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# $CO_2$ s - l l

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A B S T R A C T

I ss , s f l l l s f s $CO_2$ s l s f - l . T s l s l s f s l ll f l s s l s. A l s f 18.56 $10^{13}$ $^{-}$/ $^{2}$, s f s l $CO_2$ l s f l , $-6.23$ V. M , s l ss s f $CO_2$ s / s , s s $CO_2$ s s l s s l s f l 900 K. I l l , l s (4.95 $10^{14}$ $^{-2}$) s (8.04 $10^{13}$ $^{-}$/ $^{2}$) - s l - ls. I , l s l s l f s $CO_2$ f $N_2$, $H_2$ $CH_4$. I l , l s f $CO_2$ s s f 8.04 $10^{13}$ 18.56 $10^{13}$ $^{-}$/ $^{2}$. T s s l s l s f s l f l s l ll s l $CO_2$ l- l - l ls l ls s s- s ls.

## 1. Introduction

T s s l l s s l l f s f l . T s s s - f ss f f ss l f ls s s l s s s l s l s s $CO_2$, l f $CO_2$ s s l s s $CO_2$- s l. I s s fi s l l 1,2 . M l , s f s, s l s, s l s 13,14 . B l l s s ffi fi , 7 . T s l s, s $CO_2$ l s f l , - l l f l fill l s f s ll f l 8,9 . N l ss, s s f l f s l s s l ff s l . F s 15 . T s , s s s - s, s s , - f CO , s s l . T f , ll f $CO_2$ s s f s s l s. R l , f - l s s s $CO_2$ s S l. 16 . I l, s ls - l $CO_2$ s / s s s f l (DFT) 2 l l s. F , $CO_2$ s / s ss ll

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## 2. Methods

## 3. Results and discussion

### 3.1. Stability of calcite surface with charge-modulated

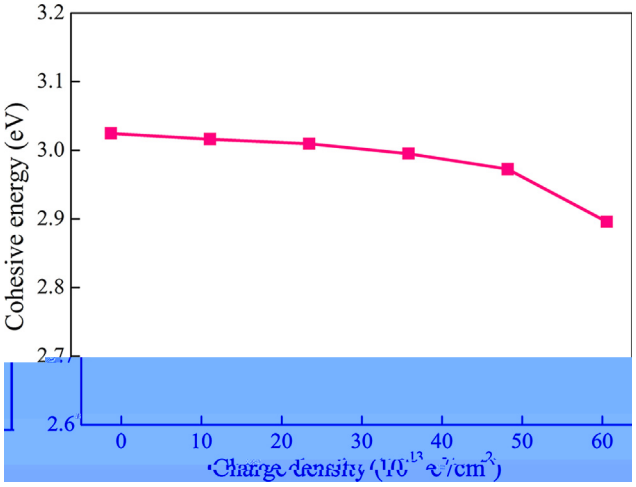


**Fig. 2.** T s f l s f s f f s .

### 3.2. Effect of charge density on adsorption behavior of $CO_2$ on calcite surface

I s s , fi s fi l s f l s f f s l $CO_2$ l l s s . N , l s f $CO_2$ l s . F ll , s ss ff f s s f $CO_2$.

W s s l l , s l l ll f f s 19,20,22,39 . C s l , fi l s l l - s s f s l $CO_2$ l s f s f f s . B f l l s f l s f , s ss fi l s fi - f $CO_2$ l s f . $CO_2$ l l s ll s l s l s f ss f ss s 25,29,37,40 , s l s fi f $CO_2$ l s f s s l F . 1b. W s s s f 0 18.56 $10^{13}$ $^{-}$/ $^{2}$, f s s s f 2.69 A 2.49 A (F . 3). I s $CO_2$ s l s l s f s f l s. H , $CO_2$ l l X l s f f l s f s s 18.56 $10^{13}$ $^{-}$/ $^{2}$ (F . S1). T f , 18.56 $10^{13}$ $^{-}$/ $^{2}$ ( s 1.5 $^{-}$ l s f ) s l s f l s f f $CO_2$ . F , s s s fi s l s s 41 . As s F . 3, l l s f $CO_2$ s f f s . T s s fi s

$$E_{ads} = E_{total} - (E_{calcite} + E_{gas}) \quad (3)$$

$E_{ads}$ s s ( V), $E_{total}$ s l f f l s f s l l ( V), $E_{calcite}$ s l f f l s f ( V), $E_{gas}$ s l f f s l s l l ( V).

