Smart adsorbents for CO₂ capture: Making strong adsorption sites respond to visible light

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ABSTRACT Due to the good controllability and high energy efficiency in adsorption processes, photoresponsive adsorbents are intriguing for CO₂ capture. Nevertheless, most reported photoresponsive adsorbents are designed based on weak adsorption sites, regulating CO₂ adsorption through structural change or steric hindrance. In addition, ultraviolet (UV) light is commonly involved in the regulation of adsorption capacity. Here we report for the first time the smart adsorbents for CO₂ capture, which makes strong adsorption sites respond to visible (Vis) light. The adsorbents were fabricated by introducing primary amine and Dispersed Red 1 (DR1, a kind of push-pull azobenzene that responds to Vis light rapidly) units to mesoporous silica, which act as strong adsorption sites and triggers, respectively. The primary amine sites make the adsorbents highly selective in the adsorption of CO₂ over CH₄. Without light irradiation, azobenzene is in the form of *trans* configuration, which leads to decreased electrostatic potential of primary amines and subsequently, exposure of active sites and liberal adsorption of CO₂. Upon Vis-light irradiation, *cis* isomers are formed, which results in increased electrostatic potential of primary amines and subsequently shelter of active sites. Even on such strong adsorption sites, the alteration of CO₂ adsorption capacity can reach 40% for the adsorbent with and without Vis-light irradiation. Moreover, the *trans/cis* isomerization of DR1 units can be triggered reversibly by Vis light. The present smart system endows adsorbents with selective adsorption capacity and avoids the employment of UV light, which is unlikely to be achieved by conventional photoresponsive adsorbents.

Keywords: CO₂ adsorption, strong adsorption sites, selective adsorption, push-pull azobenzene, visible light response

INTRODUCTION

Natural gas has attracted increasing attention as a cleaner energy source compared with other fossil fuels [1–5]. Methane (CH₄) is the active component of natural gas and carbon dioxide (CO₂) is a predominant impurity. The coexistence of CO₂ is almost unavoidable regardless of the geographical origin, which not only reduces the calorific value of natural gas but also leads to the corrosion of equipment [6–8]. To remove CO₂, amine scrubbing is currently employed in industry [9–11]. Albeit effective, this technique has some shortcomings like high energy consumption for regeneration and corrosiveness of aqueous amine solutions [12]. In recent years, adsorption using porous solid adsorbents such as zeolites [13], activated carbons [14], and metal-organic frameworks (MOFs) [15–18] is of great interest as an alternative for CO₂ capture. Currently, pressure and temperature swings are the two typical approaches used to vary the adsorption capacity, thus realizing adsorption/desorption cycles. It is known that pressure and temperature swings are the most energy-consuming sections in adsorption processes. Despite challenges, it is extremely desirable to develop an energy-efficient method to tailor the adsorption capacity of solid adsorbents.

Stimuli-responsive materials that can respond to temperature, redox potential, pH, or light have gained much attention in recent years [19–25]. Among different stimuli, light is conspicuous for its rapid and remote controllability with high precision [26–32]. Azobenzene is a typical photoresponsive group that can be introduced to porous materials without compromising the light-responsive characteristic [33]. This offers the possibility of regulating the adsorption capacity of porous materials

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through the isomerization of azobenzene groups induced by light irradiation, providing a potential energy-efficient alternative to pressure and temperature swings. One typical example was reported by Zhou's group [34], they functionalized the ligands with azobenzene groups and got PCN-123 with pending photoresponsive motifs. The regulation of CO₂ uptake was achieved by the positional change of photoresponsive motifs. Another case from Hill's group [35] reported the incorporation of azobenzene motifs into the framework of a Zn-based MOF. Upon light irradiation, structural variation of the MOF took place, which led to the change in CO₂ adsorption capacity. These pioneering studies show interesting results on the regulation of CO₂ adsorption capacity by light instead of conventional pressure and temperature swings. However, such adsorbents are fabricated based on weak adsorption sites, regulating CO₂ adsorption through structural change or steric hindrance. The adsorption isotherms of CO₂ are almost linear [34,35], making these adsorbents unsuitable for practical applications in which selective CO₂ capture is required. To date, the regulation of adsorption capacity of photoresponsive adsorbents with strong adsorption sites has remained a pronounced challenge. In addition, ultraviolet (UV) light is commonly involved in the regulation of adsorption capacity, since unfunctional azobenzenes are used. Typically, irradiation with UV and visible (Vis) light causes azobenzene groups to isomerize between *trans* and *cis* configurations reversibly. The report on adjustment of adsorption capacity by utilizing only Vis light is very scarce, if any.

