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Introduction

Ammonia (NH_3) is indispensable in our lives today for producing artificial fertilizers and several military and commercial products, including explosives, refrigerants, pharmaceuticals, and synthetic fibers. NH_3 is also a potential fuel, providing a way to store and transport hydrogen owing to its exploitable energy density. However, the unavoidable leakage of NH_3 during its utilization has huge adverse impacts on the environment and human health. In these applications associated with the critical risks of this gas, effective adsorbents possessing the ability to store more NH_3 have been attracting substantial attention.

Porous materials with high surface areas, such as active carbon¹ and zeolites,²⁻⁴ have been used as NH₃ adsorbents; however, they suffer from relatively low affinity and limited capacity for NH₃. Simultaneously, porous materials, including metal–organic frameworks (MOFs),^{5,6} porous organic polymers

Porous acid-base hybrid polymers for enhanced NH₃ uptake with assistance from cooperative hydrogen bonds[†]

Xiaoyan Luo, (1)*** Yibang Liu, ** Mingxing Li, ** Renhui Ling, ** Ling Ye, ** Xuegong Cao** and Congmin Wang (1)***

Carboxylic acid-modified materials are a common means of achieving efficient NH₃ adsorption. In this study, we report that improved NH₃ adsorption capacity and easier desorption can be achieved through the introduction of substances containing Lewis basic groups into carboxylic acid-modified materials. Easily synthesized mesoporous acid-base hybrid polymers were constructed with polymers rich in carboxylic acid and Lewis base moieties through cooperative hydrogen bonding interactions (CHBs). The hybrid polymer PAA-P4VP presented higher NH₃ capacity (18.2 mmol g⁻¹ at 298 K and 1 bar NH₃ pressure) than PAA (6.0 mmol g⁻¹) through the acid-base reaction and the assistance from CHBs with NH₃, while the NH₃ desorption from PAA-P4VP was easier for the reformation of CHBs. Based on the introduction of CHBs, a series of mesoporous acid-base hybrid polymers was synthesized with NH₃ adsorption capacity of 15.8–19.3 mmol g⁻¹ and high selectivity of NH₃ over CO₂ ($S_{NH_3/CO_2} = 25.4-56.3$) and N₂ ($S_{NH_3/N_2} = 254-1068$), and the possible co-existing gases, such as SO₂, had a lower effect on NH₃ uptake by hybrid polymers. Overall, the hybrid polymers present efficient NH₃ adsorption owing to the abundant acidic moieties and CHBs, while the concomitant Lewis bases promote NH₃ desorption.

(POPs),7 covalent organic frameworks (COFs),8 and hydrogenbonded organic frameworks (HOFs),9 were developed as efficient NH₃ adsorbents owing to their highly porous nature, strong stability, and designable abundant binding sites.¹⁰ The modification of porous materials with functionalized moieties was expected to result in superior adsorbed amounts. Functionalized UiO-66-A/B/C11 and UiO-66-ox synthesized via postsynthetic modification with free carboxylic acids indicated their positive utilization in NH3 capture,¹² likewise the NH3 adsorption performance of Zr-based UiO-66 analogues.13,14 Various Brønsted acidic groups, such as -CO₂H and -SO₃H, were used to functionalize the water-stable framework UiO-66 and were reported with improved NH3 capacity.15 Acid-loaded porphyrin-based MOFs¹⁶ for capturing NH₃ show remarkable stability and the isoreticular porphyrin-based MOFs17 were reported with rod-like secondary building units of Brønsted acid bridging hydroxyl groups for NH₃ sorption. Similarly, the zirconium-based MOF, NU-300 with free Brønsted acid sites benefited the binding of NH₃ even at low pressures.¹⁸ Recently, carboxylic-functionalized mesoporous copolymers PDVB-xAA were developed for fast, highly efficient, selective, and reversible NH3 adsorption.19 These studies revealed that NH3 capture relies on the interplay of the functional groups, especially the -COOH of adsorbents.