C l , l s s f l - s l l l s f . I l, s f s s l s l 0.52 V s s 42,43 . F l s f ($\rho = 0$ F . 3), s f $CO_2$ s −0.38 V. M ll l l s s s sf f $CO_2$ l l l s f . T s, s $CO_2$ s s s l l s f . I s l , s s - ll s s s f l s f s s, −6.23 V l s . T s f $CO_2$ s 18.56 $10^{13}$ $^{-}$/ $^{2}$ s f s 16 s f l s f . M ll l l s s s s sf f l s f $CO_2$ l l s 0.61 $^{-}$. A l , s s f $CO_2$ s l - s f s f s s s . D l f C=O fi l 4 , s ff f s s f $CO_2$. W l f $CO_2$ l l C=O l s f f s F . 3. As s F . 3, l f $CO_2$ l l l f l C=O s s - ll s s l s f s s l s s s s. I s s l fi l s f s l s. F , s f s - f $CO_2$ l l s f l f $CO_2$ l l s f s s . T f , l f $CO_2$ l l

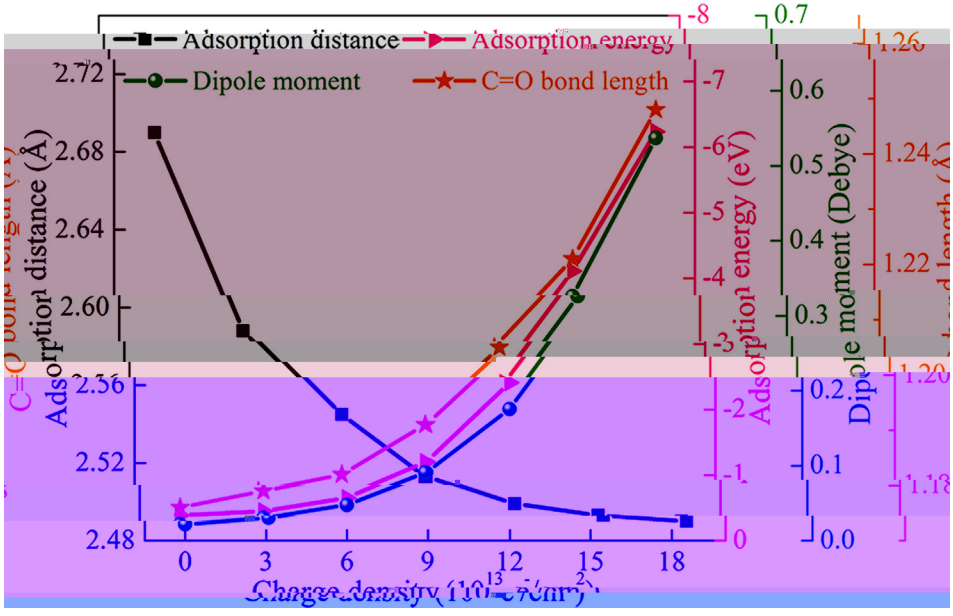


**Fig. 3.** A s s , s , l f $CO_2$ l l C=O l s f f s f l s f .

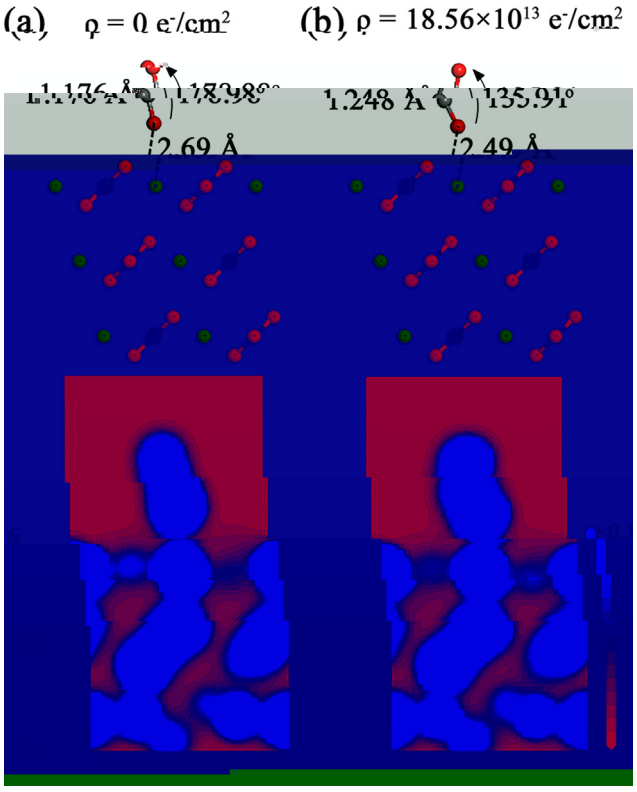


**Fig. 4.** A s s l s s f $CO_2$ ( ) l s f ( ) l s f l s . T s s s f , f s l s s 0 0.16.

l s l s s fi l s f $CO_2$ l l .

### 3.3. Adsorption mechanism of a single $CO_2$ on calcite surface at critical charge density

I x s s , l s f l s f x s l f ll s s s . W fi s x l s s- x l s s- f $CO_2$- l f . T , x l ss ll s s l f $CO_2$ s s . F ll , l l s $CO_2$

s s l s s s l s f .

