Review of H_2S selective oxidation over carbon-based materials at low temperature: from pollutant to energy storage materials

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Abstract: Carbon materials for the room-temperature selective oxidation of H_2S have attracted growing attention in recent years. The recent development of carbon-based desulfurization catalysts is reviewed, including activated carbon modified by alkalis, porous carbon doped with nitrogen or modified with functional groups, and carbon composites with other species such as alkaline metal oxides. The oxidation mechanisms for H_2S on the various catalysts are discussed, and the important function of carbon in desulfurization are emphasized, including its large specific area, porous structure and adjustable surface chemistry. In addition to the catalytic oxidation of H_2S, the extended use of the spent catalysts, sulfur/carbon composites, as sulfur cathode materials for high-performance lithium-sulfur batteries, is discussed as a way to add extra value to the sulfur-containing pollutants. Finally, the outlook for using carbon-based materials for room-temperature desulfurization and the key challenges to its large-scale use are explored.

Key words: Carbon-based materials; H_2S; Catalytic oxidation; High value-added transformation; Lithium-sulfur battery

1 Introduction

Hydrogen sulfide (H_2S) is one of the most toxic and malodorous pollutants, which mostly comes from chemical industries, such as natural gas purification and utilization, sulfurized dye, petroleum refining, coal chemistry, sewage treatment, papermaking, and a small part comes from organic corruption process[1–5]. Industrial gas containing H_2S has great bad effects on the chemical process including poisoning catalysts and corroding engines[6–8]. It is estimated that the annual H_2S emissions from industrial production are as high as 1×10^7 tons/year, which, even worse, can spread in the air, thus posing a hazard to people and the environment. As a strong neurotoxin, H_2S with a high concentration ($>700\times10^{-6}$) can cause human death[8]. With the continuously increasing demand for energy, the release of H_2S is becoming more and more widespread, and the resulting environmental pollution problems must be addressed.

Various desulfurization strategies based on wet or dry technology have been adopted to treat the H_2S-containing tail gas[9–14]. The wet method such as using ammonia, alcohol-ammonia and hot potash alkali as reactants is mature for H_2S removal in industrial production[9–10], which, however, suffers from the problem of high cost, low desulfurization precision ($c_{H_2S}>2\times10^{-5}$ *v*/*v*), and low efficiency. Given that the continued growth in demand of environmental protection, sulfur recovery has become increasingly significant. H_2S selective oxidation is regarded as the general strategy to extract elemental sulfur (S), which is a non-toxic, pollution-free and valuable product. Claus process is a common selective oxidation technology for treating the high concentration pollutants, in which typical sulfur recovery efficiencies are 90%-95% for a two-stage reactor plant and 99% for a super Claus process[11]. Limited by thermodynamic kinetic of reaction, low concentration of H_2S is still left in the tail gas, and extra purification processes are urgently needed for further purifying the Claus tail gas. The method of using carbon-based materials as desulfurization catalyst is regarded as the most promising strategy to eliminate H_2S with relatively low concentration in view of its mild reaction conditions, effi-

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cient removal ability, and high reactivity[15–16]. This oxidation process could thermodynamically reduce H_2S at room temperature to a subparts-per-million level and realize the directional conversion to elemental S[13], which is widely used in Claus tail-gas treatment, sewage treatment, and coke oven gas purification[17–18]. The irreversible reaction process is as follows (equation 1 is the main reaction and equations 2 and 3 are the side reactions):

$$H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O \quad (1)$$

$$\frac{1}{n}S_n + O_2 \rightarrow SO_2 \quad (2)$$

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \quad (3)$$

The catalyst in the system can play a double role as the initiator for the direct reaction of H_2S with O_2, then as the storeroom to accumulate solid S within the pore structure. Due to the controllable surficial chemistry and developed porous structure, the carbon-based catalysts can exhibit higher activity for catalytic H_2S oxidation and larger sulfur capacity compared to other metal/metal oxide-based materials at relatively low temperature[19–23]. Specifically, the confined space supplied by ultra-micropores (arises from the tight arrangement of graphene walls) promotes the O＝O bond distortion and O_2 activation, while the electron transfer of conductive sp^2-conjugated graphene to the outer orbit of activated-O_2 further facilitates the generation of oxygen radical, which exhibits a much higher redox potential than its parent product and can react with dissociated HS^- into solid S[24]. The produced S can be stored further in the nanopores or adhered on the carbon surface[25–29]. Therefore, some essential conditions, such as the suitable chemical environment for H_2S dissociation, the adequate micropores for gas adsorption and activation, and the developed meso-macropores for reactants transfer as well as the S storage, are needed for carbon-based catalysts in the desulfurization system.

Achieving H_2S efficient conversion is a prerequisite for the subsequent utilization of S resources to realize its high value-added utilization. The highly selective conversion of H_2S to solid S can not only reduce air pollution but also bring considerable economic benefits. As global energy scarcity intensifies, the need for high-performance energy storage devices is continuously increasing. Known for the overwhelming energy density (2 600 Wh kg^{-1}) and theoretical capacity (1 675 mAh g^{-1}), eco-friendly lithium-sulfur batteries (LSBs) using S as the cathode, are expected to be a next-generation energy storage system to substitute the traditional lithium-ion batteries[30–32]. The S-related multiphase conversion covers the reduction of solid sulfur units (S_8) to solid lithium sulfide (Li_2S), with the generation of a series of dissolvable intermediates, lithium polysulfides (LiPSs), and the reversible oxidation process. The cooperation of carbon materials with S realize the effective mitigation of poor conductivity of S, volume change and shuttle effect of LiPSs during discharge and charge processes in LSBs[30–31]. Given that the reaction of H_2S oxidation over carbon-based catalysts could realize *in-situ* S deposition and its chemical immobilization, the produced carbon/sulfur composites would be the promising cathode candidate for LSBs.

In recent decades, a broad range of carbon materials have been severed as the room-temperature catalysts for H_2S selective oxidation. This review summarizes the carbon materials used in the subject of room-temperature desulfurization, and different carbon-based materials are shown to explore the theories of efficient H_2S oxidation. It is indicated that the high selectivity of H_2S to elemental S can be achieved based on carbon materials through the pore structure optimization, surficial modification and coupling of heterogeneous components (Fig. 1). More importantly, the expended application of the *in-situ* generated carbon/sulfur composite after desulfurization is developed in energy storage system. The aim is to review the development of carbon-based materials on H_2S catalytic oxidation at room temperature, and to provide theoretical guidance for designing novel materials to realize the high added-value transformation of H_2S pollutants.

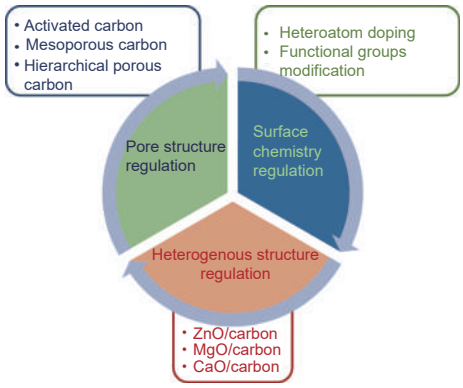

Fig. 1　Modulation strategies of carbon-based catalysts for H_2S selective oxidation at room temperature.

2　Modulation strategies of carbon materials for H_2S selective oxidation

Carbon materials are characterized by developed porous structure, large specific area and modifiable surface chemistry. When they are used as room-temperature desulfurization catalysts, the mechanism of H_2S oxidation upon carbons can be summarized as following steps: (1) the water in the feed gas is adsorbed by the porous structure and forms a water film on its surface; (2) H_2S and O_2 diffuse into the nanopores and are adsorbed, then dissolve in water-film; (3) H_2S dissociates to HS^- ions, meanwhile, O_2 is activated to oxygen radicals and further reacts with HS^-. In recent years, several attempts including three aspects of pore structure, surface chemistry and carbon-based composite designing have been adopted to adjust the adsorption characteristics and dissociation of H_2S, the activation of O_2 as well as the storage capacity of produced S, for improving the desulfurization performance.

2.1　Pore structure regulation

Based on the definition of pore structure by International Union of Pure and Applied Chemistry (IUPAC), the pores in carbon can be divided into micropore (< 2 nm), mesopore (2-5 nm) and macropore (> 50 nm), and micropores can further be divided into ultra-micropore with a pore size less than 0.7 nm and super-micropore with a pore size more than 0.7 nm. Achieving effective regulation of pore size plays an essential role in catalytic H_2S oxidation, as manifested in the adsorption of reactants, the formation of water film, the activation of oxygen, and storage of oxidation products.

Studies have shown that the pores less than 1 nm in carbon have a strong physical adsorption on H_2S and O_2 gas molecules[33]. The activation of O_2 based on carbon involves two steps of strong physical adsorption and electrons transfer. In the case of ultra-micropores (<0.7 nm), the adsorption is enhanced by the potential overlapping of the interactive pore walls, facilitating the O=O bond distortion and O_2 activation[24]. However, these small pores (<1 nm) with limited pore volume cannot act as nano-reactors for the H_2S dissolution and accommodate the oxidation products. The dissociation of H_2S to HS^- is a prerequisite for the selective oxidation[34]. For pores larger than 3 nm, their physisorption of H_2S is too weak[35], and only pore smaller than 5 nm can be filled with water at 80% relative humidity[36], so the H_2S molecules can only be effectively adsorbed and dissociated in the pores of 1-3 nm[37]. After the reaction of oxygen radicals with HS^- ions, the obtained elemental S can be detached from the active sites with the flow of water-film and accumulated to S clusters, which are stored in the larger pores. Compared to micropores, the exist of mesopores in carbon can not only provides a large storage space for oxidation product but also reduces the mass transfer resistance and facilitates the gas diffusion. For example, Zhang et al.[38] used a hard template method to prepare the ordered mesoporous carbon to analyze the effect of pore diameter and volume on H_2S selective oxidation, confirming that the presence of mesopores is beneficial for the growth of elemental S. Furthermore, the hierarchical macro-meso-microporous structure further promotes the H_2S adsorption-diffusion kinetics, which is also instructive for H_2S catalytic oxidation studies. Wang's group[26] investigated the desulfurization performance of carbon nanofibers with a multistage pore structure, finding that the meso-macropores could provide the channel for rapid H_2S diffusion and a rich stored room, while micropores mainly contributed to the supply of nano-reactors for efficient catalytic oxidation.

2.2 Surface chemistry regulation

Surface chemical modulation, such as heteroatom doping and functional group grafting, is one of the important strategies to improve the catalytic oxidation of porous carbons. On the one hand, as an acidic gas, the dissociation of H_2S can be promoted by the enhanced surface alkalinity. On the other hand, there are plenty of π* electrons in conductive sp^2-conjugated carbons, and the exist of defective sites in carbon lattice can boost the electron-donating ability to adsorb O_2, further facilitating the generation of active oxygen species[26, 27, 39].

