

# SCIENTIFIC REPORTS

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## A GdAlO<sub>3</sub> Perovskite Oxide Electrolyte-Based NO<sub>x</sub> Solid-State Sensor

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Received: 20 March 2016  
Accepted: 02 November 2016  
Published: 25 November 2016

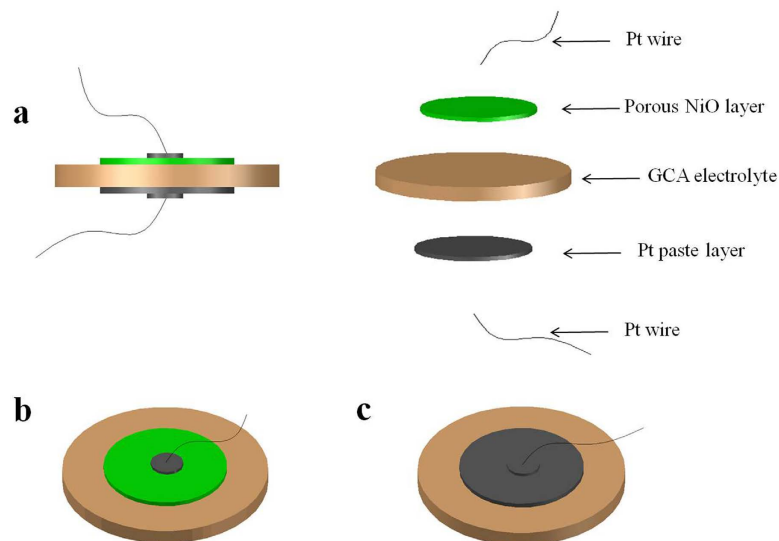
NO<sub>x</sub> is a notorious emission from motor vehicles and chemical factories as the precursor of acid rain and photochemical smog. Although zirconia-based NO<sub>x</sub> sensors have been developed and showed high sensitivity and selectivity at a high temperature of above 800 °C, they fail to show good performance, and even don't work at the typical work temperature window of the automotive engine (<500 °C). It still is a formidable challenge for development of mild-temperature NO<sub>x</sub> detector or sensor. Herein, a novel amperometric solid-state NO<sub>x</sub> sensor was developed using perovskite-type oxide Gd<sub>1-x</sub>Ca<sub>x</sub>AlO<sub>3-δ</sub> (GCA) as the electrolyte and NiO as the sensing electrode. NO<sub>x</sub> sensing properties of the device were investigated at the temperature region of 400–500 °C. The response current value at –300 mV was almost linearly proportional to the NO<sub>x</sub> concentration between 300 and 500 ppm at 500 °C. At such a temperature, the optimal sensor gave the highest NO<sub>2</sub> sensitivity of 20.15 nA/ppm, and the maximum response current value reached 5.57 μA. Furthermore, a 90% response and 90% recover time to 500 ppm NO<sub>2</sub> were about 119 and 92 s, respectively. The excellent selectivity and stability towards NO<sub>x</sub> sensing showed the potential application of the sensor in motor vehicles.

The nitrogen monoxide (NO) and nitrogen dioxide (NO<sub>2</sub>), referred as NO<sub>x</sub>, are one kind of the most hazardous air pollutants causing acid rain and photochemical smog<sup>1</sup>. A major source of NO<sub>x</sub> emission is from automobile exhaust, and as a result, the NO<sub>x</sub> emission sharply inclined due to the rapid increase of the amount of automobiles worldwide. Therefore, detection and monitoring of NO<sub>x</sub> gas is an important operation in environmental protection. Computerized control of internal combustion engines has improved the work efficiency and decreased the emission of NO<sub>x</sub> gas, where the sensor tracing nitrogen oxide (NO<sub>x</sub>) is the key to the closed loop feedback control of the emissions<sup>2</sup>.