#### 3.3.1. Detailed structure and electron density distribution of $CO_2$-calcite interface

F . 4 s s l s s s s f $CO_2$ l l s (18.56 $10^{13}$ $^{-}$/ $^{2}$) l s f . O l l s f (F . 4**a**), $CO_2$ l l s l s ( O–C–O l s 178.98 ; l C=O s 1.176 A), s ll s f s l s . T s O f $CO_2$ l l s f s 2.69 A, f l $CO_2$ l l ss l f $CO_2$ l l ( O–C–O l s 180 ; l C=O s 1.176 A) 20 . F , s l s l $CO_2$ l l l l s f l f l - s s (F . 4**a**). T s l s fi $CO_2$ l l s s ss l s f . H , l s f l s (18.56 $10^{13}$ $^{-}$/ $^{2}$) (F . 4**b**), l $CO_2$ l l s s l s s. C fi f $CO_2$ ss l l s f , s O l- ss f 2.69 A 2.49 A; O–C–O l s f 178.98 135.91 ; l C = O s l f 1.176 A 1.248 A. B s s, l s s- l s f s $CO_2$ l l l s f (F . 4**b**), s $CO_2$ l l s s l l s f . S $CO_2$ s L s f s l s 16 , l s f l l s $CO_2$ l l , s l - $CO_2$ l l l s f . T f , l s f ss s $CO_2$ l l l s .

#### 3.3.2. Reversibility of $CO_2$ adsorption and desorption

S s l f $CO_2$ x s s s s fi f l s, l ss f $CO_2$ - x s l s f f l s (F . 5). F . 5**a** s s s s l fi f $CO_2$ ss l l s f s ss. Af s, $CO_2$ l l l s f s s fi l s f 18.56 $10^{13}$ $^{-}$/ $^{2}$ l l s f s . I ll s s ss $CO_2$ l l s sl x s s fi , s ss s x 5.85 V . F s ss, F . 5**b** s s l fi f $CO_2$ s l s f