Doping nitrogen (N) atom is the most common doping option for carbon materials, which has a similar size and a higher electronegativity (3.04) than carbon atoms (2.55). When N atoms are doped in carbon lattice and bonded with sp^2 carbon atoms, it exists in three main forms as follows: pyridine-N, pyrrole-N and graphitized-N[40]. Among them, pyridine-N is sp^2 hybridized, which replaces a defective atom in the hexagonal carbon ring and provides one *p*-electron to π system. Pyrrole-N means the sp^3-hybridized N atom that replaces a defective carbon atom of the five-membered ring and contributes two *p*-electrons to π system, while graphitized-N replaces a carbon atom of hexagonal ring. It is demonstrated that the doped N in carbon lattice can create the local tension of hexagonal skeleton, leading to structural deformation[41]. Moreover, the lone-pair electrons of N atoms can supply negative charge to sp^2 hybrid carbons, thus enhancing its electron donating and chemical reaction activity[42]. Electron-rich N doping can modify the energy-band configuration of carbon, lower its valence-band and improve the chemical stabilization, while the electron density at Fermi-energy level can be increased[43]. Additionally, the doped-N atoms not only affect the physical properties of carbons (e.g. electrical conductivity), but also can change the chemical properties, such as enhancing the Lewis basicity of carbon[44]. The charge delocalization induced by N atoms can also change the model of O_2 adsorption on carbon materials: from end-point adsorption mode (Pauling model) to lateral adsorption mode (Yeager model), which can effectively weaken the O＝O bond, thus favoring oxygen activation[45]. Beside that, the exist of functional groups on surface also impact the chemical properties of a catalyst a lot. For example, the introduction of amine (－NH_2) group are effective for increasing the number of basic sites of carbon and enhancing the interplay with H_2S[25, 46], the O-containing functional groups on the alkaline-impregnated carbon can anchor alkali sites by hydrogen bonds[47], which both can promote catalytic H_2S oxidation.

2.3 Heterogeneous structure regulation

Although the activated O_2 molecule can react with many substances such as CO, H_2S, and organics, it often suffers from poor stability, leading to its short lifetime and limiting its catalytic performance[48]. Thus, enhancing the stability of the activated oxygen species is urgently needed in the existing systems. Some dipolar aprotic solvents are demonstrated useful to stabilize the generated superoxide, based on the prevention of the disproportionation reaction[49–50], which can effectively improve the catalytic performance in various systems. However, compositing these additives with the metal-free catalysts for heterogeneous catalysis is rather difficult. Accordingly, the methods of physical/chemical trapping are usually adopted to achieve the stability of oxygen radicals[24].

Some metal oxides, such as MgO, TiO_2, and ZnO with high electron affinity, are speculated to have the ability to bond with oxygen radicals strongly[24, 51–53]. It is shown that the improved stability leads to a longer lifetime and higher concentration of oxygen free radicals in system. Nevertheless, the $O_2^{\bullet-}$ cannot format on these metal oxides without other stimulation (photocatalysis or electrocatalysis, et.al) at room temperature[24]. Thus, compositing the active phase of oxygen-activated, porous carbon, with the trapping phase of oxygen radical, metal oxide, can effectively solve this problem of stabilizing and enriching $O_2^{\bullet-}$ radicals. Moreover, the heterogenous composite of basic metal oxide with carbon matrix can not only boost the utilization of activated oxygen species, but also increase the alkalinity of carbon, that is, improving the desulfurization activity from two aspects of H_2S dissoci-

ation and oxygen activation together.

3 Carbon materials for H_2S selective oxidation

3.1 Carbon materials with different porous structures

Depending on the pore size, the desulfurization carbon-based catalysts can be divided into activated carbons, mesoporous carbons and hierarchical porous carbons. Given that the surface inertness of pristine carbon will hinder the step of H_2S dissociation, alkaline impregnation was adopted as a common method to increase the alkalinity of water-film, facilitating the formation of HS^- ions. The H_2S removal over the carbon without alkaline modification, whose desulfurization ability mainly arises from the physical adsorption by micropores rather than catalytic oxidation, is not discussed in this review.

3.1.1 Activated carbons

Activated carbon is generally abundant in micropores, whose diameter fits the scale of small molecules and is suitable for adsorbing gas molecules. Such as, the kinetic diameter of O_2 is around 0.346 nm, which can be adsorbed by micropores of carbon and further be activated by ultra-micropores[24]. Compared to the original state, the reactive oxygen with a much higher redox potential can boost the reaction kinetics of H_2S oxidation. Alkaline-modified activated carbons have been studied as room-temperature desulfurization catalysts for several years, and there has been a widely debated about the mechanism of H_2S oxidation over activated carbons. In general, two steps are included in the oxidation process:

(1) Physical adsorption step: firstly, H_2S is adsorbed on the micropores of carbon, dissolving in water-film and dissociating in an adsorbed state.

$$H_2S\ (g) \rightarrow H_2S\ (ads)$$
$$H_2S\ (ads) \rightarrow H_2S\ (ads\text{-}liq)$$
$$H_2S\ (ads\text{-}liq) \rightarrow HS^-(ads) + H^+$$

(2) Oxidation step: the adsorbed-H_2S reacts with O_2 to form elemental S, with the side reaction of sulfur dioxide (SO_2) and sulfate (SO_4^{2-}) generation in the presence of water.

$$HS^- + O^*(ads) \rightarrow S\ (ads) + OH^-$$
$$HS^- + 3O^*(ads) \rightarrow SO_2\ (ads) + OH^-$$
$$SO_2\ (ads) + O^*\ (ads) + H_2O\ (ads) \rightarrow H_2SO_4\ (ads)$$
$$H^+ + OH^- \rightarrow H_2O$$

The dominant product is highly active S atoms, which can self-assembly to a stable unit (S_8)[54–55]. These small S clusters grown in water-film could diffuse along the carbon surface and are stored in larger pores finally. The catalyst is not deactivated until the active sites are covered or the nanopores are blocked. Sulfur capacity (Q_S) is a key indicator to evaluate the catalytic performance of a catalyst, which represents the weight of H_2S oxidized by the unit weight of the catalyst (g H_2S/g catalyst). Ling's group used Na_2CO_3-impregnated activated carbon fibers (ACFs) to research the impact of pore structure on desulfurization performance[56], indicating that the smaller micropores could act as the initiator of reaction and the Q_S was dominated by the nanopores with the diameter larger than 0.7 nm (Fig. 2a). Additionally, it was found that the diameter of pores even guides the products of H_2S oxidation. The obtained ACFs with more pores larger than 0.7 nm could produce more elemental S, while those with smaller pores could produce more sulfur oxides (Fig. 2a-b). It is speculated that the edge (or defect) of carbon atoms should be the active sites of H_2S oxidation, on which the electron density is intensified thus the O_2 can be readily captured and activated. The alkaline impregnation has been verified to accelerate the H_2S dissociation, thus facilitating the subsequent oxidation of HS^- ions to S. The catalytic reaction process is shown in Fig. 2c.

The flow of water-film upon the carbon surface can transfer the produced S, continuously cleaning the active sites for maintaining the activity of a catalyst[13, 57]. Bagreev et al. proposed that the process may also happen at sulfur sites, that is, the as-formed elemental S might also as the reactor for H_2S oxidation when the original active site is covered[54–55, 58]. In larger nanopores, the oxidation process can happen as follows:

$$S_x + HS^- \rightarrow HS_xS^-$$
$$HS_xS^- + \frac{1}{2}O_2 \rightarrow HS_xS^-O^*$$
$$HS_xS^-O^* + HS^- \rightarrow HS_{x+1}S^- + OH^-$$

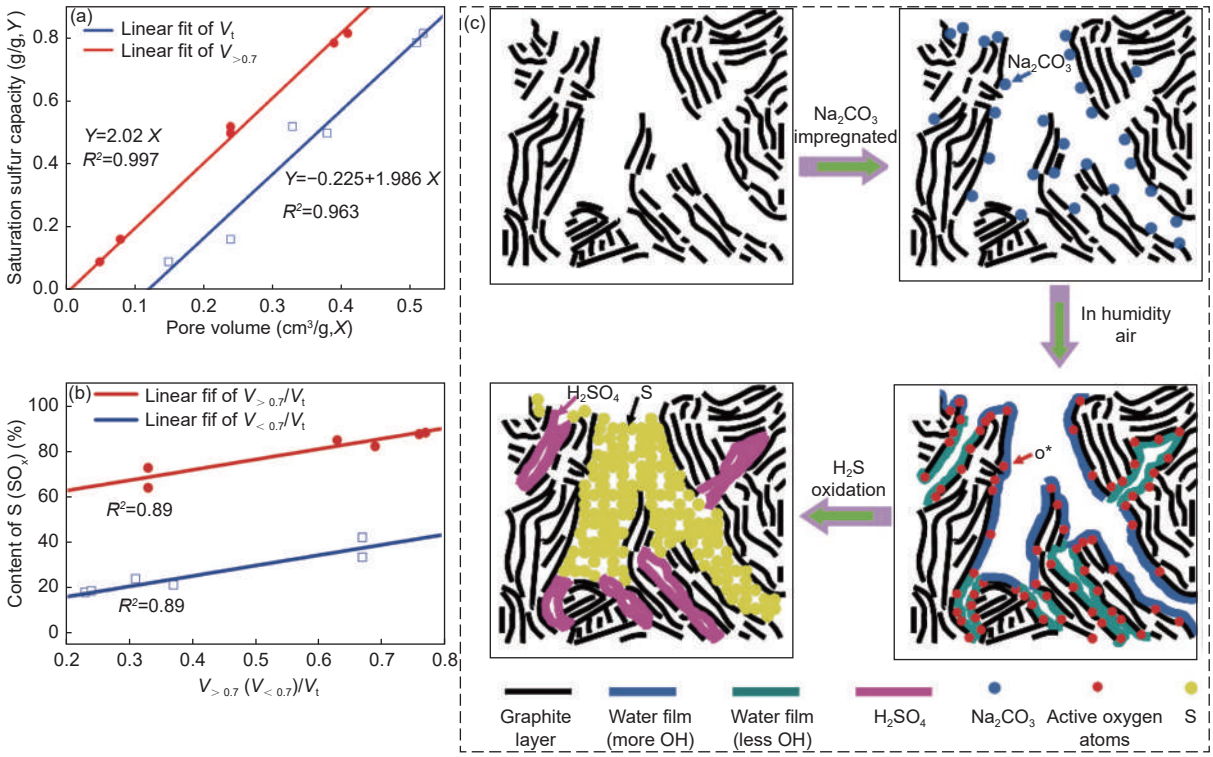

Fig. 2 (a) Relationships between saturation sulfur capacity (Q_S) and pore volume. (b) Relationships between the content of S (SO_x) and the ratios $V_{>0.7}/V_t$ and $V_{<0.7}/V_t$. (c) Schematic diagram of H_2S oxidation and sulfur species deposition in the nanopores of ACFs[56]. (Reprinted with permission by American Chemical Society, Copyright 2010).

$$HS_xS^-O^* + \frac{1}{2}O_2 \rightarrow HS_{x-1}S^- + SO_2$$

$$SO_2 + \frac{1}{2}O_2 + OH^- \rightarrow SO_4^{2-} + H^+$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

where HS_xS^- ($HS_{x-1}S^-$) and $HS_xS^-O^*$ represent polysulfides and adsorbed radicals at S sites, respectively. The accumulated S clusters can spontaneously assemble to larger S particles, then deposited in the large nanopores. That is to say, the value of Q_S mainly depends on the nanopores with larger volume. Thus, the alkaline impregnated activated carbon desulfurizer was limited at 0.2-0.8 g H_2S/g catalyst due to their small micropore diameter and pore volume that cannot accommodate much more solid S[56], which limits their industrialized applicability.