It was found that the COFs modified with weak acid groups and hydrogen bonding interactions presented more efficient NH₃ uptake than strong acid-functionalized COFs. BBP-5, a COF

[&]quot;Xiamen Key Laboratory of Optoelectronic Materials and Advanced Manufacturing, Key Laboratory of Molecular Designing and Green Conversions (Fujian Province University), College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, P.R. China. E-mail: chemistrylxy@163.com

^bDepartment of Chemistry, Center of Chemistry for Frontier Technologies, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: chewcm@zju.edu.cn

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with carboxylate acid group showed more efficient and reversible NH₃ uptake than PPN-6-SO₃H due to the existence of cooperative hydrogen bonds (CHBs) along with the acid-Lewis base interactions between carboxylic acid and NH₃, which indicated that multiple chemical interactions were optimized to single strong interactions.²⁰ Similarly, urea-functionalized Zn-MOFs with an increased number of hydrogen bonds²¹ were also reported to have outstanding NH₃ adsorption. HOFs, mainly constructed by the self-assembly of organic molecules via intermolecular hydrogen bonding interactions, were explored as a potential corrosive gas trapping agent because of their abundant CHBs and porous structure. Jancik²² explored UNAM-1 constructed of hydrogen-bonded frameworks, which achieved the porosity required for reversible SO2 uptake. Kang9 reported a hydrogen-bonded network KUF-1 for NH₃ capture with a sigmodal adsorption isotherm and achieved the NH₃ capacity of 6.67 mmol g^{-1} at 1 bar. They found that the design of an adsorbent/absorbent with a flexible hydrogen bonding network presented superior NH₃ capacity and desorption regeneration. However, the refined design and cost-intensive synthesis of MOFs, COFs, and HOFs are very real problems against their application.

It was found that the hydrogen bonding interactions between the ionic liquids (ILs) and NH₃ were the key to the significant increase in NH3 capacity according to Palomar's work.23 Therefore, protic ILs24,25 and ILs substituted with hydroxyl groups,23,26 and poly ionic liquids (PILs) served as adsorbents of ammonia.27,28 In our previous work,29,30 amidine and pyridine-based protic ILs constructed with CHBs presented sigmodal isotherms, and the results indicated a high NH₃ capacity of 7.5–9.3 mmol g⁻¹ at 1 bar, 30 °C; furthermore, the threshold pressure could be regulated through the CHBs. Deep eutectic solvents (DESs), known as new ILs analogues, consist of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) in suitable molar ratios based on hydrogen bonding interactions and other intermolecular noncovalent interactions.31-38 It has been proposed that DESs are very promising NH3 absorbents through Lewis acid-base and hydrogen bonding interactions.39 For instance, choline chloride-composed DESs were developed for NH_3 absorbents,⁴⁰⁻⁴² and choline chloride/resorcinol/glycerol (1:3: 5) presented the NH₃ absorption capacity of 13 wt% at 313.2 K and 0.1 MPa for the internal hydrogen-bonded network of DESs.⁴⁰ Alcohol, phenol,^{43,44} and sugar⁴⁵ were also selected as components of DESs by taking advantage of their hydroxyl groups for effective NH₃ absorption. Protic DESs with NH₄SCN, ethylamine hydrochloride and ethanolamine hydrochloride as HBAs were reported as excellent NH₃ absorbents through strong hydrogen bonding interactions,46,47 and the influences of HBA of EDSs on the NH₃ absorption performances were systematically investigated. According to the weak acidity of azole, azolebased DESs were also used as NH3 absorbents;48-50 it was found that the greater acidity of the azole benefited the NH₃ capacity but went against the reversibility.⁵¹ Recently, it was reported that DESs involving metal chlorides including LiCl,⁵² M(II) Cl₂,^{53,54} and M(III)Cl₃,⁵³ could achieve greater NH₃ capacity for the coordination of NH₃ with metal and hydrogen bonding



Fig. 1 (a) A diagram showing the idea of developing acid–base hybrid polymers for NH_3 uptake. (b) Structures of the agents used for synthesizing hybrid polymers.

interactions. For instance, it was found that the CHBs-rich ILs/ DESs had a good trapping effect on NH_3 , while the NH_3 absorption capacity would be enhanced by 18.1–36.9% when a small amount of metal chlorides was added to Res/EG (1:2) DES.⁵⁴

The reports of sorbents substituted with carboxylic acid for efficient NH_3 adsorption and the utilization of hydrogen bonds to improve NH_3 desorption inspired us to construct selfassembled hybrid polymers based on the formation of CHBs between carboxylate acids and Lewis bases (Fig. 1a), which would enhance the affinity for NH_3 as well as promote NH_3 desorption by the reconstruction of CHBs. To obtain this target, various acid–base hybrid polymers (Fig. 1b) were explored to analyze the effects of the interactions between acidic and basic groups on NH_3 uptake.

