cycles of CO_2 adsorption/desorption for Mg_2SiO_4 (1) and the PEI@Mg_2SiO_4 at 50 °C.

The successive CO_2 adsorption−desorption cycle may provide an assessment of the regeneration stability of the materials. The trend of cycle curves is consistent with that of other studies[53, 61-62] (Fig. 5B). During four cycles, the CO_2 capture amounts decrease from 0.94 to 0.75 mmol/g with the PEI@Mg_2SiO_4 but from 0.74 to only 0.46 mmol/g with Mg_2SiO_4. The CO_2 adsorption capacity of the PEI@Mg_2SiO_4 regenerated decreases by only 15 to 20%. In addition, from curve 1 more than 18% CO_2 is always left on the Mg_2SiO_4 every cycle. On the contrary, from curve 2 the desorption rate of CO_2 remains more than 91% with the PEI@Mg_2SiO_4.

Prediction of NACs Adsorption Uptakes in the PEI@Mg_2SiO_4

As described the above, the PEI@Mg_2SiO_4 carries a great deal of positive charges. It may adsorb strongly NACs, e.g. NP, DNP and TNP *via* the electric attraction. Moreover, there are many the electron−withdrawing groups (nitro group) in NACs, which is in favour of being adsorbed by the PEI@Mg_2SiO_4. The NP, DNP and TNP are tried to be adsorbed by the PEI@Mg_2SiO_4 hybrid composite and the adsorption obeys the Langmuir isotherm model (Fig. 6B), $1/q_e = 1/(K_aC_eq_\infty) + 1/q_\infty$. From Table 1, q_∞ value is positively related to $\lg K_{o/w}$ value e.g. 2.40 mmol/g for NP ($\lg K_{o/w}$ = 1.91), 2.66 mmol/g for DNP ($\lg K_{o/w}$ = 1.54), 4.85 mmol/g for TNP ($\lg K_{o/w}$ = 2.03), which is superior to the other traditional absorbents.[63-67] The ζ−potential of the hybrid composite approaches +7.29 mV, +6.43 mV and -0.39 mV after adsorption of NP, DNP and TNP respectively. The +/- charge attraction plays a primary role in the adsorption of NACs,[6] i.e. PEI embedding into the hybrid composite captured NACs from aqueous solution.

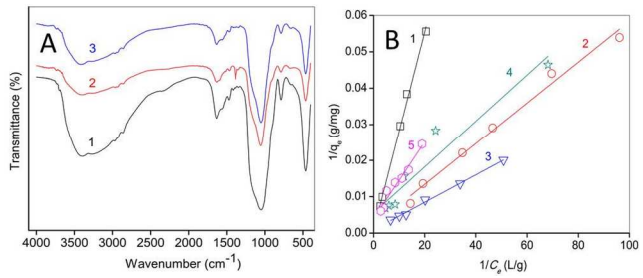

Fig. 6 IR spectra (A) of the PEI@Mg_2SiO_4−NP (1), the PEI@Mg_2SiO_4−DNP (2), the PEI@Mg_2SiO_4−TNP (3), the PEI@Mg_2SiO_4 (4), Mg_2SiO_4 (5) and adsorption of NP (B1), DNP (B2), TNP (B3), *p*−cresol (B4) and *p*−chlorophenol (B5).

Nitro groups can increase the electronegativity of the phenolic hydroxy groups so that the amino groups of PEI@Mg_2SiO_4 can combine with the phenolic hydroxy groups of NACs more efficiently.[68] Such NACs with more nitro groups often exhibit the higher adsorption capacity. In addition, the electron−withdrawing effect of chlorine group is less than nitro groups. Methyl groups can reduce the electronegativity of the phenolic hydroxy groups, which weights against the combination between the amino groups of the PEI@Mg_2SiO_4 and the phenolic hydroxy groups of *p*−cresol. Therefore, the absorption ability of pollutants from high to low is: TNP > DNP > NP > *p*−chlorophenol > *p*−cresol. The $\lg(K_a)$ values of NP, DNP and TNP are calculated to be 2.52, 2.66 and 3.05 respectively, which are superior to their $\lg K_{o/w}$. And there are many long hydrophobic chains i.e. $-[CH_2-CH_2-N^+]-_n$ in PEI, which indicates the PEI@Mg_2SiO_4 carries decent hydrophobicity[69]. Therefore, the hydrophobic interaction occurs between the hydrophobic groups of NACs and the long alkyl chains of embedded PEI in the PEI@Mg_2SiO_4 besides the electrical charge interaction.