3.1.2 Mesoporous carbon materials

Due to its excellent structural characteristics, mesoporous carbon has been widely used in adsorption[59], catalysis[60], electrochemistry[61], and other fields. Compared to the activated carbons, the mesoporous carbons can additionally provide enough space for product storage and highly open channels for promoting the diffusion of gases, which is more favorable for H_2S catalytic oxidation[62]. Zhang et al. used the silica-templating synthesis method to prepare alkaline mesoporous carbons (AMCs) for room-temperature desulfurization (Fig. 3a)[38]. The produced AMCs have both good H_2S dissociation ability and, more importantly, enough mesopores for elemental S storage (Fig. 3b-c), which leads to a high Q_S of 4.49 g H_2S /g catalyst. Long's group prepared a kind of millimeter-sized mesoporous carbon spheres (MCSs) and used the MCSs as a support to load different alkalis for efficient H_2S catalytic oxidation[63]. It was found that upon various alkalic impregnates such as Na_2CO_3, K_2CO_3, NaOH and KOH, the catalyst impregnated with MgO could exhibit a much higher Q_S (2.46 g H_2S/g catalyst) than that with conventional basic salts (Fig. 3d). It should be ascribed to the different solubilities of various basic salts in water. During the catalytic oxidation, the alkalic MgO is slightly soluble in water, releasing the OH^- continuously and facilitating the H_2S dissociation for a long time (Fig. 3e). Contrast-

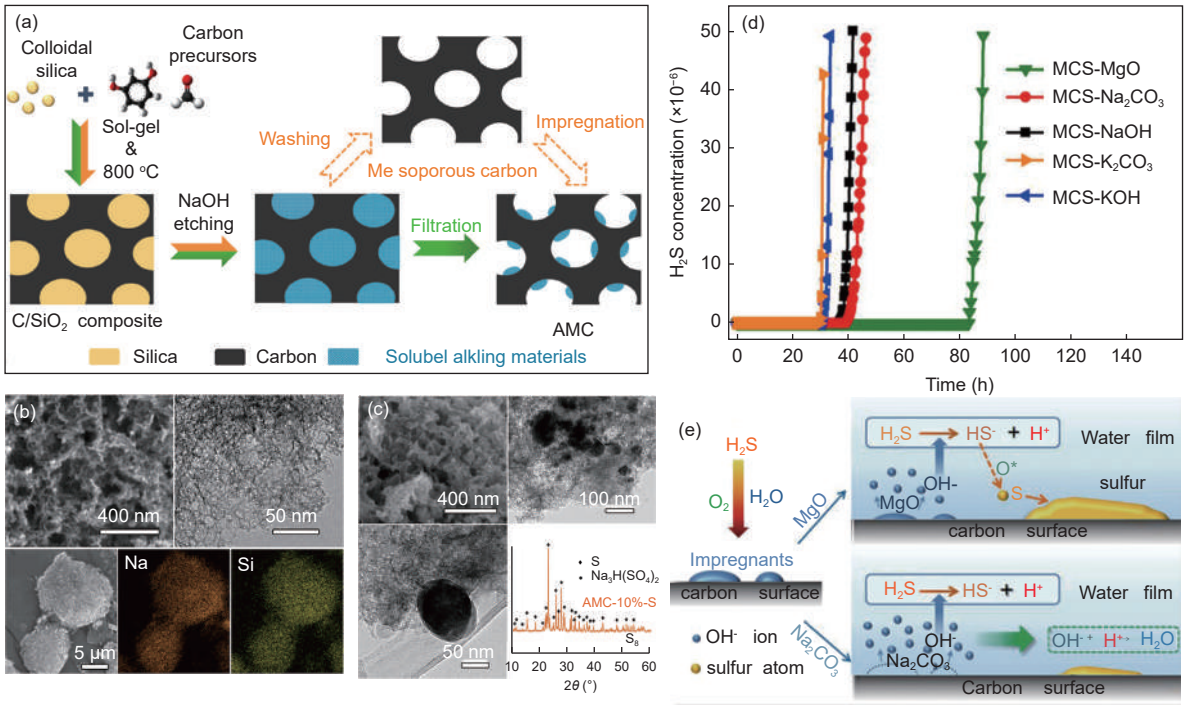

Fig. 3　(a) Preparation schematic of AMCs. (b) SEM, TEM and elemental mapping images of pristine AMC-10%. (c) SEM, TEM and XRD pattern of the catalyst after H_2S oxidation (AMC-10%-S)[38]. (Reprinted with permission by American Chemical Society, Copyright 2016) (d) H_2S breakthrough curves of the catalysts with various alkalic impregnates. (e) Schematic diagram of H_2S oxidation over MCSs with MgO and other soluble bases[63]. (Reprinted with permission by Elsevier, Copyright 2016).

ively, the normal basic salts are highly soluble in water and forming OH^- ions immediately, which not only facilitate the dissociation of H_2S to HS^-, but also are easily consumed *via* an acid-base neutralization. Similarly, Yan et al. investigated the effect of alkali-impregnation on H_2S oxidation and the oxidation mechanism is remarkably different upon carbons modified by various alkaline species[64].

3.1.3　Hierarchical porous carbon materials

Moreover, carbon with a hierarchical micro-mesoporous structure has attracted lots of attentions given that the combined advantages of two kinds of pores can achieve a synergistic effect of promoting H_2S oxidation. A catalyst of Na_2CO_3-impregnated carbon aerogel with a hierarchical porous structure was designed by Chen's group, the micro- and mesoporous structures were regulated by the sol-gel conditions and CO_2 activation, and their respective roles on H_2S catalytic oxidation were further explored[65]. Studies showed that the micropores can act as the microreactor for desulfurization, and meso-macropores as storage for elemental S. Moreover, with the increase of mesopore sizes, the utilization efficiency of mesopores decreased, and the catalytic oxidation can achieve the best when the volumes and sizes reach a compromise. This phenomenon can be accounted as follows (Fig. 4a): the S clusters could be readily coalesced to large agglomerations in the mesopores with small diameters (2-30 nm), allowing the epitaxial growth of S clusters rather than covering the active surface. While the S clusters could be isolated or hardly be coalesced in the mesopores with large sizes (>30 nm), leading to the growth of S clusters directly along the active surface. In 2019, Sun et al. fabricated the hierarchical porous carbon nanofibers (N-PCNFs) *via* a simple electrospinning method[26]. Owing to the action of interfacial stress arising from different pyrolysis properties of two precursors (PAN, ZIF-8), numerous mesopores are generated, further resulting in the formation of macropores, which can act as the passage for H_2S molecules to the accessible micropores. Meanwhile, due to the volatilization of coordinated zinc from the original ZIF-8 and the chemical activation of KOH (Fig. 4b-c), the micropores will be gener-

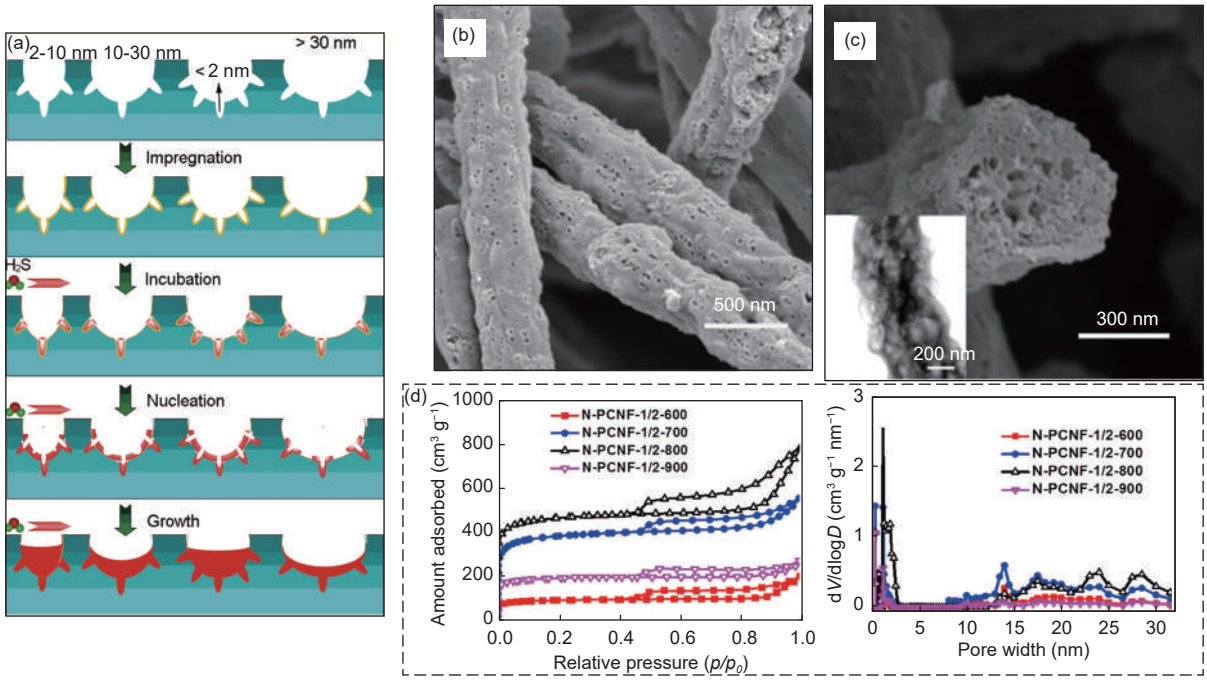

Fig. 4 (a) Schematic diagram of sulfur species disposition upon carbon aerogel with various microstructures[65]. (Copyright 2011, Elsevier) (b, c) FESEM images of typical N-PCNF-1/2-800 sample, the inset in (c) is the TEM image of sample. (d) N_2 adsorption-desorption isotherms and pore-size distributions of samples prepared at different temperatures[26]. (Reprinted with permission by Elsevier, Copyright 2019).

ated, which facilitate the formation of water-film to dissociate the adsorbed-H_2S. The porosity, especially the volume percentage of micropores (v_{mic}/v_{tot}) of materials greatly affects the performance of desulfurization. The carbonization temperature varied from 600 to 900 °C, enabling effective regulation of hierarchical porous structures (Fig. 4d), the optimum N-PCNFs catalyst exhibits ultra-high activity with the Q_S up to 3.57 g H_2S/g catalyst. It should be attributed to the synergistic effect of the micro-mesoporous structure of carbon materials, during which micropores act as the micro-reactors for triggering H_2S oxidation and mesopores serve as the passage for reactants and storehouse for elemental S[26, 56, 65] .

3.2 Chemically modified porous carbons

3.2.1 Nitrogen-doped porous carbon

Heteroatoms doping is considered as another efficient strategy for promoting the catalytic process of carbons[45, 66–68]. The doped nitrogen (N) in carbon can act as alkalic sites, enhancing the electron donating of carbon lattice, further increasing its redox reactivity[45, 68]. Long's group prepared a kind of N-rich mesoporous carbon (NMC), which exhibits the high-efficient desulfurization activity at room temperature[27]. It is suggested that the N content and the bonding configurations are both responsible for H_2S oxidation performance (Fig. 5a-b). Pyridinic-N atoms, which are located at the edges of carbon lattice, are favorable for the O_2 adsorption and the subsequently oxidation reaction. Actually, the pyridinic-N were previously reported to be active for catalytic oxygen reduction[69] and sulfur dioxide removal[70]. Based on the mechanism of vapor-liquid-solid for H_2S oxidation (Fig. 5c), the presence of pyridinic-N groups could act as Lewis-basic sites to enhance the basicity of carbon, facilitating the H_2S dissociation and the generation of HS^- ions (pK 6.89). Moreover, the spent NMC can be regenerated by CS_2 washing or thermal treatment[27]. After that, a series of N-rich carbon with various dimensional structures are designed as desulfurization catalysts. Sun's group synthesized one-dimensional (1D) N-doped hierarchical porous carbon nanofibers (N-PCNFs) as a desulfurization catalyst[26]. Studies proved that the special design of 1D nanofibers can act as a highway for the rapid migration of gas reactants, and the synergy between N-rich and hierarchical meso-micropores to efficient desulfurization has been demonstrated. The doped N atoms, especially pyridinic-N