Results and discussion

The reagents, preparation and characterization of hybrid polymers, and the NH₃ adsorption and desorption experiments are described in the ESI File[†] in detail.

The characterization of hybrid polymers

To explore the feasibility of the utilization of CHBs in enhancing the NH_3 uptake by acid–base hybrid polymers, PAA and PVBA with carboxylic acid groups were hybridized with P4VP/PVIm containing Lewis base groups to synthesize hybrid polymers as NH_3 adsorbents. The CHBs were further proposed from the optimized structures calculated through the DFT method as shown in Fig. S2.† The interaction energies between these acid and basic moieties were between -40.23 and -46.90 kJ mol⁻¹ as listed in Table 1, which allows the possibility to self-assemble the acid–base hybrid polymers. For PAA–P4VP, the interactions between PAA and P4VP were calculated through propionic acid and 4-ethylpyridine, the reaction enthalpy was -40.23 kJ mol⁻¹ and the Gibbs free energy was -1.28 kJ mol⁻¹, which indicate the possibility of interaction between PAA and P4VP.

The elemental contents of C, N, and H listed in Table S1[†] correspond with the theoretical data calculated from the molar ratio of acid and base moieties of 1:1, indicating that the hybrid polymers self-assemble in the equimolar reaction of – COOH and Lewis base. The IR spectra of acid-base hybrid polymers in Fig. S3[†] exhibit the changes in the vibration of

Table 1	The interaction energies between	acidic and basic groups and the N	H ₃ desorbed active energy from the TPD test
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Entry	Complex	Interaction energy ^{a} (kJ mol ^{-1})	TDP peak (°C)	Desorbed active energy ^{b} (kJ mol ⁻¹)	
1	PAA-P4VP	-40.23	78	104.0	
2	PAA-PVIm	-46.90	90	107.6	
3	PVBA-P4VP	-40.05	75	103.2	
4	PVBA-PVIm	-46.75	87	106.8	
5	PAA	—	112	114.3	

^{*a*} The interaction energies between acidic and basic groups were obtained through DTF calculations on the B3LYP basis set at the 6-31G++ level. ^{*b*} The active energies of NH₃ desorption were calculated based on the Redhead method⁵⁵ according to the desorption temperature from NH₃-TPD.

C=O as compared with acid polymers for the formation of CHBs. The IR spectra of PAA and PAA-P4VP in Fig. S3a[†] show that the stretching vibration of –COOH at 1698 cm⁻¹ was blue shifted to 1713 cm⁻¹ with the hybridization with P4VP (marked with a star). According to the 2D correlation IR spectra in Fig. S4,[†] the absorption of ν (COOH) was correlated with the vibration of the pyridine group at about 1600 cm⁻¹ (marked with a red star), which indicates the interaction between PAA and P4VP.

The SEM images in Fig. 2a present the mesoporosity of these hybrid polymers. The BET surface areas of hybrid polymers according to N_2 adsorption at 77 K in Fig. 2b and S5† range from 11.2 to 23.6 m² g⁻¹ (Table 2) and their pore size distribution is 2–30 nm, which explains the mesoporous structure of these hybrid polymers. On comparison of the SEM images and N_2 adsorptions of nonporous PAA in Fig. S6b† and 2b, it was concluded that the porosity of PAA–P4VP was due to the multiple interactions between PAA and P4VP.

NH₃ uptake of PAA-P4VP vs. pure PAA

It was reported that materials rich in CHBs are suitable for efficient NH₃ uptake; thus, hybrid polymers were used for NH₃ uptake. Interestingly, PAA–P4VP presents a higher NH₃ uptake capacity of 18.2 mmol g⁻¹ than PAA (6.0 mmol g⁻¹) from Fig. 3a, and the NH₃ trapped in PAA–P4VP would be released feasibly. From the reported data according to the properties of DESs, ILs, and acid-modified MOFs listed in Table S2,† the hybrid polymer showed excellent NH₃ uptake capacity and mild desorption conditions. The comparison of the IR spectra of fresh and NH₃ saturated samples in Fig. 3b indicates that –COOH reacts with NH₃ to form –COONH₄ according to the vibration of –COO⁻ at



Fig. 2 (a) The SEM images of hybrid polymers. (b) The N_2 adsorption isotherm curve at 77 K and the pore distribution (inner picture) of PAA and PAA–P4VP.