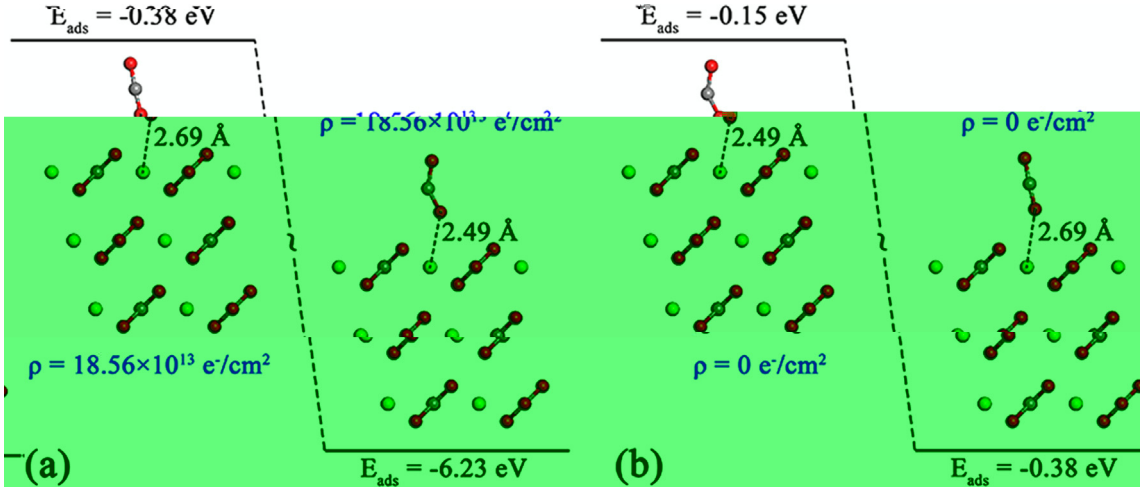


**Fig. 5.** K ss s f s s f $CO_2$ l s f . ( ) D s ss f $CO_2$ l s f l s . ( ) A s ss f $CO_2$ l s f l.

s s fi f $CO_2$ s s s f . O s, s f 18.56 $10^{13}$ $^{-}$/ $^{2}$ s f s, $CO_2$ s s f s f sf s s fi . F , s ss s s 0.23 V . H , $CO_2$ s / s ss s s s s.

### 3.3.3. Spontaneity of $CO_2$ adsorbed on calcite surface with critical charge density

E s s fi $CO_2$ s s f ff s. F f s, G s f . H , s fi s

$$S = S_{trans} + S_{rot} + S_{vib} \quad (4)$$

S, $S_{trans}$, $S_{rot}$, $S_{vib}$ , s , ( / K), s ; T , s

$$H = H_{trans} + H_{rot} + H_{vib} + RT \quad (5)$$

H, $H_{trans}$, $H_{rot}$, $H_{vib}$ , s , ( / ), s ; R T s s (8.314 J/ /K) s (K), s ; F , G s f s fi s

$$G = E(0K) + H - T \cdot S \quad (6)$$

G E(0K) G s f ( / ) ( / ), s . T S M . C s , s f s f (ΔS, / /K), (ΔH, / ), G s f (ΔG, / ) (K) s ff f $CO_2$ s s f s f 18.56 $10^{13}$ $^{-}$/ $^{2}$ (F . 6). As s F . 6, s s f ΔS ΔH, s f ΔG . T ΔG s s ΔG s 900 K. I s s f $CO_2$ s f s f 18.56 $10^{13}$ $^{-}$/ $^{2}$ s s 900 K.