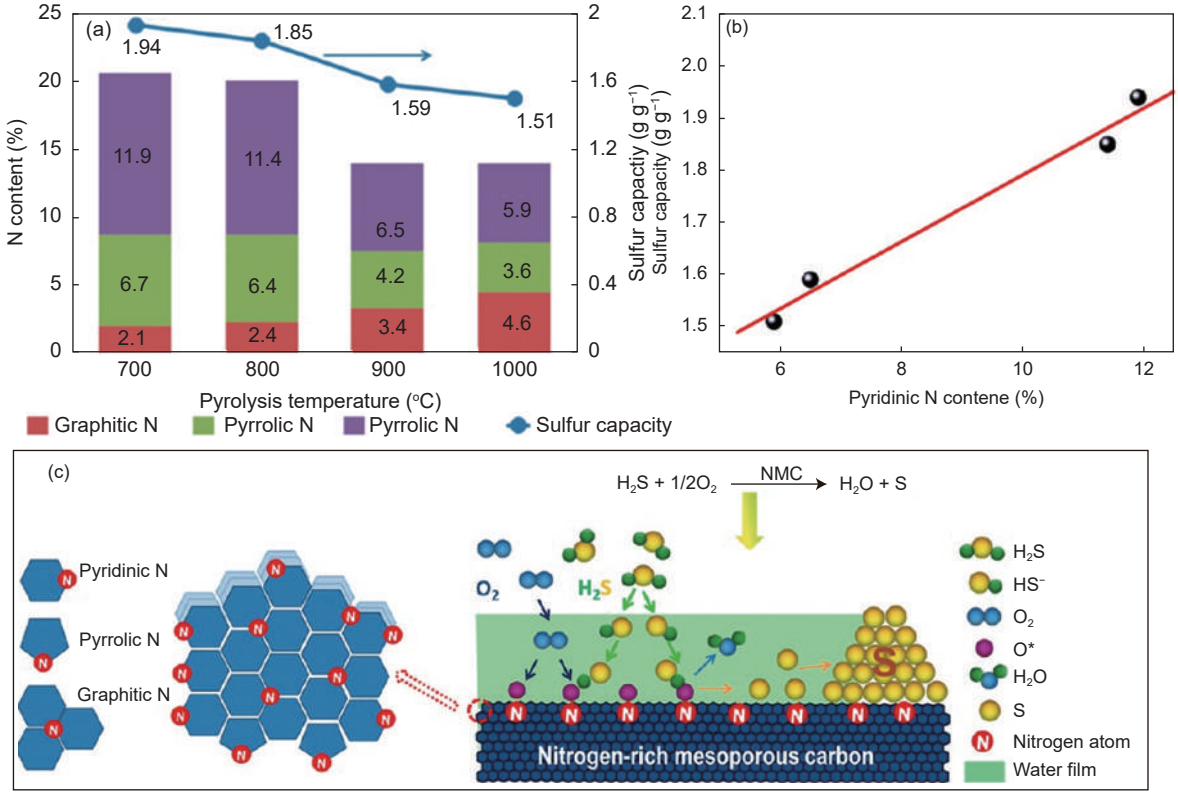

Fig. 5　(a) The configuration of N in NMC prepared at different temperatures. (b) Relationship between sulfur capacity and pyridinic-N content. (c) Schematic diagram of H_2S oxidation and sulfur deposition on NMC[27]. (Reprinted with permission by American Chemical Society, Copyright 2013).

and pyrrolic-N, can offer rich alkalic-sites for binding acidic molecules, and enhance the reactivity of carbon for O_2 activation. Yu et al. reported a kind of two-dimensional (2D) N-rich mesoporous carbon nanosheets (NMCS) as a room-temperature H_2S oxidation catalyst[39]. The thin nanosheets shorten the diffusion distance of reactants, and the mesopores on nanosheets are convenient for the growth of S clusters.

3.2.2　N-containing group functionalized porous carbons

Besides the N-doping, N-containing functional group grafting can also increase the desulfurization activity by enhancing the alkalinity of water film. Wang et al. prepared the N-functionalized mesoporous carbon nanosheets (MCNs) by grafting polyethyleneimine (PEI) upon graphene oxides (GO) nanosheets[46]. The N-containing group of PEI create the basic environment upon GO, favoring the H_2S dissociation and resulting in the high desulfurization performance of MCNs-PEI (Fig. 6a). Furthermore, the concentration of active free radicals in the system has been increased due to the introduction of active sites upon GO, which is favorable for O_2 activation and further boosts the H_2S oxidation (Fig. 6b). With increasing the loading content of PEI, the sulfur capacity gradually raises and a maximum Q_S of 13.68 mmol H_2S/g catalyst is realized with 25% PEI.

Similarly, Sun et al. produced a kind of amino-functionalized lotus-root-like carbon nanofibers (NH_2-PLCNFs) assisted by dielectric barrier discharge (DBD) plasma technology[25]. As the diffusion highway, the inside channels also allow nanofibers great S storage and physical confinement abilities, while the porous structure in carbon wall increases the reactive area of catalysts and, to a certain extent, guarantees the entry of gaseous reactants. Together with the synergistic contribution between unique structure and -NH_2 functionalities, the catalyst exhibits efficient desulfurization abilities with Q_S of 3.49 g H_2S/g catalyst. (Fig. 6c). The whole process of H_2S selective oxidation upon NH_2-PLCNFs are as follows: (i) the water-film formation on the basis of capillary effect, (ii) H_2S adsorption and reaction with $-NH_2$ to form HS^- and

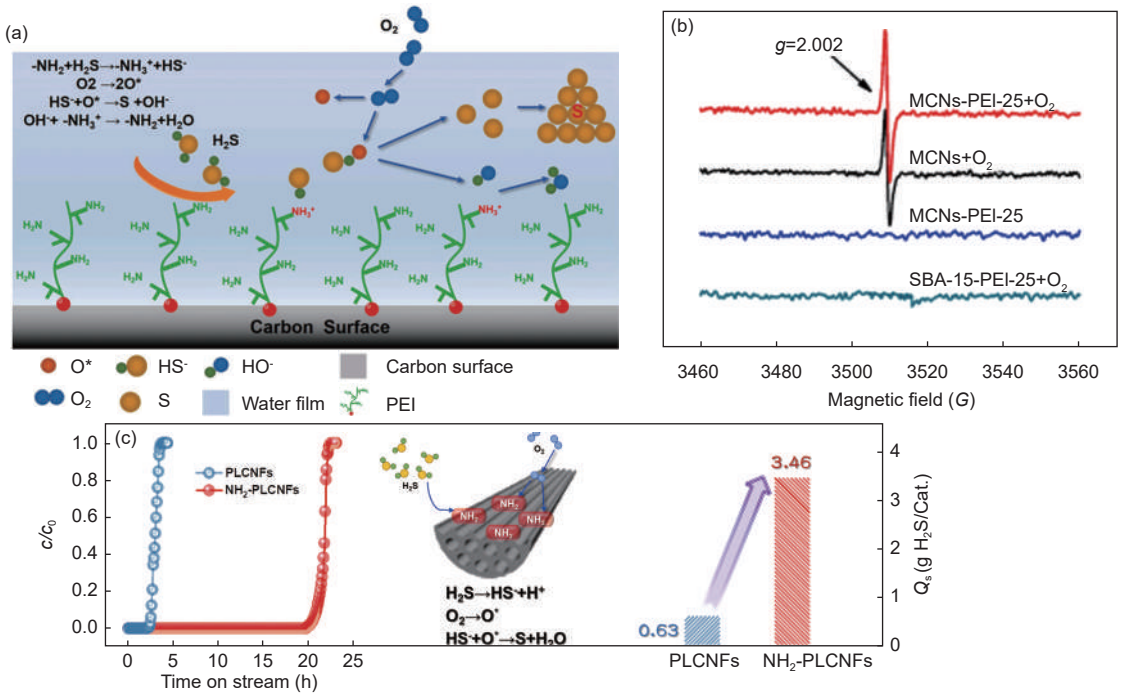

Fig. 6 (a) Schematic diagram of H_2S oxidation and sulfur deposition on MCNs-PEI-25. (b) EPR spectra of various catalysts under different conditions[46]. (Reprinted with permission by Elsevier, Copyright 2016) (c) Comparison of the desulfurization performance between NH_2-PLCNFs and PLCNFs[25]. (Reprinted with permission by WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2022).

$-NH_3^+$, (iii) O_2 activation to active free radical, (iv) HS^- reaction with oxygen radical for generation of S and OH^-, (v) the storage and fixation of as-formed S in lotus-root-like nanochannels.

3.2.3 O-containing group functionalized porous carbons

As a special carbon, graphene oxide with lots of O-containing functional groups and structural defects has been regarded as an ideal playground for catalysis, and has been widely used as a desulfurization catalyst in recently years. It is reported that the 2D plane could achieve the more S deposition than that in pores[71], which is favorable for improving the desulfurization performance. Hence, the thin 2D plane with more reactive sites endows GO with excellent reactivity and processability[72–77]. Nevertheless, the graphene nanosheets prefer to stack to form graphite-like bulks due to the action of strong π-π interaction, which would remarkedly reduce the effective utilization of graphene units. Constructing a three-dimensional (3D) interconnected network is verified as a useful method to enhance the practicality of graphene nanosheets. Inspired by this, 3D alkaline graphene aerogels (AGAs) produced by GO have been firstly used in the field of desulfurization by Long's group[47]. The open network of AGAs promotes the gas diffusion, and the O-containing functional groups on surface, with the effect of hydrogen bonds, would uniformly anchor the alkali substance (Fig. 7a) and facilitate the capture of H_2O molecules to form the water-film (Fig. 7b). Finally, a saturated capacity of 3.19 g H_2S/g catalyst has been achieved. Additionally, Yang's group demonstrated that the aqueous GO suspension was favorable for dispersing the hydrophilic GO monolayers, guaranteeing the full contact between H_2S and GO for further redox reaction[78]. During this process, H_2S was oxidized to elemental S that deposited on the reduced GO (RGO) nanosheets, eventually producing a H_2S-reduced graphene oxide/sulfur (HRGO/S) composite.

