Removals of aqueous sulfur dioxide and hydrogen sulfide using CeO₂-NiAl-LDHs coating activated carbon and its mix with carbon nano-tubes

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HIGHLIGHTS

- Mixture of activated carbon and nano-tubes support with good adsorption and conduction.
- NiAl/layered double hydroxide catalyst-sorbent.
- CeO₂ is used as a promoter in redox reactions.
- Ce-doped NiAl/layered double hydroxide/activated carbon catalyst-sorbents.
- Removal of aqueous sulfur dioxide and hydrogen sulfide using adsorption and electrochemical method.

GRAPHICAL ABSTRACT

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ABSTRACT

Ce-doped NiAl/layered double hydroxide was coated at activated carbon by urea hydrolysis method (CeO₂-NiAl-LDHs/AC) in one pot, which was characterized by X-ray diffraction, infrared spectra, field emission scanning electron microscope and electrochemical techniques. CeO₂-NiAl-LDHs/AC shows good uptake for aqueous sulfur dioxide (483.09 mg/g) and hydrogen sulfide (181.15 mg/g), respectively at 25 °C. Meanwhile, the electrochemical removals of aqueous sulfur dioxide and hydrogen sulfide were respectively investigated at the mix of CeO₂-NiAl-LDHs/AC and carbon nano-tubes modified homeod paraffin-impregnated electrode. Both sulfur dioxide and hydrogen sulfide could be effectively oxidized to sulfuric acid at 1.0 V in alkaline aqueous solution.

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1. Introduction

Hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) often come from process streams of industry production, processing and refining of fossil fuels [1,2]. Emissions of these compounds could form

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acid rain and destruct the ozone layer [3]. Besides, H_2S is a corrosive gas towards pipelines and equipment, as well as one of main poisons for many industry catalysts [4]. Therefore, their treatments are significant in terms of industry, environment and human health. Among various treatment methods including oxidation [2,4,5], reduction [6], adsorption [1,3,7] and precipitation [8], both the oxidation and adsorption are effective ways. Many metal based oxide catalysts such as titanium [9], chromium [10], iron [11] and vanadium [12–14] were proposed for the selective oxidation of H_2S to elemental sulfur. But the deactivation for the catalysts lost treatment efficiency and economic advantage. Meanwhile activated carbon was used as adsorbent for H_2S and SO_2 removals [15,16]. Further some catalyst-sorbents formed by activated carbon and metal oxides including V [12], Mn [17], Fe, Co, Ni, Ce and Cu [18] were developed to enhance the removals. Recent reports showed that layered double hydroxides (LDHs) such as Ni/Al-LDHs [1,19], $\text{CeO}_2/\text{MgAl-LDHs}$ [20] and MgFeAl-LDHs [21] are better catalyst-sorbents for SO_2 and H_2S removals. But their micron sizes could result in difficulties in regeneration and separation. Moreover, cerium oxide (CeO_2) is used as a promoter in various redox reactions due to its reducibility and high oxygen storage capacity [16,22]. Therefore, Ce-doped NiAl-LDHs/activated carbon composite may be a promising catalyst-sorbent for the removals, but there has not been any report up to now.

On the other hand, electrochemical oxidation treatment offers an environmentally attractive method to remove SO_2 and H_2S [23–33,34,11,35–37]. Many researches have related the redox of SO_2 and oxidation of H_2S (sulfide) [23]. SO_2 could be oxidized to sulfuric acid [24], and reduced to elemental sulfur [23] or polysulfides [25]. The oxidation product of H_2S (S^{2-}) could be elemental sulfur [27–29,11], SO_3^{2-} [30,33] or a mix of S, S_2^{2-} and SO_4^{2-} [32]. The electrode materials involved in carbon [24], Pt [23,25], Au [31] $\text{Ti}/\text{Ta}_2\text{O}_5\text{-IrO}_2$ [32], V_2O_5 [27], B [29], $[\text{SbVO}(\text{CHL})_2]\text{Hex}$ [30], ferrocyanide [6], cobalt pentacyanonitrosylferrate [34], Fe and Ti mix metal oxide [11], 2,6-dichlorophenolindophenol [33], N,N-diphenyl-p-phenylenediamine [35], 2-(4-fluorophenyl)indole-modified xerogel [36] and hematoxylin [37]. Since the removals could be performed at atmospheric temperature, atmosphere and aqueous, these make electrochemical method very attractive candidates for the removals of aqueous sulfur dioxide and hydrogen sulfide.