In this paper, we report for the first time the smart adsorbents for CO₂ capture, making strong adsorption sites respond to Vis light. The adsorbents were fabricated by incorporating primary amine and Dispersed Red 1 (DR1, Fig. S1) units to mesoporous silica (MS), which act as strong adsorption sites and triggers, respectively (Scheme 1). It is noticeable that DR1 is a kind of push-pull azobenzene responsive to Vis light rapidly, which is different from unfunctional azobenzenes that undergo *trans/cis* isomerization upon UV-light irradiation. Upon Vis-light irradiation, *cis* DR1 isomers are formed, which results in increased electrostatic potential of primary amines and subsequently shelter of active sites. Once Vis light is removed, DR1 isomerizes to *trans* configuration, which leads to decreased electrostatic potential of primary amines and subsequently, exposure of active sites and liberal adsorption of CO₂. Even on such strong adsorption sites, the alteration of CO₂ adsorption capacity can reach 40% for the adsorbent with and without Vis-light irradiation. Furthermore, the primary amine sites make

Scheme 1 Vis-light-triggered CO₂ adsorption on smart adsorbents with strong adsorption sites *via* the interaction between primary amine and DR1 motifs. (a) Without Vis-light irradiation, photoresponsive motif is in *trans* configuration, which results in decreased electrostatic potential of primary amines and CO₂ molecules can be adsorbed liberally; (b) with Vis-light irradiation, photoresponsive motif is in *cis* configuration, which results in increased electrostatic potential of primary amines and active sites are sheltered.

the adsorbents highly selective in the adsorption of CO₂ over CH₄. We realize the regulation of CO₂ adsorption capacity on strong adsorption sites while avoiding the utilization of UV light, which is impossible for conventional photoresponsive adsorbents.

EXPERIMENTAL SECTION

Chemicals

DR1, triethylamine, cetyltrimethylammonium bromide (CTAB), and 3-(triethoxysilyl)propyl isocyanate (TPI) were purchased from Sigma-Aldrich. (3-Aminopropyl) triethoxysilane (APTES) and tetraethylorthosilicate (TEOS) were purchased from Aladdin. Hydrochloric acid (HCl, 37 wt%) and sodium hydroxide (NaOH) were purchased from Adamas. The above chemicals were used directly. Toluene, tetrahydrofuran (THF), ethanol, and *n*-hexane were purchased from Sinopharm and dehydrated before use. The deionized water used in the experiment was produced by an ultrapure water purification system.

Materials synthesis

The DR1-containing precursor used for grafting 2-[ethyl [4-[2-(4-nitrophenyl)diazanyl]phenyl]amino] ethylester (DR-TPI, Fig. S1) was prepared by silane-modification. Firstly, TPI (1.24 g, 5 mmol) and DR1 (0.78 g, 2.5 mmol) were dissolved in THF (15 mL), and two drops of triethylamine was added to the solution. The mixture was refluxed in N₂ atmosphere overnight. Finally, the obtained solid was washed with *n*-hexane and dried in va-

cuum. ^1H nuclear magnetic resonance (^1H NMR) of DR-TPI is shown in Fig. S2, and the result indicates that the DR1-containing precursor was successfully prepared.

The MS MCM-41 used as the support was prepared by the sol-gel method [36]. CTAB (0.5 g, 1.37 mmol) and NaOH (1.75 mL, 2 mol L $^{-1}$) were added to water (240 mL) with stirring, and the mixture was heated to 80°C followed by the addition of TEOS (2.5 mL, 11.5 mmol) within 5 min. After 2 h, the white colloidal suspension was separated and washed with water. For removing CTAB from the products, the obtained powders were dispersed in a mixed solution containing HCl (1 mL, 1 mol L $^{-1}$) and ethanol (80 mL), and refluxed overnight. The white solid was washed and dried for further use.

