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Realizing both selective adsorption and efficient regeneration using adsorbents with photo-regulated molecular gates[†]

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A new generation of smart adsorbents was designed by grafting photo-responsive molecules onto the pore entrances of mesoporous silica. These molecules act as the gates of the mesopores, which are reversibly closed/opened upon light irradiation. Our smart adsorbents thus realize both selective adsorption and efficient desorption, which is highly expected for adsorption but impossible for traditional adsorbents with fixed pore entrances.

Separation is one of the most important unit operations in the chemical industry. Being the opposite process of mixing, which is favored by the second law of thermodynamics, separation is normally not a spontaneous procedure. Consequently, conventional separation techniques are often somewhat expensive and energy-intensive. At present, the dominating separation method is distillation, which consumes more than 50% of the total production energy.¹ Adsorption is well-positioned to play a key role in the development of many future energy and environmental technologies, because of its low equipment investment, easy operation, and high energy efficiency.² The design and fabrication of efficient adsorbents is crucial for adsorption processes.3 Micropores and mesopores are two predominant pore systems for traditional adsorbents.⁴ Microporous materials with pore diameters of <2 nm (e.g. zeolites) display excellent performance in selective adsorption with a high steric effect (Fig. 1A).⁵ In this case, only small and properly shaped molecules can diffuse into the channels, whereas other molecules are totally excluded. However, the regeneration process of microporous adsorbents is relatively slow and difficult.⁶ In the case of mesoporous materials (with pore diameters of 2-50 nm), their large pore entrances allow efficient desorption but at the expense of adsorption selectivity (Fig. 1B). From the viewpoint of practical applications, an ideal adsorbent is expected to possess small



Fig. 1 (A) Scheme of conventional microporous adsorbents with high adsorption selectivity but low desorption efficiency, (B) scheme of conventional mesoporous adsorbents with high desorption efficiency but low adsorption selectivity, (C) smart adsorbents with photo-regulated molecular gates for selective adsorption and efficient regeneration, and (D) the schematic structure of molecular gates when closed and open caused by photo-dimerization (>310 nm light irradiation) and cleavage (254 nm light irradiation) of a coumarin derivative.

pore entrances to achieve selectivity in the adsorption process, while show enlarged pore entrances to facilitate desorption in the regeneration process. Unfortunately, traditional adsorbents with fixed pore entrances are unlikely to realize both of the requirements. Despite great challenges, it is extremely desirable to develop a new type of adsorbent possessing pore entrances that are adjustable during adsorption/desorption.

Inspired by sophisticated biological systems, the implementation of switchable molecules in artificial systems would lead to a variety of advanced stimuli-responsive properties.⁷ The regulation of the behavior of switchable molecules upon external stimuli

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(such as light, temperature, and pH) has attracted great attention, not only in relation to biological supramolecular machines but also for the development of materials science.⁸ In comparison with other types of external stimuli, light has several additional advantages.⁹ It can be used to control the behavior of switchable molecules remotely, and can be delivered to a precise location, and applied/removed instantaneously. Consequently, light has been investigated extensively as a type of external stimulus, which results in a mass of photo-controlled materials for various applications.¹⁰

Here we report the fabrication of a new generation of adsorbents by grafting a coumarin derivative 7-[(3-triethoxysilyl)propoxy]coumarin (TPC) onto the pore entrances of mesoporous silica. The TPC molecules act as photo-regulated molecular gates for the mesopores, which are reversibly switched on and off upon UV irradiation (Fig. 1C). Upon irradiation using light with wavelengths >310 nm, intermolecular dimerization takes place and produces cyclobutane coumarin dimers in anti-head-to-head configuration (Fig. 1D),¹¹ which obstructs part of the pore entrances. The sizes of the pore entrances are thus reduced, through which the adsorbates with smaller diameter can easily pass but the larger ones are blocked, achieving the selective adsorption of two molecules with different diameters. Further irradiation with 254 nm UV light causes photo-cleavage of dicoumarins, which makes the molecular gates open, and thus the desorption of adsorbates is facilitated. Accordingly, the smart adsorbent exhibits the ability to undergo both selective adsorption and efficient desorption, which is highly expected for adsorptive separation but impossible to realize using traditional adsorbents with fixed pore entrances.