In this work, Ce-doped NiAl-LDHs/activated carbon composite ($\text{CeO}_2\text{-NiAl-LDHs/AC}$) was prepared by urea method in one pot. The removals of aqueous SO_2 and H_2S were respectively investigated by adsorption and electro-oxidation methods using $\text{CeO}_2\text{-NiAl-LDHs/AC}$ and its mix with carbon nano-tubes modified paraffin-impregnated electrode ($\text{CeO}_2\text{-NiAl-LDHs/NAC/WGE}$). Here, carbon nano-tubes (CNTs) could improve the conductivity of $\text{CeO}_2\text{-NiAl-LDHs/AC}$.

2. Experiment

2.1. Chemicals and apparatus

Activated carbon (AC) was obtained from Hengxin Environmental Protection Material Company of Huaibei City (Huaibei City, China). Carbon nanotubes (CNTs) were purchased from Sun Nanotech. Co. Ltd. of China and were synthesized by catalytic decomposition of CH_4 on a NiMgO catalyst. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and all other chemicals were Chemical Reagent Company of Shanghai products (China, Shanghai). Doubly distilled water was used to prepare all solutions.

All electrochemical experiments were performed with a CH660B electrochemical workstation (Chenhua, Shanghai, China). A conventional three-electrode electrochemical system was used

for all electrochemical experiments, which consisted of a home-made paraffin-impregnated electrode (WGE), a twisted platinum wire counter electrode, and a saturated calomel reference electrode (SCE). All potentials reported are versus SCE. Field emission scanning electron microscope (FE-SEM) images were obtained on a JSM-600 field emission scanning electron microanalyser (JEOL, Japan). X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX-rB diffractometer with Cu K α radiation. Infrared spectra (IR) were measured at IR 200 (Nicolet America).

2.2. Preparation of $\text{CeO}_2\text{-Ni/Al-LDHs/AC}$

AC was firstly coated with tetraoxalyl ethylenediamine melamine resin to adhere the LDHs (labeled MFT/AC) [38]. 10 g AC was impregnated in 100 mL of mixed acid solution of nitric acid and perchlorate acid (7:3). The mixed solution was ultrasonically agitated for 7 h to form carboxyl-activated carbon; the AC was washed with distilled water to neutral pH, and dried in vacuum at 100 °C with 4 h. In 100 mL flask, the 5 g AC were quickly added in 50 mL 1 mM ethylenediamine. Ethylenediamine modified AC could be obtained with amidation reaction or adsorption. It was centrifuged, washed with acetone and distilled water, and dried in vacuum at 40 °C in 6 h. 5 g ethylenediamine modified AC was quickly put in 50 mL aqueous solution including 1.5 g tetraoxalyl ethylenediamine and 1.8 g melamine, 20 mL 15% formaldehyde and 0.1 g sodium dodecylsulfate with dipping of 4 h, finally tetraoxalyl ethylenediamine modified melamine resin could be evenly coated at the surface of AC under ultrasonic of 1 h at 25 °C. It was collected, washed thoroughly with hot water, cold water, ethanol and acetone, and dried in vacuum (signed MFT/AC).