The smart adsorbents containing primary amine and DR1 units were prepared by grafting. DR-TPI (50, 100, or 150 mg), APTES (50 mg), and MCM-41 (0.25 g) were mixed in toluene (40 mL) under N $_2$ atmosphere, and then heated at 80°C with stirring for 12 h. After filtration and washing with ethanol three times, the obtained powders were denoted as AP $_m$ @MS, where A and P mean amines and photoresponsive motifs, respectively, and m varies from 1 to 3 corresponding to the different contents of photoresponsive motifs. The grafting densities of photoresponsive motifs and amines were calculated based on the results of elemental analysis, thermogravimetric (TG) analysis, and surface areas. The results show that the density of amines in each sample is 0.32 per nm 2 , while the densities of photoresponsive motifs in AP $_1$ @MS, AP $_2$ @MS, and AP $_3$ @MS are 0.14, 0.27, and 0.40 per nm 2 , respectively (Table 1). For reference, adsorbents functionalized with individual amines (A@MS) and photoresponsive motifs (P $_2$ @MS) were prepared as well (Table S1). The synthetic processes are similar to AP $_m$ @MS except that only one rather than both of APTES or DR-TPI was added.

Material characterizations

^1H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer in dimethyl sulfoxide. PerkinElmer Lambda 35 was used to record the UV-Vis spectra of the

samples in the range of 250–700 nm. A Japan Rigaku D/MAX- γ A diffractometer was employed to record the X-ray diffraction (XRD) patterns of different samples. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed on JEM-2010 UHR and Hitachi SU8010, respectively. Energy dispersive X-ray (EDX) analysis was also carried out during the TEM analysis. N $_2$ adsorption-desorption isotherms were recorded on an ASAP 2020 system at -196°C . Before each analysis, the sample was evacuated at 80°C for 12 h. The Brunauer-Emmet-Teller (BET) surface area (S_{BET}) was calculated based on the data in the relative pressure ranging from 0.04 to 0.20. The total pore volume (V_{p}) was calculated from the adsorption capacity at a relative pressure of 0.99. The pore size (D_{p}) distribution was calculated by using the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared (FTIR) spectra were measured by using a Nicolet Nexus 470 spectrometer. The Vario Micro Cube elemental analyzer was chosen to perform elemental analysis (C, H and N). TG analysis was carried out on a thermobalance (STA-499C, NETZSCH), where the heating rate was 20°C min $^{-1}$ with the temperature ranging from 25 to 1000°C under an air atmosphere.

Adsorption experiments

An ASAP 2020 analyzer was used to measure the adsorption isotherms of CO $_2$ and CH $_4$. For testing the adsorption performance of the samples with photoresponsive motifs in *cis* configuration, Vis light was used to irradiate the sample tube during the tests. Vis light was generated by a xenon lamp (CEL-HXUV300). For testing the adsorption performance of the samples with photoresponsive motifs in *trans* configuration, Vis light was removed and the sample tube was covered by silver paper to make sure that adsorption was conducted in dark. To calculate the isosteric heat (Q_{st}) of CO $_2$, the adsorption data measured at 15 and 25°C were fitted by the Virial equation (Equation (1)), where P is the pressure, T is the temperature in Kelvin, N is the amount adsorbed, a_i and b_i are temperature-independent em-

Table 1 Physicochemical parameters and elemental compositions of different samples

Sample	S_{BET} (m 2 g $^{-1}$)	V_{p} (cm 3 g $^{-1}$)	D_{p} (nm)	Elemental content (wt%)			Density of amine (A) (number per nm 2)	Density of photo-responsive motif (P) (number per nm 2)
				C	N	H		
MCM-41	1066	1.04	2.86	–	–	–	–	–
AP $_1$ @MS	685	0.56	2.38	10.26	3.26	2.49	0.33	0.14
AP $_2$ @MS	547	0.41	2.13	14.42	4.47	2.50	0.32	0.27
AP $_3$ @MS	495	0.30	1.94	16.45	5.10	2.67	0.32	0.40

pirical parameters, and m and n are the number of terms. Q_{st} was estimated by Equation (2), where R refers to the universal gas constant [37–39].