4 Carbon supported heterogeneous materials for H_2S selective oxidation

Coupling carbon with metal oxides for improving the desulfurization performance has been developed in the last few years. A strategy has been re-

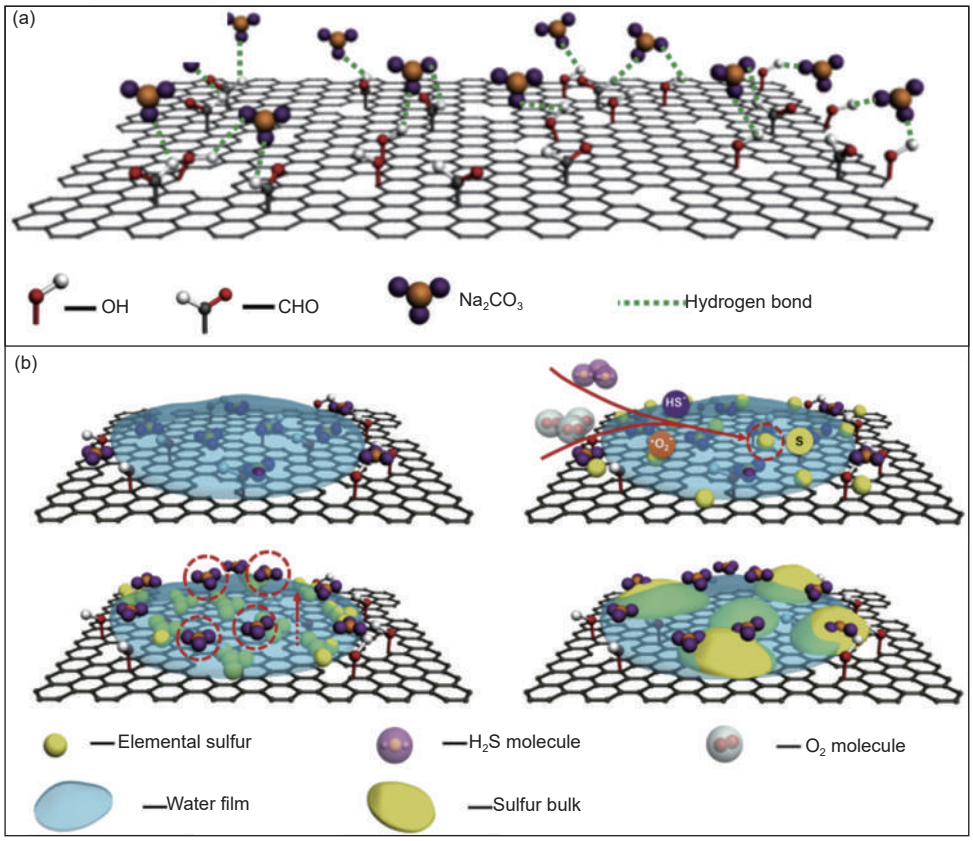

Fig. 7　(a) A proposed mechanism of Na_2CO_3 deposition on graphene nanosheets. (b) Schematic diagram of H_2S oxidation and sulfur deposition on AGAs[47]. (Reprinted with permission by Elsevier, Copyright 2020).

ported by Fan's group for enhancing the catalytic activity by varying the interaction between N-doped carbon and ZnO[79]. The coal-based activated carbon (AC) is used as the matrix, whose interaction with ZnO is modulated by the amount of introduced N species on its surface. It is demonstrated that such interaction can reduce the electron density of ZnO, some defect sites, such as oxygen vacancies, are thus generated[80]. These defective sites are confirmed to boost the adsorption of free radicals. After the water vapor in the feedstock condenses on the surface, the hydroxylation of ZnO occurs on its surface and provides a weak alkali environment for the dissociation of H_2S to HS^-[81–82], which is further oxidized by the adsorbed oxygen-free radicals to elemental S.

Pan et al. designed the catalyst of MgO-loaded porous carbon (PC/MgO) and demonstrated by DFT calculations that the couple of MgO with carbon can realize the surficial enrichment of produced free radicals (Fig. 8a-b), the radical detection analysis with electron paramagnetic resonance (EPR) characterization also confirms this point (Fig. 8c)[24]. In addition, MgO with weak alkaline could promote the H_2S adsorption and its dissociation. Compared to other alkali-modified porous carbon including PC/Na_2CO_3 and PC/NaOH, whose EPR intensities are almost indistinguishable from that of pure PC. Whereas the EPR intensity enhances obviously when PC is coupled with MgO (Fig. 8d), indicating the effect of MgO for radical enrichment and promotion of H_2S oxidation (Fig. 8e). Furthermore, Bandozs's group[83] synthesized a series of bifunctional ZnO-MgO/activated carbon desulfurizers (Mg_xZn_{1-x}/AC) with developed porous structure and high dispersion of metal oxides. Owing to the weak water-solubility of ZnO and MgO, their basicity makes H_2S-dissociation continuously be promoted. Thus, the desulfurization capacity could be enhanced.

Recently, the heterostructure of 2D CaO/carbon nanosheets was synthesized as room-temperature desulfurization catalysts[71], whose superior Q_S up to 9.1 g H_2S/g catalyst is caused by the comprehensive boosting for the enrichment of free radical, the dissociation

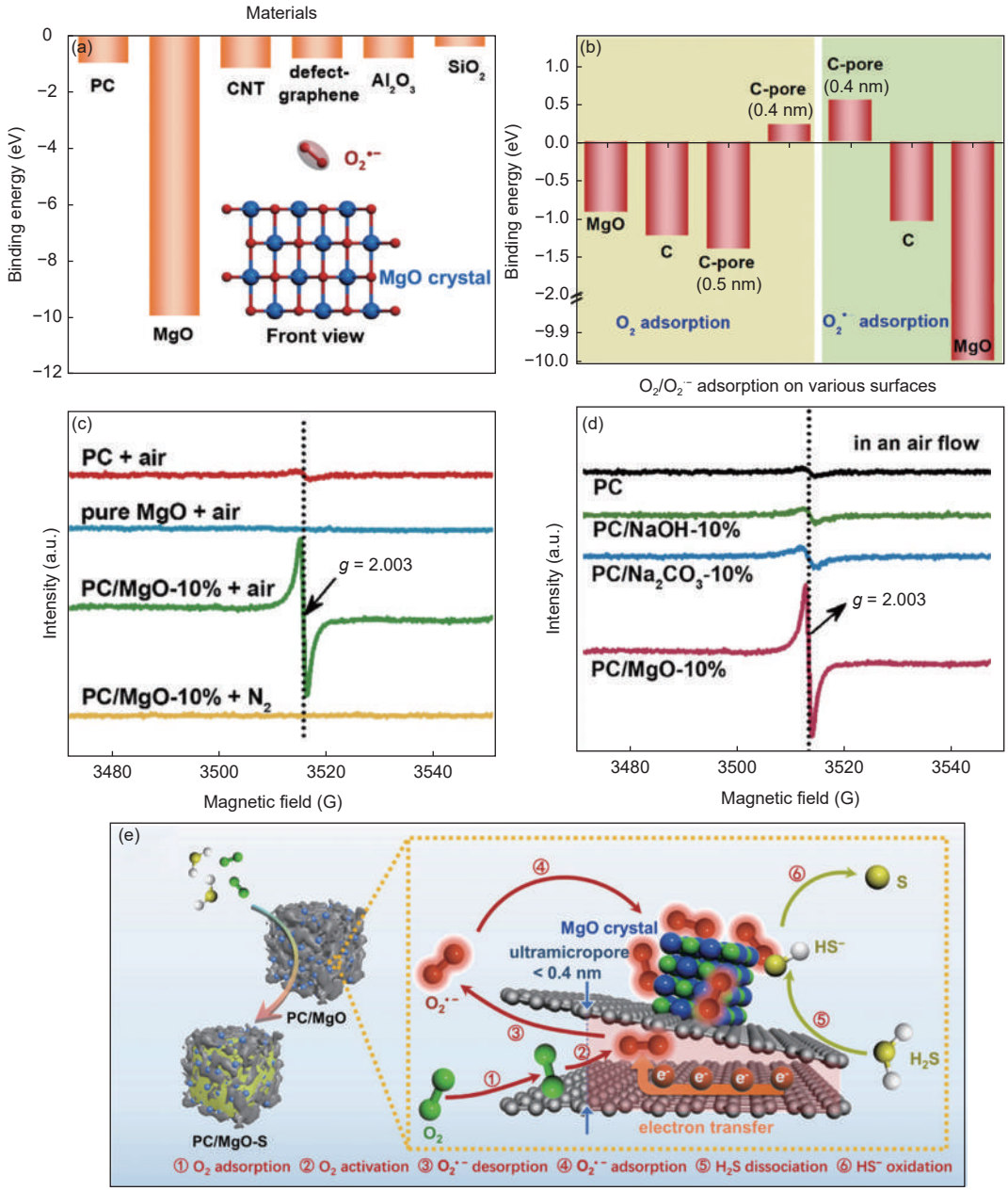

Fig. 8 (a) Binding energy of $O_2^{\bullet-}$ radical on the surface of various catalysts, the inset in (a) is the front view of the adsorption model. (b) Comparison of the binding energy of O_2 and $O_2^{\bullet-}$ radical adsorbed on various surfaces. EPR spectra of (c) different systems and (d) various alkali-modified PC catalysts in an air-flow. (e) Schematic diagram of H_2S oxidation and sulfur deposition on PC/MgO catalysts[24]. (Reprinted with permission by American Chemical Society, Copyright 2021).

of H_2S, and the storage of S. It can be suggested from the EPR results that the carbon matrix is responsible for the O_2 activation and the superoxide radical's generation. The couple of CaO with carbon can enhance the trap of the generated oxygen radicals and increases the alkalinity of carbon matrix for promoting the H_2S dissociation. Moreover, the 2D plane of the heterostructure is favorable for exposing more active sites, thus boosting the catalytic reaction.

The desulfurization performances of carbon-based materials mentioned above are summarized in Table 1, and the related parameters of reaction systems are also listed and compared.

5 Applications of spent desulfurization catalyst in Li-S batteriess

The chemical-reaction-induced S deposition is expected to realize the *in-situ* S growth to produce the

Table 1　Carbon-based catalysts for the selective oxidation of H_2S to elemental sulfur at low temperature.

Catalysts	Reaction conditions	$Q_S(g_{H_2S}/g_{catalyst})$	Reference
Na_2CO_3-impregnated activated carbon fibers	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	0.2-0.8	[56]
Alkaline mesoporous carbons	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 25 °C; flow rate 150 mL min^{-1}.	4.49	[38]
Na_2CO_3-impregnated carbon aerogels	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	2.26	[65]
Millimeter-sized mesoporous carbon spheres	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	2.46	[63]
N-rich mesoporous carbon	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	2.77	[27]
N-doped porous carbon nanofibers	H_2S 1000×10^{-6}; O_2 2%; RH 70%; 25 °C; flow rate 100 mL min^{-1}.	3.57	[26]
N-doped mesoporous carbon nanosheets	H_2S 1000×10^{-6}; O_2 2%; RH 70%; room temperature; flow rate 200 mL min^{-1}.	1.37	[39]
Graphene aerogels	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	3.19	[47]
N-functionalized mesoporous carbon nanosheets	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 25 °C; flow rate 150 mL min^{-1}.	0.47	[46]
Amino-functionalized lotus-root-like carbon nanofibers	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 25 °C; flow rate 25 mL min^{-1}.	3.46	[25]
ZnO/N-modified AC	H_2S 600 mg/m^3; pre-humidified for 1.5 h using the moist N_2 (ca. 3% moisture); 30 °C; flow rate 100 mL min^{-1}.	0.06	[79]
MgO-loaded porous carbon	H_2S 1000×10^{-6}; O_2 1%; RH 80%; 30 °C; flow rate 150 mL min^{-1}.	2.40	[24]
ZnO-MgO/activated carbon	H_2S 850 mg/m^3; pre-humidified for 1.5 h using the moist N_2 (ca. 3% moisture); 30 °C; flow rate 100 mL min^{-1}.	0.11	[83]
CaO/carbon nanosheets	H_2S 1000×10^{-6}; O_2 1%; RH, 80%; 30 °C; flow rate 150 mL min^{-1}.	9.10	[71]

carbon/sulfur composite, which could be regarded as the ideal cathode candidate of LSBs. In 2014, Yang's group achieved the reduction of GO and the oxidation of H_2S pollutant simultaneously in a liquid environment, and the graphene/S hybrid was prepared by this chemical process (Fig. 9a)[78]. During the process, GO is effectively reduced while H_2S is oxidized to elemental S that uniformly distributed on the graphene layers, and the 2D graphene/S plane (HRGO/S) are interconnected with each other to form a convoluted structure (Fig. 9b-d). The obtained composite is expected to be an ideal candidate for LSB cathodes, presenting the outstanding electrochemical performance and cycling stability (Fig. 9e-f). Two points are responsible for the excellent power properties: the evenly deposition of S on the tightly convoluted graphene layers, and the presence of O-containing functional groups, which leads to a far superior rate performance to the cathode of GN/S (prepared by the method of molten S diffusion, Fig. 9g). Then, using the similar method of redox-triggered S deposition and self-assembly of GO, followed by the strategy of evaporation-induced volume shrinkage, Yang et al. further prepared a compact graphene/sulfur composite for high-density LSBs[84]. This assembly delivers a much higher volumetric capacity than other common carbon/sulfur cathodes.