$\text{CeO}_2\text{-NiAl/LDHs/AC}$ was prepared by urea hydrolysis method [1]. 50.0 mL of a solution ($\text{M}^{2+}/\text{M}^{3+}=2$, $\text{Al}^{3+}/\text{Ce}^{3+}=4$, $\text{Ni}^{2+}+\text{Al}^{3+}+\text{Ce}^{3+}=0.06\text{ M}$, urea/M=4) was prepared. 3 g MFT/AC was vacuumed in 4 h to decrease inner pressure, and quickly put in the solution. MFT/AC could be fully dipped in the solution with less time under an aid of pressure atmosphere in 1 h. Then the mixture was added into a three-neck flask and stirred at 298 K. The flask was soaked in an oil bath previously heated at 363 K to start the hydrolysis reaction. The reaction was stopped by quenching it in a cold-water bath after 48 h under stirring. The resulting material was washed several times with deionized water, and dried at 323 K (labeled as $\text{CeO}_2\text{-NiAl-LDHs/AC}$).

2.3. Specific surface area and pore properties of AC

The specific surface area and pore structure of the carbon samples were determined by N_2 adsorption–desorption isotherms at 77 K (Micrometrics ASAP 2020 system) after being vacuum-dried at 100 °C overnight. The specific surface areas were calculated by the conventional BET (Brunauer–Emmett–Teller) method. The pore size distribution (PSD) plots were recorded from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model.

2.4. Batch of adsorption studies of aqueous sulfur dioxide and hydrogen sulfide

Batch experiments included adsorption equilibrium isotherm, adsorption kinetic and temperature were performed. The purpose was to investigate the uptake of the composite towards aqueous sulfur dioxide and hydrogen sulfide.

Sulfur dioxide (hydrogen sulfide) aqueous solutions were prepared by adding adequate amounts of solid Na_2SO_3 (Na_2S) or by injecting a certain volume of an SO_2 (H_2S)+0.5 M HClO_4 solution into the test solution [23]. For the determination of the amount H_2S (SO_2) in the liquid sample, an excess amount of iodine was

Fig. 1. SEM of AC (A, inset), CeO₂-NiAl/LDHs/AC (A) and (B), mix of CeO₂-NiAl/LDHs/AC with carbon nano-tubes (C).

added to react with H₂S (SO₂) in an acid solution. The amount of excess iodine was determined by titration using sodium thiosulfate (starch as indicator) [2,37]. The determination based following reactions (1)–(3).

2.5. Electrochemical oxidation of aqueous sulfur dioxide and hydrogen sulfide

After CeO₂-NiAl-LDHs/AC was ground into powder, it was mixed with carbon nano-tubs (CNTs) to improve the conductivity. 1 g mixture was dispersed in 25 mL ethanol and 0.5 wt.% nafion with an aid of ultrasonic agitation to give the black suspension. WGE was polished step-by-step to a mirror-like finish with fine wet emery paper (grain size 400, 800), followed by sonication in ethanol and water for 15 min, respectively. After cleaning, 30 μ L suspension was directly cast at WGE and evaporated in the solvent at room temperature (labeled as CeO₂-NiAl-LDHs/NAC/WGE).

Electrochemical oxidation of aqueous sulfur dioxide (hydrogen sulfide) was investigated using cyclic voltammograms (CVs) or potentiostatic method at CeO₂-NiAl-LDHs/NAC/WGE in 0.1 M NaOH. All the electrochemical experiments were carried out at room temperature in N₂ atmosphere.

3. Result and discussion

3.1. Characterization of CeO₂-NiAl-LDHs/AC

Fig. 1 shows FE-SEM of AC (A, inset), CeO₂-NiAl/LDHs/AC (A) and (B) and mix of CeO₂-NiAl-LDHs/AC with carbon nano-tubes (C). The origin AC gives a rough and porous surface in Fig. 1A, inset. After CeO₂-NiAl-LDHs/AC was coated at AC, it could be readily seen that petal-like structures with many cavities evenly distributed at the surface of AC in Fig. 1A and B. Meanwhile CNTs could be observed in mix of CeO₂-NiAl-LDHs/AC with carbon nano-tubes in Fig. 1C.