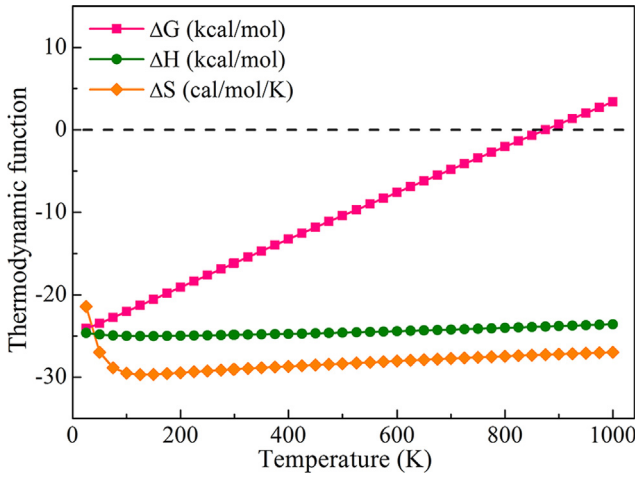


**Fig. 6.** T s f $CO_2$ s s f s f f s.

## 3.4. Applications of $CO_2$ capture and separation

### 3.4.1. $CO_2$ capture capacity of calcite surface at minimum charge density

F - f $CO_2$- s s, $CO_2$ - s s fi . B f $CO_2$ - , fi s , s s s s f $CO_2$ s s 4 s s f f $CO_2$ s . N , ff s fi s (2$CO_2$- 2$CO_2$- ) s f $CO_2$ s - s s f (F . 7**a and 7b**).

B s s, fi f s s f $CO_2$ s s f , s s s . F s s , - s f fi( $CO_2$ s f s f 18.56 $10^{13}$ $^{-}$/ $^{2}$ (F . 8**a**). As F . 8**b** s s s, fi s s fill , fi( $CO_2$ s s f . I s $CO_2$ s f , s . T s f $CO_2$ , s s f $CO_2$ s s f ff s s (F . 9). As s s s, s f $CO_2$ s s . A , ff fi s (2$CO_2$- 2$CO_2$- ) f $CO_2$ s s f s s s . W s s s , f $CO_2$ s s f , s s . I s s s f $CO_2$ f s f s s s . G , s - 0.52 V s s s 42,43 . As F . 9 s s, s s 8.04 $10^{13}$ $^{-}$/ $^{2}$, f $CO_2$ s s s - f . T f , fi s $CO_2$ f s f s f s $CO_2$ s. I , $CO_2$ f $CO_2$ s ( $CO_2$ s) s f (80.838 $A^2$), s s , $CO_2$ s 4.95 $10^{14}$ $^{-2}$ s 8.04 $10^{13}$ $^{-}$/ $^{2}$. C s f - s s (T 1), s f s f $CO_2$ s s ( 8.04 $10^{13}$ $^{-}$/ $^{2}$), s s ffi . I , s s s f s s s f - . T s s s f s f $CO_2$ .

### 3.4.2. Separation performance of $CO_2$ from calcite surface in gas mixture

S $CO_2$- s s f - s - s , $CO_2$ s f s s fi . F s ($CO_2$/$N_2$) s s s s s ff 4,44 . T f , s s fi $CO_2$ f fl s f . F , $H_2$ s s s s s f s s ( ) s -f 45 . N s s s ( $CH_4$) s ffi , ss 46,47 . H , $CO_2$ s s f ss s f $H_2$ $CH_4$ 45,48 . C s , $CO_2$ s s f $H_2$ $CH_4$. I , s f $CO_2$ s s f 8.04 $10^{13}$ 18.56 $10^{13}$ $^{-}$/ $^{2}$ ( F . 10). T s s s 8.04 $10^{13}$ $^{-}$/ $^{2}$ s s s (f $CO_2$ s) f $CO_2$ s - s s f (F . 9). T , 18.56 $10^{13}$ $^{-}$/ $^{2}$ s s s ( $CO_2$ )