 1500 cm^{-1} , and new peaks at 850 cm^{-1} (marked with #) ascribed to the hydrogen-bonded NH₃.¹⁹ From the NH₃-TPD detection curve in Fig. 3c, the most ammonia was released from PAA-P4VP when the temperature reached 78 °C, while the NH₃ desorption peak occurred at 112 °C for PAA, indicating that the NH₃ release from PAA-P4VP was easier. It should be noted the peaks at about 200 °C, which arise from polymer fragments, collapsed according to the TGA results as shown in Fig. S6;† this indicates that the weights of PAA and PAA-P4VP begin to decline from 207 and 198 °C, respectively. The comparison of the IR spectra of the fresh and recovered samples after NH₃ desorption in Fig. 3b indicates that the PAA-P4VP could be recovered, and it is probably facilitated by the exothermic CHB formation between PAA and P4VP.^{29,56} The -COONH₄ remains in PAA for the obvious absorption of COO^{-} at 1540 cm⁻¹ (marked with pink shadow), which demonstrates the better properties of PAA-P4VP as an NH₃ adsorbent as compared to PAA. For 8 consecutive cycles of NH₃ adsorption-desorption experiments (Fig. 3d), the efficient NH₃ capacity of PAA-P4VP remained steady while there was an obvious decrease for PAA, which might be due to part of the unrecovered carboxylic acid in PAA. The uptake of NH₃ and other gases by PAA-P4VP in Fig. S7[†] shows that there was not considerable CO₂ or N₂ adsorption, and the selectivity of NH3 as compared to CO2 and N2 was 54.0 and 408, respectively. As can be seen, the acid-base hybrid polymer PAA-P4VP presented enhanced NH₃ adsorption and desorption as compared with PAA and high selectivity for NH₃, which indicate the potential application of acid-base polymers as NH₃ adsorbents.

The effects of CHBs on the NH₃ uptake of PAA-P4VP

To investigate the effects of P4VP on the NH₃ uptake of PAA– P4VP, other complexes including PAA-BPY and PAA-PS were synthesized (Fig. S8a†). PS has the same chainlike structure like P4VP but without the Lewis base moieties, while BPY has the same Lewis base moieties as P4VP. The PAA-BPY and PAA-PS are non-porous as seen from the SEM in Fig. S8b,† which indicates that the Lewis base moieties and the chainlike structure are important for forming porous complexes. The FT-IR spectra in Fig. S9a† show a blue shift of ν (COOH) when PAA reacts with BPY but it was less affected by PS, indicating the formation of the CHBs between PAA and BPY. The NH₃ uptake properties from Fig. S10† show that the adsorption capacity and desorption of PAA-PS are close to those of PAA, indicating that there

Table 2 The BET surface areas and gas uptake capacities of hybrid polymers and PAA

Entry	Complex	$S_{\rm BET}^{a} \left({ m m}^2 { m g}^{-1} ight)$	Gas capacity (mmol g^{-1})			Selectivity ^d	
			NH ₃ ^b	$N_2^{\ c}$	$\mathrm{CO_2}^c$	NH_3/N_2	NH ₃ /CO ₂
1	PAA-P4VP	23.6	18.2	0.0445	0.396	408	54.0
2	PAA-PVIm	11.2	19.3	0.0181	0.398	1068	48.6
3	PVBA-P4VP	23.0	18.4	0.0723	0.557	254	33.0
4	PVBA-PVIm	23.6	15.8	0.0478	0.622	331	25.4
5	PAA	0.7	6.0	_	_	—	—

 a The specific surface areas were calculated by the Brunauer–Emmett–Teller equation according to the N₂ adsorption–desorption isotherm at 77 K. b The NH₃ uptake was operated under the self-made device at 25 °C. c The N₂ and CO₂ adsorptions were detected *via* Micromeritics BAFLEX surface characterization measurements at 25 °C. d The selectivity of NH₃ over N₂ (CO₂) was calculated based on the capacity of NH₃ divided by the capacity of N₂ (CO₂).