Development of NO<sub>x</sub> sensors based on solid electrolytes has attracted great attention recently<sup>3</sup>. The solid electrolytes mainly include two categories: fluorite (AO<sub>2</sub>)-type and perovskite (ABO<sub>3</sub>)-type electrolyte. The traditional solid electrolytes for sensing NO<sub>x</sub> are zirconia-based ceramics with the fluorite (AO<sub>2</sub>)-type structure. Until recently, Yttria stabilized Zirconia (YSZ) based sensors aroused great attention due to their great sensitivity, excellent selectivity, response signal testability, simple structure, the superiority on a wide gas test range, and particularly, the operating ability under high-temperature and hazardous conditions<sup>4–11</sup>. Miura *et al.*<sup>12</sup> fabricated an amperometric-type NO sensor using YSZ substrate with oxide electrode (CdCr<sub>2</sub>O<sub>4</sub>), which showed quick and selective response to NO. Park *et al.*<sup>13</sup> reported a mixed-potential-type NO<sub>x</sub> sensor using the YSZ electrolyte with a CuO electrode showing good transient responses and large response values. However, the YSZ-based sensors show high oxygen-ion conductivity only above 800 °C. The high operating temperature can lead to a series of problems such as electrode aging<sup>14</sup>, adverse reactions and interfacial diffusion between electrode and electrolyte<sup>15</sup>, weak long term stability and high cost of interconnects<sup>16</sup> and other issues. This greatly limits the application of such sensors in NO<sub>x</sub> detection. Therefore, it is urgent to search an alternative solid electrolyte material that can work for sensing NO<sub>x</sub> at a mild temperature.

Recently, many mild-temperature NO<sub>x</sub> sensors have been studied. For example, Wang *et al.*<sup>17</sup> investigated the Pt/La<sub>10</sub>Si<sub>5</sub>NbO<sub>27.5</sub> (LSNO)/NiO sensor and showed that the sensor had a very high sensitivity to NO<sub>2</sub> at the operating temperature of 450–600 °C. Dai *et al.*<sup>18</sup> also fabricated an amperometric-type NO<sub>2</sub> sensor using Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (CGO) substrated with La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3-δ</sub> (LSCM) sensing electrode, which gave the high NO<sub>2</sub> sensitivity of 134 nA/ppm at 500 °C. In addition, Ueda *et al.*<sup>19</sup> reported that the electrochemical gas sensor

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**Figure 1.** (a) Schematic representation of the fabricated sensor, (b) top view of the sensor, (c) bottom view of the sensor.

Pt/YSZ/La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.98</sub>Mn<sub>0.02</sub>O<sub>3</sub>, which demonstrated the fast response to NO<sub>2</sub> at 500–600 °C, but the response current value had only 3 μA to 400 ppm NO<sub>2</sub> at 550 °C.

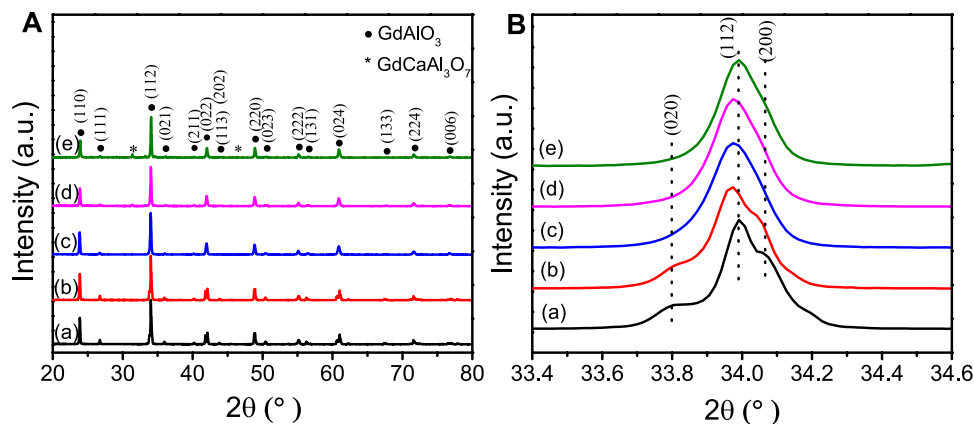
At present, perovskite (ABO<sub>3</sub>)-type oxides have been widely studied as potential candidates for gas sensing<sup>20–23</sup>. Structurally, the AO<sub>2</sub> type oxides only offer A site for aliovalent ion doping. However, not only the perovskite oxides provide A site but also B site for doping, thus vacancies in the oxygen sublattice are more easily formed and the higher conductivity can be achieved. For example, the oxide ion conductivity exhibiting in the doubly-doped La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.83</sub>Mg<sub>0.17</sub>O<sub>2.815</sub> (LSGM) perovskite oxide is three times higher than 8YSZ at 800 °C<sup>24,25</sup>. Sinha *et al.*<sup>26</sup> showed that calcium-doped GdAlO<sub>3</sub> is promising material for oxygen-ion-conducting solid electrolyte application. Among the doped systems, Gd<sub>0.85</sub>Ca<sub>0.15</sub>AlO<sub>3–δ</sub> showed a conductivity of 0.057 S/cm at 1000 °C, which was only slightly less than that of yttria-stabilized zirconia at the same temperature. Moreover, the gadolinium aluminate material was widely applied in different luminescent display systems<sup>27–31</sup>, neutron absorption, and control rod<sup>32–36</sup>. It was also reported that the gadolinium aluminate material could be applied to the solid oxide fuel cell<sup>37,38</sup>. However, to the best of our knowledge, no reports were found on NO<sub>x</sub> sensors that are prepared using calcium-doped GdAlO<sub>3</sub> system as solid electrolyte.