The gate molecule TPC was first synthesized (Fig. S1, ESI[†]) and characterized using ¹H nuclear magnetic resonance (NMR) spectra (Fig. S2 and S3, ESI[†]). The molecular length of TPC, attached to silanol groups on mesoporous silica MCM-41 is estimated to be 1.30 nm. The photo-dimerization yields cyclobutane coumarin dimers in an anti head-to-head configuration with a length comparable to the pore size of MCM-41 (2.67 nm). To graft as many coumarin molecules as possible onto the pore entrances, two factors were considered. On the one hand, as-prepared mesoporous silica (whose pore channels are occluded with the template) was used for the grafting of coumarin. On the other hand, a short grafting time (15 min) was adopted to hinder the diffusion of coumarin molecules into the pore channels and the elimination of the template in the reaction solvent. Both considerations can ensure that the coumarin molecules attach preferentially to the pore entrances rather than the inside walls (Fig. S4, ESI[†]).¹² Then an acidic alcohol solution was used to extract the template in the pore channels. The resultant materials were denoted by CM-1, CM-2, CM-3, and CM-4, representing the grafted amounts of 0.3, 1.0, 2.1, and 5.6 wt%, respectively (Table S1, ESI[†]). To confirm the point above, template-free MCM-41 was employed for grafting. The amount of coumarin is identical to the sample CM-2, and the obtained reference sample is denoted by CM'-2.

Structural characterization of the samples was performed using various techniques. In the low-angle X-ray diffraction



Fig. 2 (A) Low-angle XRD patterns, (B) IR spectra, (C) N₂ adsorption–desorption isotherms, and (D) pore size distributions of MCM-41 before and after introduction of the molecular gates.

(XRD) patterns (Fig. 2A), all of the samples show an intense diffraction line accompanied by two weak ones, which can be indexed as the (100), (110), and (200) reflections corresponding to the 2D hexagonal pore regularity of the *p6mm* space group.¹³ This indicates that the ordered mesostructure is well preserved after organic functionalization and template removal. The wide-angle XRD patterns of MCM-41 before and after introduction of the molecular gates present a single broad diffraction peak centered at 23° attributed to amorphous silica walls (Fig. S5, ESI[†]). No new diffraction peaks emerge after the introduction of TPC, suggesting the lack of long-range order in the arrangement of coumarin molecules. All samples exhibit an N₂ adsorption-desorption isotherm of type IV and a narrow pore size distribution (Fig. 2C and D), indicating that the cylindrical mesopores of MCM-41 are well maintained. Moreover, the samples before and after irradiation with UV light show identical adsorption behavior for N2 (Fig. S6, ESI⁺), suggesting that light irradiation does not damage the mesostructure and that N2 adsorption cannot probe the change of the pore entrances. Transmission electron microscopy (TEM) is another useful technique to characterize the long-range channel ordering of mesoporous materials. The images show that the periodic ordering of the mesostructure is well maintained (Fig. S7, ESI[†]). On the basis of the aforementioned results, it is clear that the obtained adsorbents show an ordered mesostructure that is comparable to pristine mesoporous silica.