Fig. 3 (a) The NH₃ uptake and residual capacity of PAA and PAA–P4VP with time. (b) FT-IR spectra of fresh, NH₃ saturated, and recovered PAA and PAA–P4VP. (c) NH₃-TPD curves of PAA and PAA–P4VP with temperature increase ratio of 2 °C min⁻¹ to 220 °C. (d) 8 consecutive NH₃ adsorption–desorption results for PAA and PAA–P4VP. NH₃ uptake at 25 °C, 1 bar. NH₃ desorption at 80 °C under vacuum.

was no obvious improvement in the NH_3 uptake of PAA for the mixture of PS. The NH_3 capacity of PAA-BPY was 13.0 mmol g⁻¹ and just 1.5 mmol NH_3 g⁻¹ remained after desorption under vacuum at 80 °C for 90 min. The superior properties of PAA-BPY as compared to PAA-PS indicate that the insertion of Lewis base moieties benefits NH_3 uptake capacity and desorption, and the competitive formation of CHBs between carboxylic acid and pyridine groups, which implies that the hybrid polymers are excellent ammonia sorbents.

NH₃ uptake of acid-base hybrid polymers

Based on the strategy of developing acid–base hybrid polymers for improved NH₃ uptake, hybrid acid–base polymers constructed with PAA and PVBA as acid polymers, P4VP and PVIm as Lewis base polymers were synthesized to investigate the effects of the interactions between acid and base moieties on NH₃ uptake properties. These hybrid polymers were used for NH₃ uptake at 1 bar and 25 °C; their NH₃ capacity was 15.8–

19.3 mmol g^{-1} from Fig. 4a and most of the fixed NH₃ could be desorbed under vacuum at 80 °C for 100 min. Simultaneously, the N₂ and CO₂ adsorption by the hybrid polymers was also measured at 1 bar and 25 °C, which showed that tiny amounts of CO₂ but non-considerable N₂ could be adsorbed, as shown in Table 2. The selectivity of NH₃ as compared to CO₂ and N₂ was 25.4-54.0 and 254-1068, respectively, which suggests the potential for the efficient separation of NH₃ from these mixture gases. Besides, some interfering gases are inevitably present in industry, and the effects of the adsorbed CO₂, SO₂, and H₂O on NH₃ uptake were investigated. Fig. 4b shows that 18.44 mmol g^{-1} NH₃ would be fixed after 0.77 mmol g^{-1} SO₂ adsorption of PAA-P4VP, and the same phenomenon for CO₂, which indicates no obvious effect of the acid gas on the NH₃ uptake by PAA-P4VP. There was a considerable H₂O uptake capacity of 7.22 mmol g^{-1} by PAA–P4VP but the subsequent ammonia adsorption capacity was reduced to 16.71 mmol g^{-1} , likely due to the active hydrogen bonding sites being occupied by H₂O.

The capacity of acid-basic hybrid polymers is susceptible to ammonia pressure and temperature; from Fig. 5, the NH₃ capacity decreases along with the increase in temperature and decrease in NH₃ pressure, which indicates that the NH₃ would be desorbed with the variation of temperature and pressure. It should be noted that there were uptake plateaus at $P/P_0 = 0.05$ of PAA–P4VP and $P/P_0 = 0.2$ of PAA-PVIm and PVBA-PVIm, and their stepwise uptake of approximately 6 mmol g⁻¹ from Fig. 5a, corresponding to about 1 equivalent of NH₃ per mol –COOH for



Fig. 4 (a) NH₃ uptake capacity of the acid-basic hybrid polymers at 25 °C and 1 bar. (b) Staged adsorption of 5% SO₂ and NH₃, CO₂ and NH₃, as well as 3.1% H₂O and NH₃ of PAA–P4VP at 25 °C. The residual gases were obtained after desorption in a vacuum at 80 °C for 100 min. The remaining capacity of adsorbate after desorption was converted into NH₃ gas.



Fig. 5 NH_3 uptake capacity of acid-basic hybrid polymers at various temperatures under 1 bar NH_3 pressure (a) and under various pressures at 25 °C (b).

the acid-base reaction to $-COONH_4$. Another 10–13 mmol g⁻¹ NH₃ uptake of these hybrid polymers probably contributed to the hydrogen interaction.