In this paper, an amperometric NO<sub>x</sub> sensor was fabricated using perovskite-type oxide Gd<sub>1–x</sub>Ca<sub>x</sub>AlO<sub>3–δ</sub> (GCA) as an electrolyte, NiO as sensing electrode (NiO-SE), and a noble metal Pt as reference electrode (Pt-RE), as illustrated in Fig. 1. The GCA powder was synthesized by citrate gel route. The advantage of citrate gel route over the conventional solid-state synthesis method, particularly for singly and doubly doped GdAlO<sub>3</sub> compositions, is that it tunes at a molecular level and produces solid powders that could be sintered to have good densities at significantly lower temperatures<sup>39</sup>. NO<sub>2</sub> sensing performance of the device was measured on the Electrochemical Workstation to study its sensitivity, selectivity and stability at the temperature range of 400–500 °C.

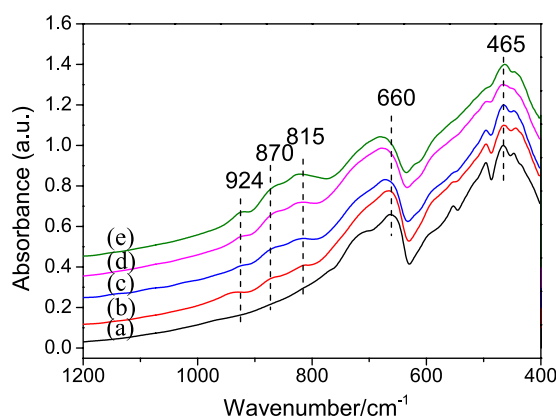
## Results and Discussion

**Characterization of the sensor materials.** XRD patterns and an expanded view around  $2\theta$  (33.6–34.4°) of the samples calcined at 1500 °C for 4 h are shown in Fig. 2A and B, respectively. As shown in Fig. 2A, when  $x$  was in the range of 0–0.1, the diffraction peaks of the resulting samples were indexed to orthorhombic crystal structure of GdAlO<sub>3</sub> phase [ICDD PDF 46–0395]. However, for  $x = 0.15$  and 0.2, additional diffraction peaks were observed in the XRD patterns, indicating the emergence of a impurity phase indexed to the tetragonal crystal structure of GdCaAl<sub>3</sub>O<sub>7</sub> [ICDD PDF 50–1808]. It showed that the Ca doping is limited in the GdAlO<sub>3</sub> lattice structure and less than 15%. The result is highly consistent with the literature<sup>26</sup>. For  $x = 0.05$ –0.15, it was noticed from Fig. 2B that the corresponding Bragg diffraction,  $2\theta$ , shifted towards lower values and the doublet (112, 200) was merged into a single peak.

We used the following Eq. 1 for further analyzing the measured XRD patterns. Based on the {110}, {112}, and {024} peaks, the lattice parameters for a given symmetry can be calculated as shown in Fig. S1. The Ca doping at  $x = 0.05$  does not change  $a$  value, whereas  $b$  decreases significantly from 8.49 Å to 5.95 Å and  $c$  increases from 6.47 Å to 7.47 Å. With increasing the Ca<sup>2+</sup> concentration to 15%, these lattice parameters don't further change, indicating that the Ca<sup>2+</sup> doping only resulted in the  $d_{hkl}$  expansion. Clearly, the  $2\theta$  shift to lower values was resulted from the lattice expansion. It was attributed to the difference in ionic size because the Ca<sup>2+</sup> (0.134 nm) ion was bigger than the Gd<sup>3+</sup> (0.127 nm) for coordination number 12<sup>26</sup>.