Moreover, according to the reaction of SO_2 + $H_2S \rightarrow S + H_2O$, the water was used as the medium to produce water-dispersed sulfur nanoparticles (WDS, Fig. 10a)[85]. Various sulfur/carbon composites with adjustable sulfur content can be easily prepared by contaminant-free WDS due to its excellent aqueous dispersibility. Based on the totally green strategy, Yang et al. dispersed multi-walled carbon nanotubes (MWCNTs) into WDS to prepare the S/MWCNT composite, which are connected with each other to build a 3D conductive architecture with very uniform S deposition (Fig. 10b-c). The S/MWCNT membranes with different S contents (S-*x*/MWCNT) can be obtained by changing the concentration of WDS, and show their excellent electrochemical performance when used as LSBs cathodes (Fig. 10d-e). Additionally, using graphene and PANI as substrates for WDS deposition, various cathodes could also be prepared, showing the practicality of this strategy in fabricating the advanced electrode materials with high-performance.

Similarly, Sun et al. used an efficient bottom-up catalytic approach to produce the sulfur/carbon composite for high-performance LSB cathodes[61]. The H_2S pollutant could be selectively oxidized to elemental S by the catalyst of a N-rich mesoporous carbon and further layer-by-layer deposited on the carbon framework. This uniform S deposition enables the strong bind between atomic S and the carbon network,

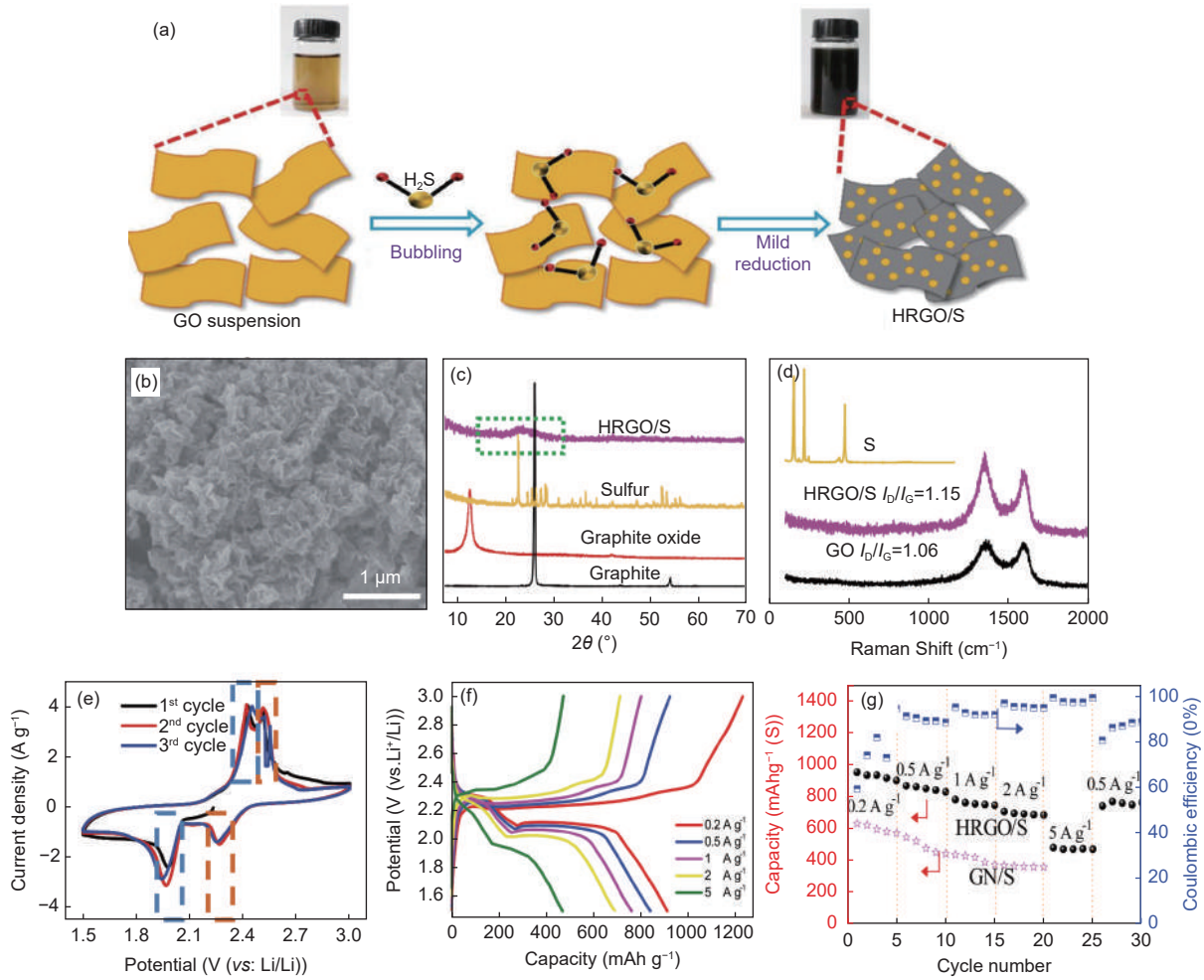

Fig. 9 (a) Preparation schematic and (b) SEM image of HRGO/S composite. (c) XRD patterns, and (d) Raman spectra of different samples. (e) CV curves (scan rate: 0.1 mV s^{-1}), and (f) discharge/charge profiles of HRGO/S cathode. (g) Rate performance of different S cathodes[78]. (Reprinted with permission by WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2013).

realizing effective immobilization of electroactive substance. In addition, the doped-N atoms can increase the interactions between carbon and polysulfides, and mitigate the shuttle effect of polysulfides effectively. When the composite was used as a LSB cathode material, a reversible capacity of 939 mAh g^{-1} at 0.2 C after 100 cycles and a superior rate capability of 527 mAh g^{-1} at 5 C after 70 cycles can be achieved.

Further enhancements have been made in the last few years. Wang's group reported the integrated strategy of H_2S selective oxidation and LSBs enabled by amino-functionalized porous lotus-root-like carbon nanofibers (NH_2-PLCNFs)[25]. The oxidation of H_2S pollutant and S growth are simultaneously realized upon the metal-free catalyst (Fig. 11a), and the spent catalyst with S deposition (S@NH_2-PLCNFs) can be regarded as an ideal cathode material for LSBs, due to its high-efficient desulfurization capacity with the Q_S of 3.46 g H_2S/g catalyst derived from the strong covalent bonding between deposited S with NH_2-functionalized carbon nanofibers. Together with the physical confinement of nanochannels to polysulfides, a reversible specific capacity of 705.8 mAh g^{-1} at 1 C after 1 000 cycles, and an excellent cycling stability was obtained when S@NH_2-PLCNFs was assembled as the LSB cathode (Fig. 11b-c). On the basis of the capillary effect on water and gas-liquid-solid chemical reaction, the uniform S growth is induced upon the nanochannels, just like the chemical vapor deposition (CVD), resulting in the superior power performance than that prepared by the physical method of traditional molten infusion (S/NH_2-PLCNF-M).

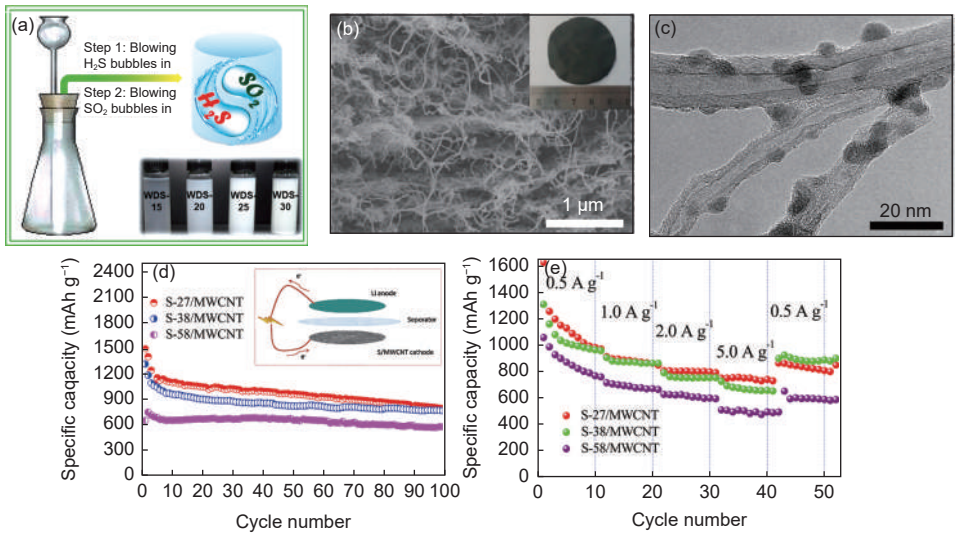

Fig. 10　(a) Preparation schematic of WDS. (b) SEM and (c) TEM images of S-38/MWCNT, the inset in (b) is a photograph of the membrane. (d) Cycling performance (current density: 1.0 A g^{-1}), and (e) rate performance of S/MWCNT cathode, the inset in (d) is the schematic of coin cell composition[85]. (Reprinted with permission by Elsevier Copyright 2017).

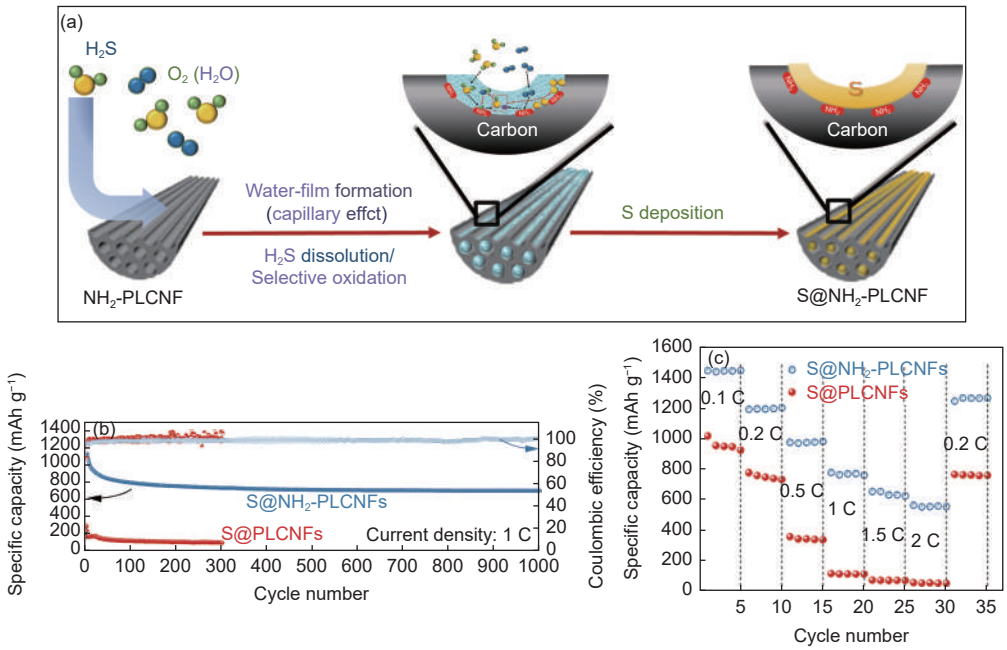

Fig. 11　(a) Schematic diagram of the *in-situ* fabrication of LSB cathodes by H_2S selective oxidation. (b) Cycling performance (current density: 1 C), and (c) rate performance of various S cathodes[25]. (Reprinted with permission by WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim, Copyright 2022).