Fig. 2 shows XRD patterns of AC (a) and CeO₂-NiAl-LDHs/AC (b). The characteristic peak at 23° matches to AC in curve a. A highly crystalline LDH phase could be seen in curve b, the (003), (006), (009), (110) and (113) diffraction peaks, which are evidences for the layered structure [34], appear at 11.2°, 23.8°, 34.9°, 60.3° and 62.2°, respectively. Furthermore, other peaks, located at 2 θ $\approx$ 28°, 35° (overlap with the LDHs), 48° and 57° correspond to the (111), (200), (220) and (311) reflection of CeO₂ in cubic fluorite structure [41]. Thus, a highly crystalline CeO₂-NiAl-LDHs/AC was acquired.

Fig. 3 shows FT-IR spectrums of acid treated AC (a), MFT/AC (b) and CeO₂-NiAl-LDHs/AC (c). In curve a, the carbonyl (C=O)

stretch at 1630 cm⁻¹ could be seen at acid treated AC. In curve b, the peak at 1630 cm⁻¹ matches to carbonyl (C=O) stretch; 1389–1296 cm⁻¹ and 871 cm⁻¹ relate to melamine, which are caused by the framework vibration and the out-of-plane ring deformation; 3317 cm⁻¹, 1630 cm⁻¹, 1430 cm⁻¹, 1156 cm⁻¹ and 717 cm⁻¹ could be traced back to tetraoxalyl ethylenediamine, which are due to the N–H stretch attached to ethylene bridge and N–H bend bridging in the secondary amine (3413 cm⁻¹, 1455 cm⁻¹ and 717 cm⁻¹), N–C=O (1156 cm⁻¹) and the C=O and –OH in COOH (1630 cm⁻¹, 1430 cm⁻¹) [38]. In curve c, a broad adsorption band around 3440 cm⁻¹ relates to the O–H stretching vibrations of interlayer water molecules and hydroxyl groups of hydrotalcite layers. The absorption band at 1380 cm⁻¹ is attributed to the antisymmetric stretching vibrations of interlayer carbonate group [39]. This characteristic peak indicates that anions of LDHs consist of carbonate besides the hydroxyl ions. The absorption band at near 1630 cm⁻¹ is originated by the bending mode of interlayer water molecules and M–OH vibration in the brucite-like layers of the LDHs, respectively [40]. In the low-frequency region, the bands at 975 cm⁻¹, 786 cm⁻¹ are ascribed to the lattice vibration modes attributed to M–O and O–M–O vibrations [16,22,41].

Fig. 2. XRD patterns of AC (a) and CeO₂-NiAl-LDHs/AC (b).

Fig. 3. FT-IR spectrums of acid treated AC (a), MFT/AC (b) and CeO₂-NiAl-LDHs/AC (c).

Table 1
Specific surface area and pore properties of AC, MFT/AC and CeO₂-NiAl/LDHs/AC.

Sample	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
^a AC	743.19	0.063	4.65
MFT/AC	333.13	0.055	3.76
CeO ₂ -NiAl/LDHs/AC	110.12	0.045	2.74

^a Acid treated coal active charcoal. **Fig. 4.** Effect of time on the adsorption capacities of SO₂ and H₂S at CeO₂-NiAl-LDHs/AC from initial concentration 0.1 M.

The physical and textural properties of CeO₂-NiAl-LDHs/AC were further investigated and the results were summarized in Table 1. The average pore sizes of 27.38 Å is comparative to origin AC and MFT/AC with obvious decrease; the surface area of 110.12 m² g⁻¹ for CeO₂-NiAl-LDHs/AC is significantly decreased compared to that of AC and MFT/AC. These illustrated that the CeO₂-NiAl-LDHs probably coated at the out and inner surface of AC.

3.2. A batch adsorption experiments

In order to investigate the absorption property of the composite, batch adsorption experiments were performed. The uptakes of aqueous sulfur dioxide and hydrogen sulfide were investigated at CeO₂-NiAl-LDHs/AC with 0.1 M initial concentration, respectively.