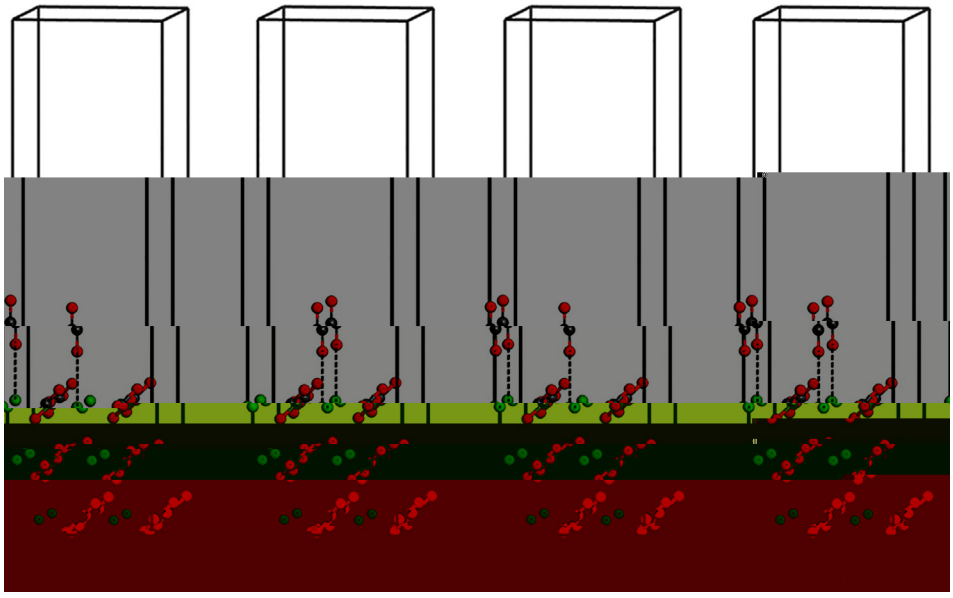

**Fig. 7.** T l s fi s f l l $CO_2$ l l s l s f .

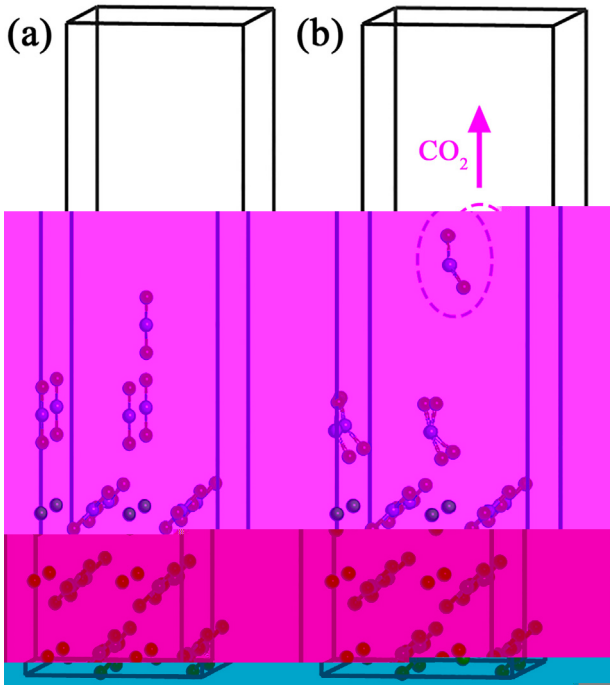


**Fig. 8.** A s f fi $CO_2$ l l s l s f l s . ( ) T l s fi f fi $CO_2$ l s f . ( ) T s s l fi f fi $CO_2$ l s f l s .

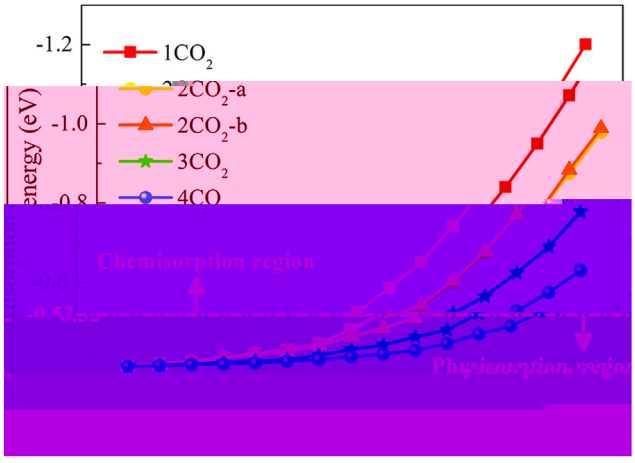


**Fig. 9.** T s s f $CO_2$ ff s s. " " " s ff s fi s (F . 7**a and 7b**), s l .

**Table 1**
C s f $CO_2$- s f f s s s l s.

| A s l s | C s ($10^{13}$ $^{-}$/ $^{2}$) | ($10^{14}$ $^{-2}$) |
|---|---|---|
| G 18 | 61.70 | 7.39 |
| B s 19 | 52.50 | 6.73 |
| N- - s 22 | 40.90 | 2.45 |
| $C_3N$ s 20 | 22.00 | 2.13 |
| **Calcite (this study)** | **8.04** | **4.95** |

f $CO_2$ l l l s f (F . 3). T fi s l f l s f f $CO_2$ , s s f $CO_2$, $N_2$, $H_2$ $CH_4$ ff s s f l s f l l (F . 10), l s fi - s f $N_2$, $H_2$ $CH_4$ l s f s F . S2. As s l l F . 10, F . S3 F . S3 , $H_2$ $CH_4$ s s l s f . O s s s - l 8.66 $10^{13}$ 10.50 $10^{13}$ $^{-}$/ $^{2}$, $H_2$ $CH_4$ f l s f s s - l l D l$^{3}$ 19 . B s s, - s f $N_2$ l s f s s s l l

s f s , s s ll s f s - s (F . S3 ). H , $N_2$, $H_2$ $CH_4$, $CO_2$ s s l s l s f l s . I l s X l s f s s s l f $CO_2$ s f s f $N_2$, $H_2$ $CH_4$.

## 4. Conclusions

I s , DFT s s s s

s s s f $CO_2$ l l-
s f . T s l s s - l l s -