6　Conclusions and outlook

In summary, we discuss the development of carbon-based materials from the modulation strategies for room-temperature H_2S catalytic oxidation, and the expanded application of spent catalysts for energy storage system. Carbon materials have the advantages of controllable surface chemistry and large specific surface area, as well as developed pores. When used as a desulfurization catalyst, carbon-based materials can thermodynamically decrease H_2S to a subparts-per-million level and realize the selective oxidation to solid S. The complete "green" transform of H_2S pollutant to precious S resource and the *in-situ* preparation of electrode for advanced energy storage devices can be achieved simultaneously. The critical factors for high-efficiency catalyst design are as follows: (i) suitable surface chemistry for H_2S dissociation, (ii) efficient catalytic center for O_2 activation, and

(iii) a developed micro-mesoporous structure for gas adsorption and storage of products. Although significant progress has been made, several key points for further development and large-scale application of H_2S selective oxidation must be considered.

(1) The design of catalytic materials. Typically, to sufficiently improve the H_2S dissociation, more than 20 wt.% of alkaline substances are needed for most carbon materials, even for some heteroatom-doped systems. Nevertheless, that's generally at the expense of covering active sites. There are a couple of strategies that can be employed to promote the H_2S anchoring and dissociation such as defect engineering, dispersity engineering of adsorptive sites, and increasing the adsorptive sites/water/H_2S contact area through inter- or intra-molecular interactions. A small amount of metal doping is promising to be a win-win approach to regulate the electronic states of the adsorptive center for adsorption-dissociation, and change the regional electron density of carbon layers for increasing the catalytic activity. Whereas the consideration of how to protect the metal species from the reaction in the oxidation process is essential, and the degree of doping involves the balance of oxidation performance and cost, should also be considered.

(2) Combination of theoretical simulation and experiment. Elaborating on the catalytic oxidation mechanism is believed to offer a basis for the design of room-temperature desulfurizer. The systematic research is absolutely essential to further define the catalytic sites, which have been mostly considered as carbon atoms in defective or edge sites, while some believe that doped heteroatoms are the origin of catalytic activity. This needs to be further clarified with the help of theoretical calculation or other advanced characterization. The clarification of the reaction mechanism can not only provide theoretical guidance to design high-efficient catalyst, but also help to avoid the production of by-products in reaction (such as SO_2 and SO_4^{2-}). Furthermore, to visualize the oxidation process and confirm the factors that control the catalytic reaction rate, advanced dynamic characterization technologies that featuring in real-time recording are necessary. For instance, synchrotron X-ray powder diffraction coupled with high-resolution electron microscopy could be applied to investigate the process of sulfur deposition upon nanopores and the structural evolution of catalysts. It is expected to offer more foundational understanding of the synergy between structural and chemical property on H_2S oxidation. While for S electrodes prepared by the reaction-reduced method, the *in-situ* characterization can provide a basis for exploring the relationship between desulfurization performance and optimal S loading, which is related to the uniformity of S growth and its electrochemical performance.

(3) Practical application test. At the current stage, the H_2S catalytic oxidation was operated as a strict stoichiometric O_2/H_2S ratio rather than at various ratios, and the flow is controlled at a fixed rate. The impact of dynamic environmental changes, for example, the composition of feed gas, humidity and partial pressure, on oxidative desulfurization is unclear, which is the greatest challenge for achieving actual industrialization. Generally, the inevitable appearance of sulfate (SO_4^{2-}) during the H_2S selective oxidation may be related to the O_2 concentration in reaction systems, thus the unclear relationship between the O_2 concentration in feed gas and the degree of H_2S oxidation needs to be explored further. Additionally, take the cost into consideration, catalyst should be designed to be scalable for mass production and be compliant with industrial production processes.

To sum up, carbon materials have the infinite possibilities and tailored abilities that can meet various demands of room-temperature H_2S oxidation (i.e. adsorption, catalytic oxidation, storage of products), it is believed that constructing a carbon-based catalyst is a prospective method for achieving the high-efficiency desulfurization. Considering the above challenges and numerous opportunities for improvement, the design of carbon for room-temperature desulfurization has great research value, and there is still a lot of work to be done in the future.

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References

[1] Ghosh T K, Tollefson E L. A continuous process for recovery of sulfur from natural-gas containing low concentrations of hydrogen-sulfide[J]. Canadian Journal of Chemical Engineering, 1986, 64(6): 960-968.

[2] Seredych M, Bandosz T J. Desulfurization of digester gas on catalytic carbonaceous adsorbents: Complexity of interactions between the surface and components of the gaseous mixture[J]. Industrial & Engineering Chemistry Research, 2006, 45(10): 3658-3665.

[3] Bandosz T J, Le Q. Evaluation of surface properties of exhausted carbons used as H_2S adsorbents in sewage treatment plants[J]. Carbon, 1998, 36(1-2): 39-44.

[4] Turk A, Mahmood K, Mozaffari J. Activated carbon for air purification in New-York-City sewage-treatment plants[J]. Water Science and Technology, 1993, 27(7-8): 121-126.

[5] Bandosz T J, Block K A. Removal of hydrogen sulfide on composite sewage sludge-industrial sludge-based adsorbents[J]. Industrial & Engineering Chemistry Research, 2006, 45(10): 3666-3672.

[6] Ni J Q, Heber A J, Diehl C A, et al. Ammonia, hydrogen sulphide and carbon dioxide release from pig manure in under-floor deep pits[J]. Journal of Agricultural Engineering Research, 2000, 77(1): 53-66.

[7] Hendrickson R G, Chang A, Hamilton R J. Co-worker fatalities from hydrogen sulfide[J]. American Journal of Industrial Medicine, 2004, 45(4): 346-350.

[8] Zhang X, Tang Y Y, Qu S Q, et al. H_2S-selective catalytic oxidation: catalysts and processes[J]. Acs Catalysis, 2015, 5(2): 1053-1067.

[9] Rebolledo-Libreros M E, Trejo A. Gas solubility of H_2S in aqueous solutions of N-methyldiethanolamine and diethanolamine with 2-amino-2-methyl-1-propanol at 313, 343, and 393 K in the range 2.5-1036 kPa[J]. Fluid Phase Equilibr, 2004, 224(1): 83-88.

[10] Sidi-Boumedine R, Horstmann S, Fischer K, et al. Experimental determination of hydrogen sulfide solubility data in aqueous alkanolamine solutions[J]. Fluid Phase Equilibr, 2004, 218(1): 149-155.

[11] Pieplu A, Saur O, Lavalley J C, et al. Claus catalysis and H_2S selective oxidation[J]. Catalysis Reviews-Science and Engineering, 1998, 40(4): 409-450.

[12] Duan H Q, Yan R, Koe L C C, et al. Combined effect of adsorption and biodegradation of biological activated carbon on H_2S biotrickling filtration[J]. Chemosphere, 2007, 66(9): 1684-1691.

[13] Xiao Y H, Wang S D, Wu D Y, et al. Catalytic oxidation of hydrogen sulfide over unmodified and impregnated activated carbon[J]. Separation and Purification Technology, 2008, 59(3): 326-332.

[14] Seredych M, Bandosz T J. Role of microporosity and nitrogen functionality on the surface of activated carbon in the process of desulfurization of digester gas[J]. Journal of Physical Chemistry C, 2008, 112(12): 4704-4711.

[15] Keller N, Pham-Huu C, Crouzet C, et al. Direct oxidation of H_2S into S. New catalysts and processes based on SiC support[J]. Catalysis Today, 1999, 53(4): 535-542.

[16] Wu X X, Kercher A K, Schwartz V, et al. Activated carbons for selective catalytic oxidation of hydrogen sulfide to sulfur[J]. Carbon, 2005, 43(5): 1087-1090.

[17] Bandosz T J, Bagreev A, Adib F, et al. Unmodified versus caustics-impregnated carbons for control of hydrogen sulfide emissions from sewage treatment plants[J]. Environmental Science & Technology, 2000, 34(6): 1069-1074.

[18] Zou H K, Sheng M P, Sun X F, et al. Removal of hydrogen sulfide from coke oven gas by catalytic oxidative absorption in a rotating packed bed[J]. Fuel, 2017, 204: 47-53.

[19] Lee E K, Jung K D, Joo O S, et al. Support effects in catalytic wet oxidation of H_2S to sulfur on supported iron oxide catalysts[J]. Applied Catalysis a-General, 2005, 284(1-2): 1-4.

[20] Huang G, He E Y, Wang Z D, et al. Synthesis and characterization of *gamma*-Fe_2O_3 for H_2S removal at low temperature[J]. Industrial & Engineering Chemistry Research, 2015, 54(34): 8469-8478.

[21] Wang J, Wang L J, Fan H L, et al. Highly porous copper oxide sorbent for H_2S capture at ambient temperature[J]. Fuel, 2017, 209: 329-338.

[22] Pahalagedara L R, Poyraz A S, Song W Q, et al. Low temperature desulfurization of H_2S: High sorption capacities by mesoporous cobalt oxide via increased H_2S diffusion[J]. Chemistry of Materials, 2014, 26(22): 6613-6621.

[23] Yang C, Kou J W, Fan H L, et al. Facile and versatile sol-gel strategy for the preparation of a high-loaded ZnO/SiO_2 adsorbent for room-temperature H_2S removal[J]. Langmuir, 2019, 35(24): 7759-7768.

[24] Pan Y K, Xu H, Chen M Q, et al. Unveiling the nature of room-temperature O_2 activation and O_2^- enrichment on MgO-loaded porous carbons with efficient H_2S oxidation[J]. Acs Catalysis, 2021, 11(10): 5974-5983.

[25] Sun M H, Wang X Z, Li Y, et al. Integration of desulfurization and lithium-sulfur batteries enabled by amino-functionalized porous carbon nanofibers [J]. Energy Environmental Materials, 2022,DOI: 10.1002/eem2.12369.

[26] Sun M H, Wang X Z, Pan X, et al. Nitrogen-rich hierarchical porous carbon nanofibers for selective oxidation of hydrogen sulfide[J]. Fuel Processing Technology, 2019, 191: 121-128.

[27] Sun F G, Liu J, Chen H C, et al. Nitrogen-rich mesoporous carbons: Highly efficient, regenerable metal-free catalysts for low-temperature oxidation of H_2S[J]. Acs Catalysis, 2013, 3(5): 862-870.

[28] Chen Q J, Wang J T, Liu X J, et al. Alkaline carbon nanotubes as

effective catalysts for H_2S oxidation[J]. Carbon, 2011, 49: 3773-3780.

[29] Chiang H L, Tsal J H, Tsal C L, et al. Adsorption characteristics of alkaline activated carbon exemplified by water vapor, H2S, and CH3SH gas[J]. Separation Science and Technology, 2000, 35(6): 903-918.

[30] Wild M, O'Neill L, Zhang T, et al. Lithium sulfur batteries, a mechanistic review[J]. Energy & Environmental Science, 2015, 8(12): 3477-3494.

[31] Peng H J, Huang J Q, Cheng X B, et al. Review on high-loading and high-energy lithium-sulfur batteries[J]. Advanced Energy Materals, 2017, 7(24): 1700260.

[32] Pang Q, Liang X, Kwok C Y, et al. A comprehensive approach toward stable lithium-sulfur batteries with high volumetric energy density[J]. Advanced Energy Materals, 2017, 7(6): 1601630.

[33] Bagreev A, Bandosz T J. On the mechanism of hydrogen sulfide removal from moist air on catalytic carbonaceous adsorbents[J]. Industrial & Engineering Chemistry Research, 2005, 44(3): 530-538.