The successful introduction of the coumarin substituents into mesoporous silica was demonstrated using different characterization techniques. In the infrared (IR) spectra (Fig. 2B), the band at 1700 cm⁻¹ corresponds to the stretching vibration of carbonyl groups, and the bands at 1557 and 1508 cm⁻¹ derive from the ring C—C vibration of the conjugated coumarin ring.¹⁴ These results indicate the successful grafting of the coumarin substituents onto MCM-41. With increasing amount of coumarin substituent (from CM-1 to CM-4), the characteristic



Fig. 3 (A) UV-vis spectra and (B) fluorescence emission spectra of the smart adsorbent CM-2 with different irradiation times. Insets in (A) are typical photographs for CM-2 before and after irradiation.

absorption bands become stronger, which is in line with the TG analysis (Fig. S8, ESI[†]) and UV-vis spectra (Fig. S9, ESI[†]). In addition, no peaks related to the template cetyltrimethylammonium bromide (CTAB) are observed, suggesting the efficient removal of the template *via* extraction (Fig. S10, ESI[†]).¹⁵ On the basis of the above-mentioned results, it is obvious that the gate molecules (TPC) are successfully introduced to the entrances of MCM-41.

Photo-dimerization of coumarin-modified MCM-41 was first examined using UV-vis spectroscopy. Coumarin and its derivatives show two characteristic absorption bands in their UV-vis spectra (Fig. 3A). Between 310 and 340 nm, an n $\rightarrow \pi^*$ like transition is observed, related to the carbonyl function. At higher energies there is a $\pi \to \pi^*$ transition between 250 and 300 nm corresponding to the conjugated π system.¹⁶ UV light irradiation (>310 nm) results in a decrease in the absorption between 310 and 340 nm as well as an increase in the absorption between 250 and 300 nm. This is due to the formation of a cyclobutane ring via the dimerization of the coumarin monomers, and the length of the conjugated π system is reduced. After irradiation for 240 min, the absorption between 310 and 340 nm almost disappears, while the absorption between 250 and 300 nm becomes quite sharp. The UV-vis spectra (Fig. S11, ESI[†]) show that in the case of CM-2, the absorption at 320 nm almost disappeared after UV irradiation, indicating the efficient dimerization of coumarin. However, the decrease in absorption at 320 nm is much smaller for CM'-2 under the same conditions. It is known that for the photo-dimerization of coumarin, two molecules must be located closely enough to combine their coumarin parts.¹² By use of the short-time grafting method with template occluded MCM-41, the coumarin molecules are likely to be densely grafted on the pore entrances, which enables efficient photo-dimerization. On the contrary, in the case of CM'-2, the relatively dispersed arrangement of the coumarin molecules on the pore channels make the photo-dimerization quite difficult, which is responsible for the small decrease in absorption at 320 nm. In addition to the UV-vis spectra, fluorescence emission spectra were also employed to monitor the photo-dimerization of the coumarin-modified samples. Coumarin derivatives with fluorophores (e.g. benzene ring, C=C, C=O, and lactone structure) have strong fluorescence. Upon excitation at 330 nm, the fluorescence emission spectra of coumarin monomers exhibit strong fluorescence emission at 388 nm (Fig. 3B).¹⁷ Upon irradiation of UV light (>310 nm), the formation of coumarin dimers led to a decrease in fluorophore C=C, then the fluorescence intensity weakened gradually. In addition, the color of the sample changed from white to light yellow due to the dimerization of the coumarin monomers (Fig. 3A, inset). These results are consistent with the UV-vis spectra, thus confirming that the photo-responsive property of the coumarin molecules is well retained even after immobilization on mesoporous silica. Because the coumarin molecules are located on the pore entrances, they might act as molecular gates and might be switched on and off *via* light irradiation. The photo-responsive property endows the adsorbents with interesting adsorption performances as shown below.