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i, \quad (1)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i. \quad (2)$$

The selectivity for CO_2 over CH_4 is defined as $S = (x_1/y_1)/(x_2/y_2)$, where x and y refer to the composition of the adsorbed and bulk phases, respectively. The ideal adsorption solution theory (IAST) was applied to analyze the adsorption of binary gas mixture in porous materials [40–42], and the dual-site Langmuir model was selected to fit the adsorption isotherms.

RESULTS AND DISCUSSION

Textural and surface characteristics

XRD, SEM, and TEM were first employed to determine

the structural properties of different samples. In low-angle XRD patterns (Fig. 1a), the support MCM-41 presents one strong peak and two weak peaks, which can be indexed to (100), (110), and (200) reflections corresponding to a hexagonal pore structure ($p6mm$). During synthesis, photoresponsive molecules and amine were introduced to the parent material MCM-41 to obtain the photoresponsive adsorbents AP@MS. Thus, MCM-41 with a pore structure analogous to AP_m@MS was selected as the control sample. After introducing primary amine and DR1 units, AP_m@MS shows similar diffraction peaks to MCM-41, suggesting that the pore structure is preserved despite the presence of functional groups. In wide-angle XRD patterns (Fig. S3), the unique broad diffraction peak at around 23° for different samples is associated with the amorphous silica walls. This also suggests that the primary amine and DR1 units are lack of long-range order in the pores. Both SEM (Fig. S4) and TEM (Fig. 1b, c) images show that the samples possess microsphere morphology with a diameter of about 120 nm. The uniform and straight channels can be observed from the

Figure 1 (a) Low-angle XRD patterns of different samples. TEM images of (b) MCM-41 and (c) AP₂@MS as well as (d) EDX-mapping images of AP₂@MS. (e) IR spectra of different samples.

TEM images, which are beneficial to mass transfer in the process of adsorption.

The surface chemistry of different samples was initially characterized by IR. As shown in Fig. 1e, the characteristic bands at 1560 cm^{-1} ($-\text{NH}_2$) and 1520 cm^{-1} ($-\text{CONH}-$) suggest the incorporation of primary amines and photoresponsive motifs, respectively [43,44]. In addition, the relative peak intensity of the $-\text{NH}_2$ band keeps constant and that of the $-\text{CONH}-$ band increases for the samples $\text{AP}_1\text{@MS}$ to $\text{AP}_2\text{@MS}$ and $\text{AP}_3\text{@MS}$. This is in line with the constant content of primary amines and gradually increased content of photoresponsive motifs (Table 1). The EDX spectrum of $\text{AP}_2\text{@MS}$ suggests the existence of C, N, O, and Si (Fig. S5), and these elements are uniformly distributed in the samples as can be seen from the element mapping results (Fig. 1d). All nitrogen adsorption-desorption isotherms (Fig. 2a) are of type-IV, suggesting the presence of mesoporous structure for the samples before and after functionalization. Fig. 2b gives the pore size distributions of the support and $\text{AP}_m\text{@MS}$. The introduction of primary amine and DR1 units leads to the decline of pore size, suggesting that functional groups are introduced to the pores rather than the external surface. Table 1 gives the detailed textual parameters calculated from isotherms. Although the surface areas of $\text{AP}_m\text{@MS}$ are not as high as that of the MS support due to the incorporation of organic units, their pore channels are still highly open. TG analysis of different samples is shown in Fig. S6. All samples have a slight loss before 125°C , corresponding to the removal of water. The severe weight loss between 300 and 700°C corresponds to the decomposition of primary amine and DR1 units. Such a weight loss increases with the increasing loading of functional groups.