Adsorption kinetics: As shown in Fig. 4, the effects of contact time on the adsorption capacities of aqueous sulfur dioxide and hydrogen sulfide were illustrated at the composite from initial concentration 0.1 M at 25 °C. The removals increase rapidly at the initial stage of adsorption. Maximum adsorption capacities respectively reach within 3 h for SO₂ and 4 h for H₂S. These are due to the decrease of adsorption sites at CeO₂-NiAl-LDHs/AC, which gradually interacted with them. In present experiments, SO₂ of 462.4 mg g⁻¹ and H₂S of 116.8 mg g⁻¹ were adsorbed at CeO₂-NiAl-LDHs/AC in 4 h.

Two kinetic models such as pseudo-first-order and pseudo-second-order are able to interpret the rate and mechanism of each

adsorption process. The pseudo-first-order model was described empirically by Lagergren Eq. (4) and theoretically by Azizian Eq. (5).

$$\log(q_{e1} - q_t) = \log q_{e1} - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \quad (5)$$

where q_e is the amount adsorbed at equilibrium, q_m is the maximum adsorption capacity of the adsorbent, t is adsorption time, k_1 and k_2 are the pseudo-first-order constant and pseudo-second-order constant. The pseudo-first-order constant (k_1), pseudo-second-order constant (k_2), and linear correlation coefficient (R^2) were listed in Table 2. The pseudo-second-order model seems to best describe the adsorption kinetics of SO₂ and H₂S. When the pseudo-second-order model is the best fit for the experimental data, the sorption mechanism involves chemisorption.

Adsorption isotherms: The equilibrium data were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich in Eqs. (6)–(9) equilibrium models in order to obtain the best fitting isotherm.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

$$q_e = RT \frac{\ln k_t}{b_t} + RT \frac{\ln C_e}{b_t} \quad (8)$$

$$\ln q_e = \ln q_D - 2B_D RT \ln(1 + 1/C_e) \quad (9)$$

where K_L is the Langmuir isotherm parameter, K_F is the Freundlich isotherm parameter, b_t and k_t are Temkin isotherm parameters, R is the gas constant and T is the absolute temperature. q_e is the amount adsorbed at equilibrium, q_m is the maximum adsorption capacity of the adsorbent, and n is the heterogeneity parameter of the adsorbent surface. B_D is related to the free energy of sorption per mole of the sorbate, and q_D is the Dubinin–Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface. The adsorption isotherms for SO₂ and H₂S at different temperatures are shown in Fig. 5, and the corresponding parameters of adsorption isotherms are presented in Table 3. The results indicate that the Langmuir isotherms are well fit to describe the SO₂ and H₂S adsorption equilibria at CeO₂-NiAl-LDHs/AC. In present results, the maximum adsorption capacities (q_m) are 483.09–510.20 mg g⁻¹ for SO₂, and 181.15–197.23 mg g⁻¹ for H₂S respectively, while the temperature varies from 25 °C to 45 °C. The maximum adsorbed capacities are increased as the adsorption system temperature rose, which mean that the increase in energy favored the adsorption at

Table 2
Parameters of the pseudo first-order and pseudo second-order for the adsorptions of aqueous SO₂ and H₂S at CeO₂-NiAl-LDHs/AC.

	Initial C (mM)	$q_{e,exp}$ (mg/g)	Pseudo-first-order-constant			Pseudo-second-order-constant		
			$q_{e1,cal}$ (mg/g)	k_1 (g/mg h)	R^2	$q_{e2,cal}$ (mg/g)	K_2 (g/mg h)	R^2
SO ₃ ²⁻	20	391.2	1229.1	0.0314	0.958	568.2	1.78E-05	0.973
	40	405.6	1112.9	0.0307	0.972	552.5	2.25E-05	0.983
	60	424.0	1038.7	0.0302	0.955	558.7	2.54E-05	0.988
	80	442.4	1124.7	0.0308	0.973	568.2	2.78E-05	0.995
	100	462.4	793.8	0.0284	0.981	581.4	2.99E-05	0.992
S ²⁻	20	104.64	274.7	0.932	0.965	146.4	0.00257	0.982
	40	106.24	296.8	0.979	0.975	146.2	0.00273	0.984
	60	108.8	282.8	0.967	0.943	142.2	0.00342	0.992
	80	112.64	243.3	0.906	0.967	139.3	0.00442	0.997
	100	116.8	210.5	0.905	0.981	156.9	0.00279	0.986