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Table 1 The adsorption capacity of the PEI@Mg_2SiO_4 to NACs with K_a and comparison with the other sorbents reported

Pollutants	Group category	Nitro groups number, *n*	q_∞ mmol/g	q_∞ mg/g	lgK_a	R^2	q_∞ comparison Sorbent	q_∞/ mg/g
TNP	electron−withdrawing groups	3	4.85	1111	3.05	0.9962	hydrotalcite	504[63]
DNP		2	2.66	455	2.66	0.9884	activated carbon fibers	417[64]
NP		1	2.40	333	2.52	0.9763	granular activated carbon	206[65]
p−chlorophenol		/	2.23	286	2.47	0.9767	/	/
p−cresol	electron−donating groups	/	1.68	182	2.26	0.9398	/	/

On the basis of the above experiments, we further carried out *in situ* IR experiments to clarify the NACs kinetics on the adsorbents. *In situ* IR difference spectra upon NACs adsorption, the absorption peaks of nitro groups at 1385 to 1565 cm^{-1} indicate that NACs are embedded into the hybrid materials (Fig. 6A). The pH of solution affected obviously the adsorption of NACs. With increasing pH 4 to 6, the q_e of NP and DNP increase by 50% and 215% respectively and remains almost constant between pH 7 to 10. The q_e of TNP increases by 20% between pH 4 to 6 and decreases by 37% at pH 10 (Fig. S4, ESI†). The adsorption of NACs increased slightly with increase of ionic strength. It is attributed to the fact that the protonation of PEI is triggered in strong acid.[70] The q_e of NP, DNP and TNP increases by 16%, 4% and 13% respectively in 0.25 M NaCl (Fig. S5, ESI†). It is attributed to the fact that ionic strength can strengthen the hydrophobic interaction between NACs and PEI. The adsorption equilibrium is completed in 8 min (Fig. S6, ESI†), which is much faster than that of activated carbon[71]. Therefore, the hybrid sorbent prepared is favorable for treatment of the highly salt and slightly alkaline wastewater.

Conclusions

This work provides a facile layered sorbent (PEI@Mg_2SiO_4) for adsorbing CO_2 and NACs by PEI hybridizing into Mg_2SiO_4. More than 11% PEI is embedded so that the sorbent contains a large numbers of reactive sites to cause an exceptional CO_2 capture capacity. The secondary amine group of PEI with CO_2 plays a key role and the experimental data fittes to the DEM. The sorbent exhibits the highest adsorption capacity for CO_2 at 50 °C e.g. approching 0.94 mmol/g. The sorbent regenerated by heat treatment exhibits a good stability with the adsorption–desorption cycling of CO_2, e.g. decreasing by 20% for fourth cycles. In addition, the desorption rate of CO_2 remains more than 91% with the PEI@Mg_2SiO_4. Moreover, such a material appears simultaneously multifunctional, e.g. adsorption, ionic exchange and flocculation. From the adsorptions of three NACs, the PEI@Mg_2SiO_4 exhibits a high adsorption capacity to NACs, where the electrostatic interaction plays a dominant role. The effect between the electron-donating groups and electron-withdrawing groups plays a supporting role. Then it adsorbs NP, DNP, and TNP according to the Langmuir isotherm model with a high q_e at 2.40 mmol/g, 2.66 mmol/g and 4.85 mmol/g, respectively. This work may suggest a new strategy for development of CO_2 capture materials and a functionalized material for treatment of NACs wastewater.