[34] Bandosz T J. On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperatures[J]. Journal of Colloid and Interface Science, 2002, 246(1): 1-20.

[35] Everett D H, Powl J C. Adsorption in slit-like and cylindrical micropores in Henrys Law region-model for microporosity of carbons[J]. Journal of the Chemical Society-Faraday Transactions I, 1976, 72: 619-636.

[36] Brennan J K, Bandosz T J, Thomson K T, et al. Water in porous carbons[J]. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2001, 187: 539-568.

[37] Kante K, Nieto-Delgado C, Rangel-Mendez J R, et al. Spent coffee-based activated carbon: Specific surface features and their importance for H_2S separation process[J]. Journal of Hazardous Materials, 2012, 201: 141-147.

[38] Zhang Z X, Jiang W Y, Long D H, et al. A General silica-templating synthesis of alkaline mesoporous carbon catalysts for highly efficient H_2S oxidation at room temperature[J]. ACS Applied Materials & Interfaces, 2017, 9(3): 2477-2484.

[39] Yu Z F, Wang X Z, Hou Y N, et al. Nitrogen-doped mesoporous carbon nanosheets derived from metal-organic frameworks in a molten salt medium for efficient desulfurization[J]. Carbon, 2017, 117: 376-382.

[40] Wei D C, Liu Y Q, Wang Y, et al. Synthesis of N-doped graphene by chemical vapor deposition and its electrical properties[J]. Nano Lett., 2009, 9(5): 1752-1758.

[41] Sun C L, Wang H W, Hayashi M, et al. Atomic-scale deformation in N-doped carbon nanotubes[J]. Journal of the American Chemical Society, 2006, 128(26): 8368-8369.

[42] Kurak K A, Anderson A B. Nitrogen-treated graphite and oxygen electroreduction on pyridinic edge sites[J]. Journal of Physical Chemistry C, 2009, 113(16): 6730-6734.

[43] Kim D P, Lin C L, Mihalisin T, et al. Electronic-properties of nitrogen-doped graphite flakes[J]. Chemistry of Materials, 1991, 3(4): 686-692.

[44] Maldonado S, Stevenson K J. Influence of nitrogen doping on oxygen reduction electrocatalysis at carbon nanofiber electrodes[J]. Journal of Physical Chemistry B, 2005, 109(10): 4707-4716.

[45] Gong K P, Du F, Xia Z H, et al. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction[J]. Science, 2009, 323(5915): 760-764.

[46] Wang J T, Ke C Y, Jia X F, et al. Polyethyleneimine-functionalized mesoporous carbon nanosheets as metal-free catalysts for the selective oxidation of H_2S at room temperature[J]. Applied Catalysis B-Environmental, 2021, 283: 119650.

[47] Pan Y K, Chen M Q, Hu M F, et al. Probing the room-temperature oxidative desulfurization activity of three-dimensional alkaline graphene aerogel[J]. Applied Catalysis B-Environmental, 2020, 262: 118266.

[48] Pirozzi D, Imparato C, D'Errico G, et al. Three-year lifetime and regeneration of superoxide radicals on the surface of hybrid TiO_2 materials exposed to air[J]. Journal of Hazardous Materials, 2020, 387: 121716.

[49] Hayyan M, Mjalli F S, Hashim M A, et al. Long term stability of superoxide ion in piperidinium, pyrrolidinium and phosphonium cations-based ionic liquids and its utilization in the destruction of chlorobenzenes[J]. Journal of Electroanalytical Chemistry, 2012, 664: 26-32.

[50] Vasudevan D, Wendt H. Electroreduction of oxygen in aprotic media[J]. Journal of Electroanalytical Chemistry, 1995, 392(1-2): 69-74.

[51] Gonchar A, Risse T, Freund H J, et al. Activation of oxygen on MgO: O_2^- radical ion formation on thin, metal-supported MgO (001) films[J]. Angewandte Chemie-International Edition, 2011, 50(11): 2635-2638.

[52] Wang D, Zhao L X, Ma H Y, et al. Quantitative analysis of reactive oxygen species photogenerated on metal oxide nanoparticles and their bacteria toxicity: The role of superoxide radicals[J]. Environmental Science & Technology, 2017, 51(17): 10137-10145.

[53] Li L, Sun T H, Shu C H, et al. Low temperature H_2S removal with 3-D structural mesoporous molecular sieves supported ZnO from gas stream[J]. Journal of Hazardous Materials, 2016, 311: 142-150.

[54] Steijns M, Derks F, Verloop A, et al. The mechanism of the catalytic oxidation of hydrogen sulfide: II. Kinetics and mechanism of hydrogen sulfide oxidation catalyzed by sulfur[J]. Applied Catalysis A-General, 1976, 42(1): 87-95.

[55] Steijns M, Mars P. Role of sulfur trapped in micropores in catalytic partial oxidation of hydrogen-sulfide with oxygen[J]. Journal of Catalysis, 1974, 35(1): 11-17.

[56] Chen Q J, Wang Z, Long D H, et al. Role of pore structure of activated carbon fibers in the catalytic oxidation of H_2S[J]. Industrial & Engineering Chemistry Research, 2010, 49(7): 3152-3159.

[57] Nhut J M, Nguyen P, Pham-Huu C, et al. Carbon nanotubes as

nanosized reactor for the selective oxidation of H_2S into elemental sulfur[J]. Catalysis Today, 2004, 91-92: 91-97.

[58] Bagreev A, Bandosz T J. A role of sodium hydroxide in the process of hydrogen sulfide adsorption/oxidation on caustic-impregnated activated carbons[J]. Industrial & Engineering Chemistry Research, 2002, 41(4): 672-679.

[59] Wang M, Yao L W, Wang J T, et al. Adsorption and regeneration study of polyethylenimine-impregnated millimeter-sized mesoporous carbon spheres for post-combustion CO_2 capture[J]. Applied Energy, 2016, 168: 282-290.

[60] Li W C, Zhang Z X, Wang J T, et al. Low temperature catalytic combustion of ethylene over cobalt oxide supported mesoporous carbon spheres[J]. Chemical Engineering Journal, 2016, 293: 243-251.

[61] Sun F G, Wang J T, Chen H C, et al. Bottom-up catalytic approach towards nitrogen-enriched mesoporous carbons/sulfur composites for superior Li-S cathodes[J]. Scientific Reports, 2013, 3: 2823.

[62] Long D H, Chen Q J, Qiao W M, et al. Three-dimensional mesoporous carbon aerogels: ideal catalyst supports for enhanced H_2S oxidation[J]. Chemical Communications, 2009 (26): 3898-3900.

[63] Zhang Z X, Wang J T, Li W C, et al. Millimeter-sized mesoporous carbon spheres for highly efficient catalytic oxidation of hydrogen sulfide at room temperature[J]. Carbon, 2016, 96: 608-615.

[64] Yan R, Chin T, Ng Y L, et al. Influence of surface properties on the mechanism of H_2S removal by alkaline activated carbons[J]. Environmental Science & Technology, 2004, 38(1): 316-323.

[65] Chen Q J, Wang J T, Liu X J, et al. Structure-dependent catalytic oxidation of H_2S over Na_2CO_3 impregnated carbon aerogels[J]. Microporous and Mesoporous Materials, 2011, 142(2-3): 641-648.

[66] Wu Z X, Webley P A, Zhao D Y. Post-enrichment of nitrogen in soft-templated ordered mesoporous carbon materials for highly efficient phenol removal and CO_2 capture[J]. Journal of Materials Chemistry, 2012, 22(22): 11379-11389.

[67] Yang S B, Feng X L, Wang X C, et al. Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions[J]. Angewandte Chemie-International Edition, 2011, 50(23): 5339-5343.

[68] Shao Y Y, Sui J H, Yin G P, et al. Nitrogen-doped carbon nanostructures and their composites as catalytic materials for proton exchange membrane fuel cell[J]. Applied Catalysis B-Environmental, 2008, 79(1-2): 89-99.

[69] Lai L F, Potts J R, Zhan D, et al. Exploration of the active center structure of nitrogen-doped graphene-based catalysts for oxygen reduction reaction[J]. Energy & Environmental Science, 2012, 5(7): 7936-7942.

[70] Mochida I, Korai Y, Shirahama M, et al. Removal of SO_x and NO_x over activated carbon fibers[J]. Carbon, 2000, 38(2): 227-239.

[71] Pan Y K, Chen M Q, Su Z, et al. Two-dimensional CaO/carbon heterostructures with unprecedented catalytic performance in room-temperature H_2S oxidization[J]. Applied Catalysis B-Environmental, 2021, 280: 119444.

[72] Yoo E, Okata T, Akita T, et al. Enhanced electrocatalytic activity of Pt subnanoclusters on graphene nanosheet surface[J]. Nano Letters, 2009, 9(6): 2255-2259.

[73] Li Y G, Wang H L, Xie L M, et al. MoS_2 Nanoparticles grown on graphene: An advanced catalyst for the hydrogen evolution reaction[J]. Journal of the American Chemical Society, 2011, 133(19): 7296-7299.

[74] Liao G F, Gong Y, Zhang L, et al. Semiconductor polymeric graphitic carbon nitride photocatalysts: the "holy grail" for the photocatalytic hydrogen evolution reaction under visible light[J]. Energy & Environmental Science, 2019, 12(7): 2080-2147.

[75] Song Y J, Qu K G, Zhao C, et al. Graphene oxide: Intrinsic peroxidase catalytic activity and its application to glucose detection[J]. Advanced Materials, 2010, 22(19): 2206-2210.

[76] Su C L, Loh K P. Carbocatalysts: Graphene oxide and its derivatives[J]. Accounts of Chemical Research, 2013, 46(10): 2275-2285.

[77] Gao Y J, Tang P, Zhou H, et al. Graphene oxide catalyzed C-H bond activation: The importance of oxygen functional groups for biaryl construction[J]. Angewandte Chemie-International Edition, 2016, 55(9): 3124-3128.

[78] Zhang C, Lv W, Zhang W G, et al. Reduction of graphene oxide by hydrogen sulfide: A promising strategy for pollutant control and as an electrode for Li-S batteries[J]. Advanced Energy Materials, 2014, 4(7): 1301565.

[79] Yang C, Yang S, Fan H L, et al. Tuning the ZnO-activated carbon interaction through nitrogen modification for enhancing the H_2S removal capacity[J]. Journal of Colloid and Interface Science, 2019, 555: 548-557.

[80] McCluskey M D, Jokela S J. Defects in ZnO[J]. Journal of Applied Physics, 2009, 106(7): 071101.

[81] Wang L J, Fan H L, Ju S G, et al. Design of a sorbent to enhance reactive adsorption of hydrogen sulfide[J]. ACS Applied Materials & Interfaces, 2014, 6(23): 21167-21177.

[82] Yang C, Wang J, Fan H L, et al. Contributions of tailored oxygen vacancies in ZnO/Al_2O_3 composites to the enhanced ability for H_2S removal at room temperature[J]. Fuel, 2018, 215: 695-703.

[83] Chao Y, Wang Y S, Fan H L, et al. Bifunctional ZnO-MgO/activated carbon adsorbents boost H_2S room temperature adsorption and catalytic oxidation[J]. Applied Catalysis B-Environmental, 2020, 266: 118674.

[84] Zhang C, Liu D H, Lv W, et al. A high-density graphene-sulfur assembly: A promising cathode for compact Li-S batteries[J]. Nanoscale, 2015, 7(13): 5592-5597.

[85] Liu D H, Zhang C, Xu Z, et al. $H_2S + SO_2$ produces water-dispersed sulfur nanoparticles for lithium-sulfur batteries[J]. Nano Energy, 2017, 41: 665-673.