Due to the combination of an electron-withdrawing group with an electron-donating group, DR1 is a kind of push-pull azobenzene. This results in permanent dipole moment and promotes the responsive rate from hours to milliseconds [45]. Vis-light irradiation causes the fast isomerization of *trans* DR1 to *cis* one; once Vis light is removed, *cis* DR1 will be transformed to *trans* isomers rapidly. Therefore, it is difficult to monitor the *cis* isomers due to the fact that the isomerization rate of push-pull azobenzene exceeds the acquisition speed of the spectrophotometer [46]. This is confirmed by the UV-Vis spectra of both the DR1-containing precursor and DR1-functionalized MS (Figs S6 and S7). The MS support does not show any characteristic bands in the wavelength of $350\text{--}600\text{ nm}$. For the DR1-containing samples, only *trans* isomers are detected regardless of the light irradiation time. Although *cis* DR1 cannot be detected in UV-Vis spectra, the adsorbents functionalized with DR1 show interesting photoresponsive adsorption behavior since adsorption is conducted *in situ* as shown below.

Photoresponsive adsorption behavior

Adsorption experiments were first performed on the support MCM-41, A@MS that functionalized singly with primary amines, and $\text{P}_2\text{@MS}$ that functionalized singly with photoresponsive DR1 motifs (the characterization data of A@MS and $\text{P}_2\text{@MS}$ are shown in Figs S8–S13). As there is no strong adsorption site in MCM-41, the adsorption isotherm toward CO_2 has a linear shape (Fig. S14). In addition, no obvious change (less than 1%) in adsorption capacity is observed for MCM-41 before and after Vis-light irradiation. In the case of $\text{P}_2\text{@MS}$, the shape of isotherm is still linear (Fig. S15); however, A@MS shows an isotherm shape similar to type I, in-

Figure 2 (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of MCM-41, $\text{AP}_1\text{@MS}$, $\text{AP}_2\text{@MS}$, and $\text{AP}_3\text{@MS}$.

dicating that strong adsorption sites for CO₂ have been introduced (Fig. S16). A@MS and P₂@MS also display negligible changes (less than 1%) in adsorption capacity before and after Vis-light irradiation due to the absence of photoresponsive motifs or specific sites for CO₂ adsorption. Interestingly, adsorbents incorporated with both primary amines and photoresponsive DR1 motifs exhibit completely different adsorption performances upon Vis-light irradiation. For the typical sample AP₂@MS, it can adsorb 32.1 cm³ g⁻¹ of CO₂ at 25°C, while the capacity decreases to 19.1 cm³ g⁻¹ after Vis-light irradiation (Fig. 3a). This means that the change in CO₂ adsorption capacity of AP₂@MS reaches 40% upon Vis-light irradiation. The adsorption capacity for CH₄ was also evaluated. Because primary amines are specific sites for CO₂, the adsorption capacity of AP₂@MS for CH₄ is quite low. Moreover, the adsorption swing of CH₄ is trivial before and after Vis-light irradiation, indicating that the isomerization of DR1 units has a negligible effect on CH₄ adsorption.

The effect of the ratio of photoresponsive motifs to primary amines on CO₂ adsorption was studied (Fig. 3b and Figs S17–S19). It is found that the change in adsorption capacity reaches a maximum when the densities of photo-responsive motifs and amines are the closest, which are 0.32 and 0.27 nm⁻¹, respectively (i.e., AP₂@MS

as shown in Table 1). The reversibility of the obtained adsorbents for CO₂ adsorption was also examined. In each cycle, the adsorption was first conducted in dark to make sure that DR1 is in the form of *trans* isomers. After saturation with CO₂, the adsorbent was regenerated and reused for adsorption upon Vis-light irradiation to make sure that DR1 is in the form of *cis* isomer. The results show that there is no obvious decrease in adsorption capacity after five cycles, and the change between *trans* and *cis* DR1 is totally reversible (Fig. 3c).

The IAST was used to analyze the selectivity (Fig. 3d). The CO₂/CH₄ selectivity is 315 at 25°C on AP₂@MS without Vis-light irradiation, which is significantly higher than that with Vis-light irradiation (75). This reveals that the selectivity of smart adsorbents can be effectively modulated by light irradiation. To investigate the affinity of AP₂@MS for CO₂, the Q_{st} was calculated by using the Virial method (Fig. 3e). The results show that Vis-light irradiation causes a great difference in Q_{st} of CO₂ adsorption. The Q_{st} of adsorption on AP₂@MS is 52.8 kJ mol⁻¹ without Vis-light irradiation, and the value decreases to 43.2 kJ mol⁻¹ on the same adsorbent irradiated with Vis light. This suggests that the configuration of photoresponsive motifs influences the interaction between CO₂ molecules and active sites greatly.