Fig. 5. Adsorption isotherm of SO₂ (A) and H₂S (B) at different temperatures (▲ 25 °C, ● 35 °C, and ■ 45 °C; – Langmuir, --- Freundlich).

Table 3
Different model parameters for the adsorption of aqueous SO₂ and H₂S at CeO₂-NiAl-LDHs/AC.

<i>T</i> (°C)		SO ₂			H ₂ S		
		<i>q_m</i> (mg/g)	<i>K_L</i> (L/mM)	<i>R</i> ²	<i>q_m</i> (mg/g)	<i>K_L</i> (L/mM)	<i>R</i> ²
Langmuir	25	483.09	0.07	0.999	181.15	0.023	0.989
	35	502.51	0.10	0.998	186.91	0.037	0.990
	45	510.20	0.15	0.997	197.23	0.047	0.993
<i>T</i> (°C)		SO ₂			H ₂ S		
		1/ <i>n</i>	<i>K_F</i>	<i>R</i> ²	1/ <i>n</i>	<i>K_F</i>	<i>R</i> ²
Freundlich	25	0.44517	65.85	0.986	0.6159	8.61	0.982
	35	0.38581	92.32	0.988	0.50175	16.16	0.994
	45	0.31486	130.58	0.992	0.49485	19.46	0.993
<i>T</i> (°C)		SO ₂			H ₂ S		
		<i>k_t</i> (L/mg)	<i>b_t</i> (kJ/mol)	<i>R</i> ²	<i>k_t</i> (L/mg)	<i>b_t</i> (kJ/mol)	<i>R</i> ²
Temkin	25	0.025	24.38	0.994	0.048	65.95	0.985
	35	0.032	26.22	0.990	0.055	68.12	0.983
	45	0.041	30.67	0.986	0.065	63.42	0.985
<i>T</i> (°C)		SO ₂			H ₂ S		
		<i>q_D</i> (mg/g)	<i>B_D</i> (mol ² /kJ ²)	<i>R</i> ²	<i>q_D</i> (mg/g)	<i>B_D</i> (mol ² /kJ ²)	<i>R</i> ²
Dubinin–Radushkevich	25	407.04	0.001089	0.979	136.24	0.00304	0.989
	35	426.75	0.000709	0.968	132.35	0.001396	0.953
	45	435.48	0.000388	0.953	150.38	0.001228	0.959

the surface of CeO₂-NiAl-LDHs/AC, and the sorption process has an endothermic character.

Thermodynamics of adsorption: The Adsorption thermodynamic parameters including Gibbs free energy change (Δ*G*[°]), enthalpy change (Δ*H*[°]) and entropy change (Δ*S*[°]) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the adsorption process. The thermodynamic constants were obtained from Eq. (10).

$$\ln K_L = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

where Δ*G*[°] is the change in free energy (kJ/mol), Δ*H*[°] is the change in enthalpy (kJ/mol), Δ*S*[°] is the change in entropy (J/(molK)), *T* is the absolute temperature in kelvin, *R* is the gas constant (8.314 × 10^{−3} J/(molK)), and *K* is the thermodynamic equilibrium constant. The values of Δ*H*[°] and Δ*S*[°] were calculated from the slope and intercept of the plot of ln *K* versus 1/*T*. The thermodynamic parameters for the adsorption are presented in Table 4. The positive value of Δ*H*[°] confirms the endothermic nature of the adsorption process, while the positive Δ*S*[°] value suggests an increase in the randomness at the solid/solution interface during the adsorption of

SO₂ and H₂S at CeO₂-NiAl-LDHs/AC. Therefore the uptake increases with the increase in temperature.