The analysis of NH₃ uptake of acid-base hybrid polymers

The IR spectra of the hybrid polymers compared with their NH₃ saturated state are shown in Fig. 6. The increase in absorption at about 3400 cm⁻¹ was due to the N-H stretching of adsorbed ammonia. Another characteristic peak at about 1470 cm⁻¹ increased after ammonia absorption, which can be attributed to the symmetric deformation of the ammonium ion.57,58 Meanwhile, the disappearance of $v_{\rm s}$ (COOH) at about 1710 cm⁻¹ (marked with *) and the increase in $v_s(COO^-)$ and $v_{as}(COO^-)$ at about 1520 cm^{-1} and 1350 cm^{-1} (marked with #) indicate the carboxylic acid of hybrid polymers forming the carboxylate salt.⁵⁹ These results support the formation of NH₄⁺ from the reaction of NH₃ with the proton of hybrid polymers.⁶⁰ A new peak at about 910 cm⁻¹ (marked with $\mathbf{\nabla}$) is ascribed to the hydrogen bonding of NH3 from PAA-PVIm and PVBA-PVIm, while that at 850 cm⁻¹ was due to PVBA-P4VP.¹⁹ The results claim the hybrid polymers from carboxylic acid polymers and Lewis base polymers achieved high NH₃ uptake capacity, which is attributed to the cooperative acid-base interaction and hydrogen bonding interactions.

The properties of NH₃ desorption from the hybrid acid–base polymers were investigated through NH₃-TPD measurements. The results presented in Fig. S11[†] indicate NH₃ desorption peak



Fig. 6 Comparison of the partial IR spectra of hybrid polymers (red solid line) with their NH_3 saturated (gray background) and desorbed states (blue dotted lines).

before 100 °C for all these hybrid polymers, the active energy of desorption of 103.2–107.6 kJ mol⁻¹ as listed in Table 1, which belonged to the NH₃ released from the NH₃ fixed by acid-base interactions. The ammonia trapped by PVBA-P4VP and PVBA-PVIm would be released completely within 200 °C, indicating the feasible desorption of NH₃ from these hybrid polymers. The IR spectra of the hybrid polymers after the NH₃-TPD test compared with the pristine sample in Fig. 6 indicate that carboxylic acid would be recovered after NH₃ desorption. The reusability of these hybrid polymers for NH₃ uptake was further investigated. Fig. S12-14[†] show that the NH₃ uptake capacity did not decrease within 6 cycles of consecutive NH3 uptake and desorption. About 2.8 mmol g^{-1} NH₃ remained in PAA-PVIm (2.3 mmol g^{-1} NH₃ remained in PVBA-PVIm) after desorption, which would not affect the subsequent NH₃ adsorption. The reversibility of these hybrid polymers indicates that the acidic polymer hybrid with appropriate basic polymer is one of the designable strategies to promote NH₃ desorption and the recovery of hybrid polymers.

Conclusions

The simple acid-base hybrid polymer PAA-P4VP presents a porous structure and superior NH₃ uptake properties as compared to PAA for synergetic NH₃ capture through acid-base and CHB interactions. Inspired by this result, a series of mesoporous acid-base hybrid polymers presenting surface areas of 11.2 to 23.6 m² g⁻¹ were synthesized according to the predicted interactions between the acidic and basic moieties. These acidbase hybrid polymers were used for efficient NH₃ uptake with the capacity of 15.8–19.3 mmol NH₃ g⁻¹ through the cooperative acid-base reaction and hydrogen bonding interactions. The trapped NH₃ can be released at 80 °C under vacuum along with the reformation of CHBs between the -COOH and Lewis base moieties. This indicates that the incorporation of the basic moiety is a feasible method for improving the NH₃ uptake and desorption of materials with the carboxylic acid groups.

Author contributions

Conceptualization, Xiaoyan Luo and Congmin Wang; data curation, Yibang Liu; formal analysis, Xiaoyan Luo and Yibang Liu; funding acquisition, Xiaoyan Luo; investigation, Xiaoyan Luo and Yibang Liu; methodology, Yibang Liu and Mingxing Li; project administration, Congmin Wang; resources, Ling Ye, Xuegong Cao and Congmin Wang; software, Xuegong Cao; supervision, Xiaoyan Luo and Congmin Wang; validation, Yibang Liu, Mingxing Li and Renhui Ling; writing – original draft, Xiaoyan Luo; writing – review & editing, Congmin Wang.

Conflicts of interest

There are no conflicts to declare.

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