The abovementioned results demonstrate that the ad-

Figure 3 (a) Adsorption isotherms of CO₂ and CH₄ on AP₂@MS possessing DR1 in *trans* and *cis* configurations at 25°C. (b) Change amount of CO₂ adsorption on different samples before and after irradiation with Vis light. (c) Five adsorption cycles of CO₂ on AP₂@MS without and with Vis-light irradiation. (d) IAST selectivity of CO₂/CH₄. (e) Q_{st} of adsorption of CO₂ on AP₂@MS possessing DR1 in *trans* and *cis* configurations.

sorption capacity on CO₂ is adjustable on strong adsorption sites by using Vis light. It can be realized on the smart adsorbents functionalized with primary amine and DR1 units, while cannot be achieved by the adsorbents modified singly with primary amine or DR1 units. The specific interaction between photoresponsive motifs and amines is confirmed by the fact that a maximum capacity change is observed when the densities of photoresponsive motifs and amines are comparable. It is observed that CH₄ is rarely adsorbed because the incorporated active sites are specific for CO₂, which results in a high selectivity of CO₂ over CH₄. Moreover, the change in adsorption capacity caused by light irradiation is reversible.

Proposed mechanism for tunable adsorption behavior

The photoresponsive motif used in the present study is DR1, and the isomerization of DR1 can be realized by applying only Vis light. This is different from the photoresponsive motifs used in reported adsorbents in which unfunctional azobenzenes are employed and UV light has to be involved [47]. DR1 is a donor-receptor substituted push-pull azobenzene with strong charge transfer characteristics in the $\pi \rightarrow \pi^*$ electronic transition. The $\pi \rightarrow \pi^*$ absorption band locates in the Vis spectrum and overlaps with the commonly much weaker $n \rightarrow \pi^*$ transition. Normally, the DR1 motifs exist in the form of stable *trans* isomers, which can be converted to *cis* isomers quickly upon Vis-light irradiation. The removal of Vis light leads to rapid recovery of *trans* configuration (within milliseconds). It is thus difficult to detect such a change by the UV-Vis spectrophotometer because the speed of isomerization is faster than that of data acquisition for the instrument [46].

The mechanism on the photoresponsive regulation of

adsorption capacity in the present system was then examined. The steric effect caused by isomerization of photoresponsive motifs is first taken into consideration [35]. If steric hindrance plays a critical role, the swing of adsorption capacity should be observed on P₂@MS. However, Vis-light irradiation causes little change in the adsorption capacity of P₂@MS, indicating that the steric effect derived from the isomerization of photoresponsive motifs does not affect CO₂ adsorption. As for the adsorbents containing photoresponsive motifs and primary amines, CO₂ can be freely captured by the exposed active sites when photoresponsive motifs are in *trans* configuration. When the *trans* isomers are converted to *cis* ones, it seems that the steric hindrance should be enhanced due to the possible shelter of active sites. However, CO₂ molecule has a small kinetic diameter of 0.33 nm, and the amount of active sites that can be blocked by azobenzene molecules should be scarce, if any.

From the analyses above, it is suggested that some unusual interactions may exist between primary amines and photoresponsive motifs. Density function theory (DFT) was employed to reveal the possible mechanism. Fig. 4 shows the simulated geometry and surface electrostatic potential of primary amine and photoresponsive motif. The free energies of the calculated *trans* and *cis* azobenzene-amines are -9.1 and -10.4 kcal mol⁻¹, respectively, indicating that both *trans* and *cis* azobenzene can interact with amine *via* van der Waals force. Generally, the surface electrostatic potentials are able to reflect the activity of adsorption sites, and a lower surface electrostatic potential corresponds to a stronger adsorption site for CO₂. When the photoresponsive motif is in the state of *trans* configuration, the surface electrostatic potential of primary amine is -0.039 eV (Fig. 4b). In the