3.3. Electrochemical oxidation of aqueous sulfur dioxide and hydrogen sulfide

Fig. 6 shows the CVs of 0.1 M aqueous sulfur dioxide at relative materials in 0.1 M NaOH. In Fig. 6A, a pair of redox peaks (0.35/0.60 V) correspond to the conversion between Ni(OOH) and Ni(OH)₂ at CeO₂-NiAl-LDHs/NAC/WGE in 0.1 M NaOH (b)

Table 4
Thermodynamic parameters of aqueous SO₂ and H₂S adsorption at CeO₂-NiAl-LDHs/AC.

	<i>T</i> (K)	Δ <i>G</i> (kJ/mol)	Δ <i>H</i> (kJ/mol)	Δ <i>S</i> (J mol ^{−1} K ^{−1})
SO ₂	298	−10.53	29.99	135.91
	308	−11.79	29.99	135.62
	318	−13.25	29.99	135.93
H ₂ S	298	−8.29	28.24	114.84
	308	−9.55	28.24	118.80
	318	−10.18	28.24	120.78

Fig. 6. (A) CVs of SO₂ at WGE (a) and CeO₂-NiAl-LDHs/NAC/WGE (c). Curve b: CV of CeO₂-NiAl-LDHs/NAC/WGE in 0.1 M NaOH. (B) CVs of SO₂ at WGE (a), CNTs/WGE (b), CeO₂-NiAl-LDHs/WGE (c) and CeO₂-NiAl-LDHs/NAC/WGE (d). (C) Oxidation peak currents of SO₂ depend on concentration potential in concentration time 5 min. (D) Oxidation peak currents of SO₂ depend on concentration time at 0.0 V. System: 0.1 M NaOH. SO₂ concentration: 0.1 M.

[42]. An obvious oxidation peak (0.7 V) could be observed at CeO₂-NiAl-LDHs/NAC/WGE (c) compared to that of WGE (a). In Fig. 6B, although the oxidation peak responses are obviously increased at CNTs/WGE (b), CeO₂-NiAl-LDHs/WGE (c) and CeO₂-NiAl-LDHs/NAC/WGE (d) compared to that of WGE (a), it is notable that the oxidation peak response at CeO₂-NiAl-LDHs/NAC/WGE (d) is the largest among the four electrodes. It illustrates that CeO₂-NiAl-LDHs/NAC/WGE shows an excellent electrocatalysis towards the oxidation of aqueous sulfur dioxide. The reasons probably relate the cooperation of CeO₂-NiAl-LDHs and CNTs, the former is a good catalyst-sorbent, and the latter improve the conductivity with good adsorption. Meanwhile, the optimum oxidation conditions of

aqueous sulfur dioxide such as concentration potential and concentration time were investigated at CeO₂-NiAl-LDHs/NAC/WGE in 0.1 M NaOH. The peak current is increased depending on the potential from −0.2 V to 0.0 V in Fig. 6C. The peak current obviously increases from 2 min to 5 min, and reaches to a platform after 6 min in Fig. 6D, suggesting a saturation adsorption. Thus, 0.0 V and 5 min could be selected as optimum concentration conditions. Further, the exhaustible electrochemical oxidation of 5 mL 0.1 M aqueous sulfur dioxide was investigated at CeO₂-NiAl-LDHs/NAC/WGE by potentiostatic method at 1.0 V with 3, 9 and 12 h. Before the electrochemical oxidation, SO₂ firstly reacted with NaOH with form of NaSO₃. SO₃^{2−} could be determined by the standard iodometric

Fig. 7. (A) CVs of H₂S at WGE (a) and CeO₂-NiAl-LDHs/NAC/WGE (c). Curve b: CV of CeO₂-NiAl-LDHs/NAC/WGE in 0.1 M NaOH. (B) CVs of H₂S at WGE (a), CNTs/WGE (b), CeO₂-NiAl-LDHs/WGE (c) and CeO₂-NiAl-LDHs/NAC/WGE (d). (C) Oxidation peak currents of H₂S depend on concentration potential in concentration time 5 min. (D) Oxidation peak currents of H₂S depend on concentration time at 0.0 V. System: 0.1 M NaOH. H₂S concentration: 0.1 M.