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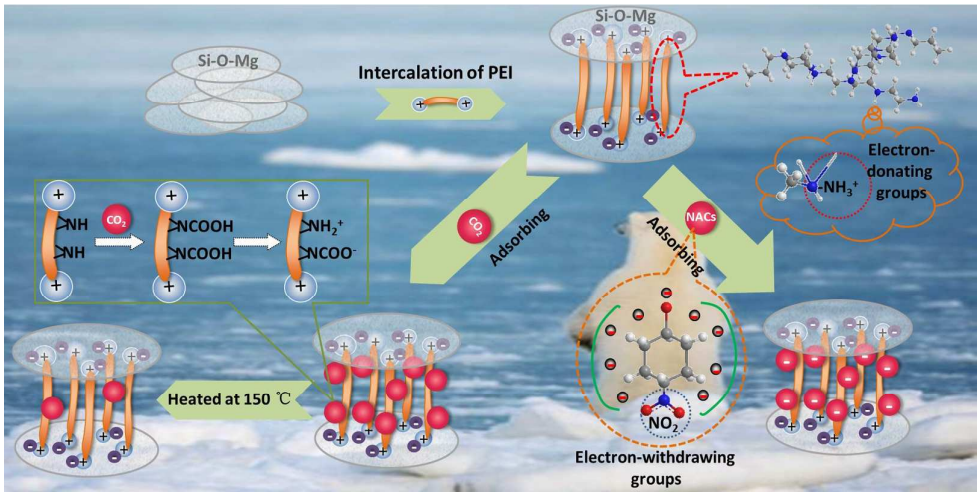
Electronic Supplementary Information (ESI)

PEI@Mg_2SiO_4: an efficient carbon dioxide and nitrophenol compounds adsorbing material

A table of contents entry



PEI@Mg_2SiO_4: an efficient carbon dioxide and nitrophenol compounds adsorbing material

Figures S1 – S3 and Table S1

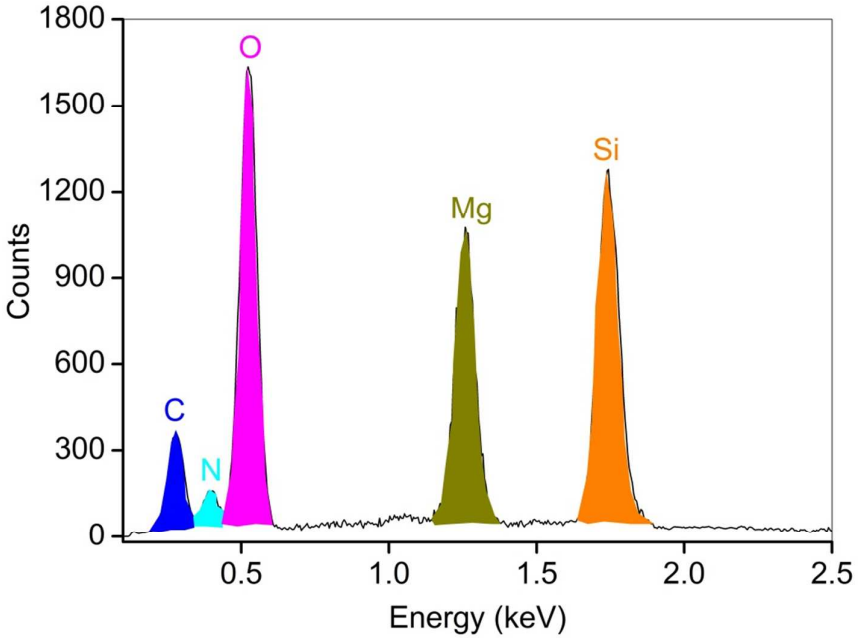


Fig. S1 EDX of the PEI@Mg_2SiO_4.