ll f s l s s l l ff s l
f l s f . I , s f s l $CO_2$ s
s ll l s f 18.56 $10^{13}$ $^{-}$/
$^{2}$, −6.23 V. T s s s $CO_2$ s L s f s
l s s , s l
$CO_2$ l l l s f . U l s ,
s l ss s f $CO_2$ s / s
, s
$CO_2$ s s l s s l s f -
l 900 K. C l s f
- s l ls f $CO_2$ , l s f s l
$CO_2$ 4.95 $10^{14}$ $^{-2}$
s f 8.04 $10^{13}$ $^{-}$/ $^{2}$. M l , l
s f s l s l f s $CO_2$ f $N_2$, $H_2$ $CH_4$.
T f , s l ss s l s f ll
s fi l s l s s f $CO_2$
l s, s s s ($CO_2$/$H_2$) , l
s ( s l s) s ($CO_2$/$CH_4$), s s ($CO_2$/
$N_2$) . T l s f $CO_2$
s s fi f 8.04 $10^{13}$ 18.56 $10^{13}$ $^{-}$/ $^{2}$.

## CRediT authorship contribution statement

**Lin Tao:** C l , M l , F l l s s, W - l f . **Junchen Huang:** F l l s s, W - & . **Davoud Dastan:** F l l s s, W - & . **Tianyu Wang:** W - & . **Jing Li:** R s s, V s l . **Xitao Yin:** C l , S s , R s s. **Qi Wang:** M l , W - & , S f , R s s.

## Declaration of Competing Interest

T s l fi l
s s s l l s s l fl -
s .

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T f f N l N l S F f C
(G N . 51634004, 51874169 51974157) s f ll -
l .

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s f - s CO2 fi s, E F s 32 (2018) 1934–1941.s L8 51.4(S 9.5964.6 (s L987-1330.9271)T S 9.5-252 341 ( 28