Figure 4 The simulated geometry and surface electrostatic potential of (a) primary amine, (b) *trans* photoresponsive motif interacting with primary amine and (c) *cis* photoresponsive motif interacting with primary amine.

case of *cis* configuration, the photoresponsive motif interacts strongly with primary amine and the electrostatic potential increases to -0.026 eV (Fig. 4c). As a comparison, A@MS shows negligible difference in capacity before and after light irradiation, indicating that the electrostatic potential of primary amine cannot be affected by Vis-light irradiation without photoresponsive motifs. Hence, in AP_m@MS the adsorption of CO₂ on the primary amine site is greatly influenced, and the isomerization from *trans* to *cis* configuration weakens the adsorption capacity of primary amine obviously. In a word, the regulation of CO₂ adsorption on the AP_m@MS adsorbents is caused by the interaction between primary amine and DR1 units. With Vis-light irradiation, the *trans* DR1 turns to *cis* one and the interaction mode of amine with azobenzene alters. This leads to the change of adsorption capacity and can be revealed by the electrostatic potential of primary amine quantitatively using DFT calculations. The steric effect of photoresponsive motifs should have a tiny (if any) effect on the regulation of CO₂ adsorption.

CONCLUSION

Smart adsorbents for controllable CO₂ capture have been successfully constructed by incorporating primary amine and push-pull azobenzene units into the MS, which makes strong adsorption sites respond to Vis light for the first time. DFT calculations show that the interactions between primary amines and photoresponsive motifs are tunable during azobenzene isomerization, which can be reflected by the change of surface electrostatic potential of primary amines. Consequently, the adsorption capacity of smart adsorbents on CO₂ can be tailored conveniently. The experimental results show that the optimal sample can be obtained when the grafting densities of primary amine and DR1 units are the closest. Since primary amines are strong adsorption sites specific for CO₂, our adsorbents exhibit high selectivity of CO₂ over CH₄. Moreover, the selectivity is adjustable upon Vis-light irradiation. Because DR1 is a kind of push-pull azobenzene, the regulation of adsorption capacity can be realized by using only Vis light, avoiding the employment of UV light that is required for reported photoresponsive adsorbents. The present investigation may open up an avenue for the development of smart adsorbents towards practical applications by using the special interactions between stimuli motifs and target-specific adsorption sites. Recently, various stimuli-responsive materials have been reported, and it is possible to utilize energy of different forms such as heat and magnet. In our next work,

thermo-responsive polymers and magnetic nanoparticles are going to be introduced into adsorbents, making adsorbents respond to temperature and magnet for efficient adsorption processes.

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Supplementary information Supporting data are available in the online version of the paper.

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用于CO₂捕获的智能吸附剂: 促使强吸附活性位响应于可见光

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摘要 基于光响应吸附剂的吸附过程可控性好、能源效率高, 其在CO₂捕获中的应用受到关注。然而, 大多数报道的光响应吸附剂是基于弱吸附位点设计的, 通过其结构或位阻的变化控制CO₂吸附。此外, 还需要用到紫外光来调节吸附能力。本文首次报道了用于CO₂捕获的智能吸附剂, 促使强吸附活性位响应于可见光。吸附剂的制备通过将伯胺和分散红(DR1, 一种响应于可见光的推-拉型偶氮苯)引入介孔氧化硅实现。伯胺作为强吸附位点促使吸附剂对CO₂的选择性高于CH₄, 而DR1则作为控制开关。光照前偶氮苯处于反式构型, 降低了伯胺的电势, 因而实现了吸附位点的暴露和CO₂的自由吸附。偶氮苯在可见光的照射下转变为顺式结构, 伯胺的电势提高, 因而活性位点被遮蔽。即使是强吸附位点, 吸附剂在光照前后对CO₂的吸附量变化也可以达到40%。此外, DR1的反式/顺式异构可以通过可见光的控制实现可逆转变。本文报道的智能系统赋予了吸附剂选择性且避免使用紫外光, 这对于传统吸附剂而言是难以实现的。