Table 5
Comparisons of SO₂ (H₂S) at different electrodes.

R	Material	Desulfurization efficiency (%)
[43]	PbO ₂ , ZnO/CFs	61.29%
[44]	Pb/PbO ₂ /CFs	55%
[45]	β-PbO ₂ /AC	87.09%
[46]	CeO ₂ /AC	83.87%
This work	CeO ₂ -NiAl-LDHs/NAC/WGE	92.7% (SO ₂), 84.1% (H ₂ S)

method [2]. In present experiment, 52.4%, 71.6% and 92.7% of SO₃²⁻ was oxidized to SO₄²⁻. The process can be expressed in Eqs. (11) and (12).

The electrochemical oxidation of 0.1 M aqueous hydrogen sulfide was followed the same performs in 0.1 M NaOH. Fig. 7A shows the CVs of aqueous hydrogen sulfide at WGE (a) and CeO₂-NiAl-LDHs/NAC/WGE (c). An obvious oxidation peak (0.4 V) could be seen at CeO₂-NiAl-LDHs/NAC/WGE (c) with a good catalysis. Fig. 7B shows that the oxidation peak response at CeO₂-NiAl-LDHs/NAC/WGE (d) is the largest compared to that of WGE (a), CNTs/WGE (b) and CeO₂-NiAl-LDHs/WGE (c), suggesting an excellent electrocatalysis and in line with Fig. 6. Fig. 7C shows that the peak current is increased with the adsorption potential from −0.2 V to 0.0 V. Fig. 7D shows that the current response is the largest at 5 min. Therefore, the optimal concentration conditions are 0.1 V and 5 min. The exhaustible electrochemical oxidation scheme of 5 mL 0.1 M aqueous hydrogen sulfide was investigated at CeO₂-NiAl-LDHs/NAC/WGE using potentiostatic method at 1.0 V with 3, 9 and 12 h. Before the electrochemical oxidation, H₂S firstly reacted with NaOH with form of Na₂S. S²⁻ could be determined by the standard iodometric method [2]. In present experiment, 43.8%, 71.9% and 84.1% of S²⁻ was oxidized to SO₄²⁻. The process can be expressed in Eqs. (13) and (14).

Moreover, the oxidation peak currents of aqueous sulfur dioxide and hydrogen sulfide were investigated depending on different ratio CeO₂-NiAl-LDHs/NAC/WGE. When the ratios of CeO₂-NiAl-LDHs and CNTs were 10:1, 20:1 and 30:1, the results showed that the peak currents of aqueous sulfur dioxide and hydrogen sulfide were larger at 20:1. As a comparison, Table 5 summarizes the electrochemical desulfurization efficiency using different electrodes [43–46]; we can find that the desulfurization efficiency at CeO₂-NiAl-LDHs/AC is comparable with their work.

4. Conclusions

CeO₂-NiAl-layered double hydroxide was successfully prepared using a urea hydrolysis method which was uniformly distributed on the surface of AC with a petal-like structure. CeO₂-NiAl-LDHs/AC composite was successfully used for the removals of aqueous sulfur dioxide and hydrogen sulfide with good uptake. Their adsorption processes were spontaneous and endothermic, which could be described by pseudo second-order kinetics equation and Langmuir equation. The mix of CeO₂-NiAl-LDHs/AC and CNTs (m:m, 20:1) shows excellent electrocatalysis towards the oxidation of aqueous sulfur dioxide and hydrogen sulfide with the formation of sulfuric acid. This work provides an environmentally attractive method to remove the aqueous sulfur dioxide and hydrogen sulfide.

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