Two dyes with different diameters (Fig. S12, ESI⁺), namely methylene blue (MB, 1.36 nm) and Coomassie brilliant blue (CBB, 1.91 nm), were utilized to probe the adsorption performance. The adsorption behavior of the support MCM-41 was first examined. The adsorption amount of the small molecule MB or the large molecule CBB does not change before/after UV irradiation (Fig. S13A and S14A, ESI[†]). In term of the equilibrium adsorption capacity of MCM-41, the selectivity of MB (small molecule) over CBB (large molecule) is calculated to be 2.1. Unlike pristine MCM-41, the coumarin-containing samples (CM-1, CM-2, CM-3, and CM-4) exhibit interesting adsorption behavior upon light irradiation. Taking CM-2 as an example, the adsorption amount of the small molecule MB is not much affected upon irradiation with UV light (Fig. 4A). However, after UV irradiation, the adsorption amount of the large molecule CBB presents a sharp decline of 75.9% (from 10.1 to 2.4 mg g^{-1} , Fig. 4B). A great difference in color is also observable for the solutions after adsorption by the adsorbent before and after irradiation (Fig. 4B, inset). This results in the high selectivity of



Fig. 4 Dynamic adsorption curves of (A) MB and (B) CBB on the smart adsorbent CM-2 before and after irradiation. (C) Change in the adsorption amount of the different adsorbents on MB and CBB. (D) Desorption curves of CBB on the smart adsorbent CM-2 before and after irradiation. Insets in (B) are the photographs for the initial CBB solution and the solution after adsorption by CM-2 with or without irradiation.

MB over CBB on CM-2 after irradiation (11.9), which is much higher than that before irradiation (2.2). The effect of the TPC content on the adsorption performance was also explored (as shown in Fig. S13 and S14, ESI†). The adsorbent CM-2 shows the largest difference in the adsorption amount of CBB (Fig. 4C). Further increasing the content of TPC, the change amount of CBB can hardly increase after photo-irradiation. In this regard, it is possible that excess coumarin monomers are randomly grafted onto the pore entrances or the outer surface of mesoporous silica. Photo-dimerization of these monomers might not affect the size of the pore entrances. Hence, the suitable content of coumarin for photo-regulated selective adsorption is about 1.0 wt% (*i.e.* the sample CM-2).

After saturation, desorption of the dye molecule CBB from the smart adsorbent CM-2 was performed (Fig. 4D). When the molecular gates are opened, 100% of the CBB molecules are desorbed, which is much superior to that desorbed from the sample with closed molecular gates (18%). In addition to the large molecule, desorption of the small molecule MB from the adsorbent was investigated (Fig. S15, ESI[†]). When the molecular gates were opened, desorption was facilitated as well. Although the difference in small molecule desorption for the adsorbent with open and closed gates is not as big as that for the large molecule, the effect of the gates on desorption is obvious. The repetition of adsorption–desorption experiments *via* light irradiation was examined (Fig. S16, ESI[†]). No obvious loss in activity is detected after five cycles, which suggests the excellent recyclability of the present adsorbents.

On the basis of the results above, it is apparent that photoregulated molecular gates endow adsorbents with a fascinating adsorption performance. Smart adsorbents can achieve both selective adsorption and efficient desorption. This unusual behavior is caused by the photo-regulated molecular gates, and thus unlikely to be realized by traditional adsorbents with fixed pore entrances. After being triggered by UV light, the molecular gates of the pore entrances are closed and the sizes of the pore entrances are effectively reduced. As a result, the adsorbate molecules with a smaller diameter can enter the pores, while the larger ones are hindered, realizing selective adsorption successfully. In contrast, when the molecular gates are opened without irradiation, efficient desorption can be realized.

In conclusion, by grafting TPC onto the entrances of a mesoporous support, smart adsorbents with photo-regulated molecular gates are successfully fabricated. Through photostimulated intermolecular dimerization of coumarin monomers, the molecular gates are reversibly closed/opened according to the irradiation conditions. The ability of both selective adsorption and efficient desorption makes the adsorbents highly promising in adsorptive separation. Our concept breaks the tradition that adsorbents always possess fixed pore entrances, resulting in the development of a new generation of adsorbents with a smart characteristic. The present strategy may open up a way for the design and fabrication of smart adsorbents by using diverse stimuli-responsive groups (*e.g.* thermo, magnet, and pH) as molecular gates, aiming to develop adsorptive separation processes with high efficiency and low energy consumption.

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