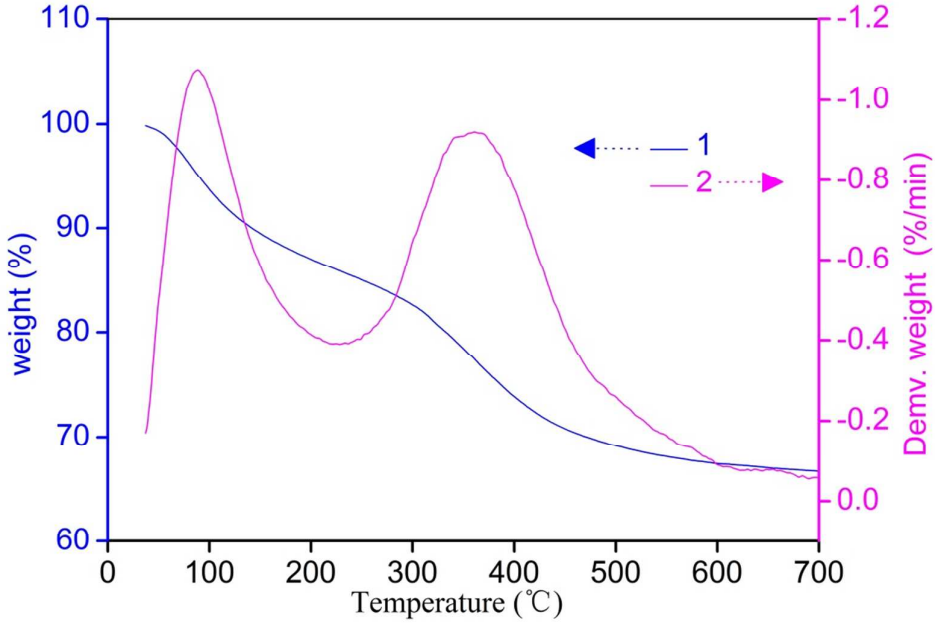


Fig. S2 TGA (1) and DTA (2) of the PEI@Mg_2SiO_4.

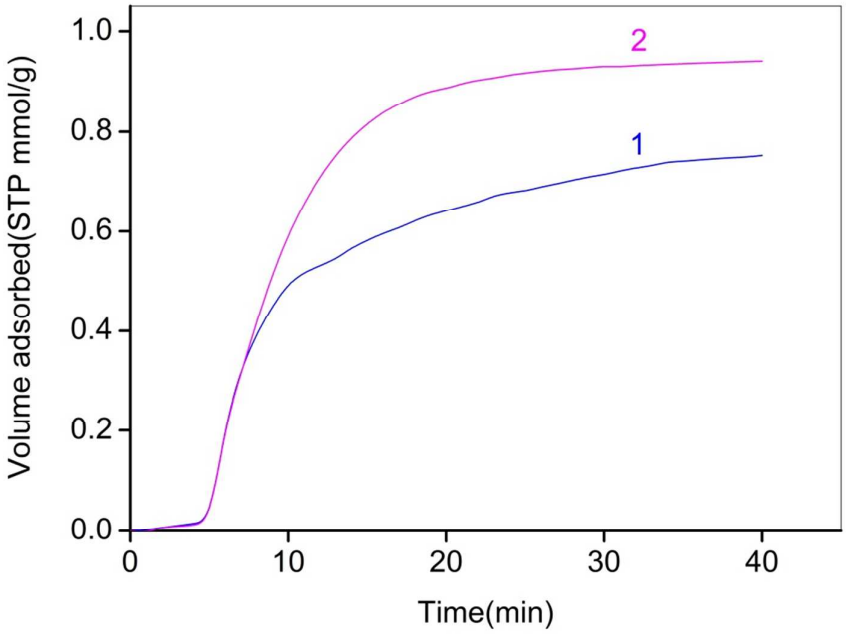


Fig. S3 Effect of time on the adsorption of CO_2 absorption for Mg_2SiO_4 (1) and the PEI@Mg_2SiO_4 (2) at 50 °C.

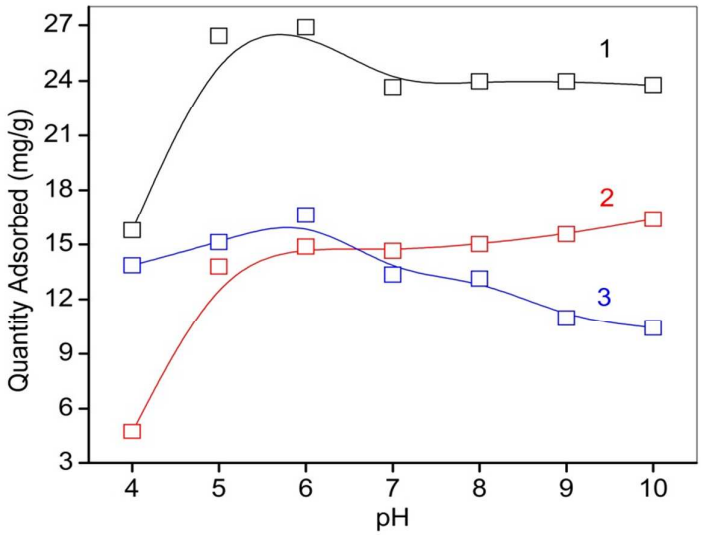


Fig. S4 The sorption curve of NACs (1-NP, 2-DNP and 3-TNP) to the PEI@Mg_2SiO_4 material at different pH.

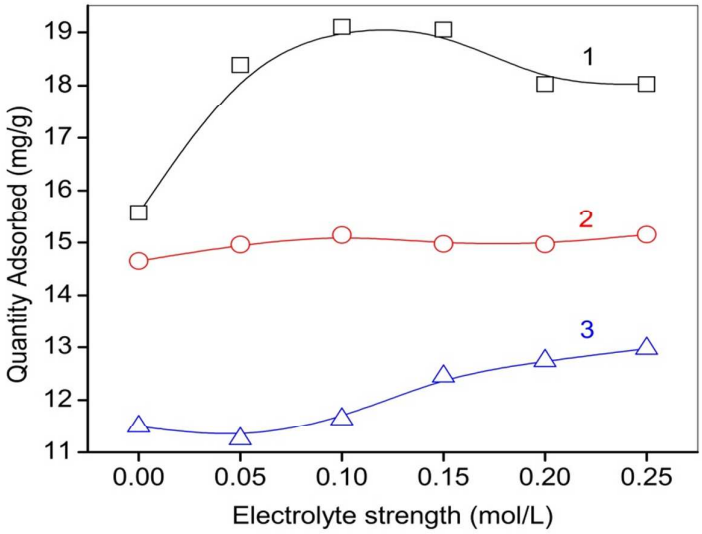


Fig. S5 Effect of ionic strength on the adsorption of NACs (1-NP, 2-DNP and 3-TNP) to the PEI@Mg_2SiO_4 material

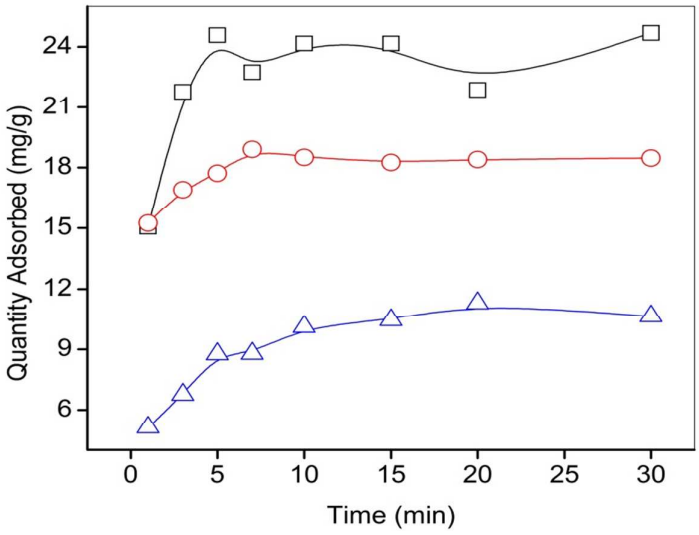


Fig. S6 The sorption curve of NACs (1-NP, 2-DNP and 3-TNP) to the PEI@Mg_2SiO_4 material at different times

Table. S1 Change of C and N contents in the PEI@Mg_2SiO_4

	C %	N %	H %
PEI@Mg_2SiO_4	7.078	3.811	4.200

Table. S2 Parameters of the DEM Kinetic Model obtained for CO_2 adsorption on the PEI@Mg_2SiO_4

Temperature (°C)	q_e (mg/g)	Fast adsorption		Slow adsorption		R^2
		D_1 (mg/g)	K_1 (min^{-1})	D_2 (mg/g)	K_2 (min^{-1})	
25	35.6	18.4	0.32	17.5	0.06	0.99
50	42.3	24.1	0.15	24.1	0.15	0.98
75	29.3	15.5	0.89	12.5	1.71	0.97
100	15.2	0.58	0.57	7.2	1.72	0.95