**Figure 2.** (A) XRD patterns of  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  powders calcined at  $1500^\circ\text{C}$  for 4 h: (a)  $x=0$ , (b)  $x=0.05$ , (c)  $x=0.1$ , (d)  $x=0.15$ , (e)  $x=0.2$ , and (B) enlarged portion at  $2\theta=33.6\text{--}34.4^\circ$ .



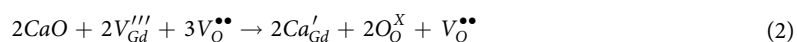
**Figure 3.** Infrared spectra of  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  powders prepared by calcinations of gel precursors for 4 h at  $1500^\circ\text{C}$ : (a)  $x=0$ , (b)  $x=0.05$ , (c)  $x=0.1$ , (d)  $x=0.15$ , and (e)  $x=0.2$ .

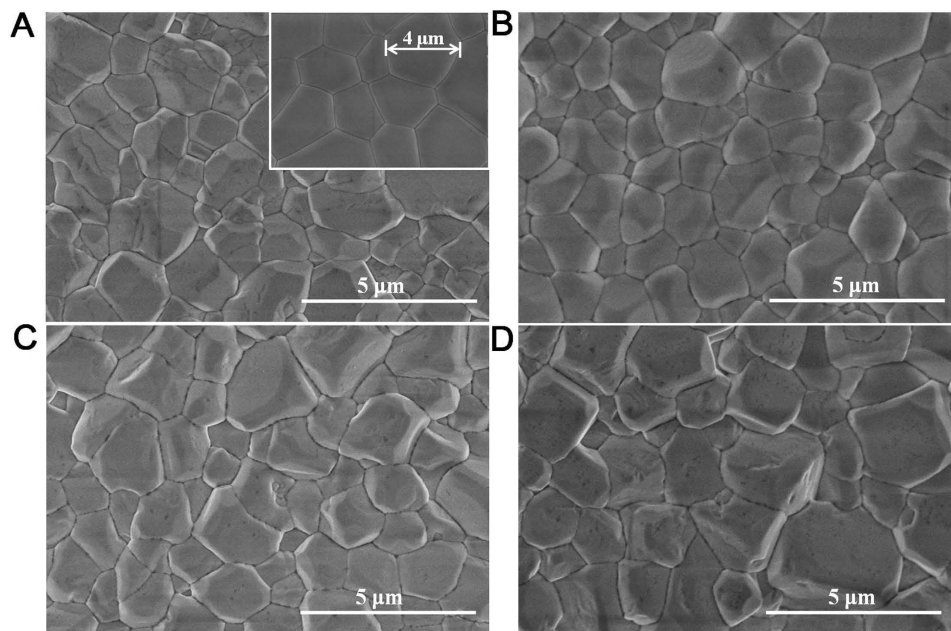
$$n\lambda = 2d_{hkl} \sin\theta, \text{ where } d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \quad (1)$$

Here,  $n$  is the diffraction order,  $\lambda$  is the x-ray wavelength,  $d_{hkl}$  is the interplanar distance,  $(hkl)$  are the Miller indices for the corresponding  $d$ -spacing and  $a, b, c$  are the lattice parameters.

Additionally, it can be observed that with increasing  $x$ , the three peaks of  $\{020, 112, 200\}$  are gradually merged into one peak and decreased in intensity. The gradual broadening and weakening are mainly originated from the lattice disordering. For  $x=0.2$ , the  $\{112\}$  Bragg diffraction peak is nearly coincided with  $x=0.0$ . It was attributed to the phase change of  $\text{GdAlO}_3$  doped with  $\text{Ca}^{2+}$  ion, leading to the formation of a new matter,  $\text{GdCaAl}_3\text{O}_7$ , due to the dissociation of doped  $\text{Ca}^{2+}$  ions from the  $\text{GdAlO}_3$  lattice structure. The most different point is that the  $2\theta$  position of the  $\{112\}$  peak recovers for  $x=0.2$ , but the broadening and weakening of these diffraction peaks are reserved, suggesting that the local structural disordering is maintained by the formation of oxygen vacancies.

Figure 3 shows the IR spectra of the samples prepared by calcinations of gel precursors for 4 h at  $1500^\circ\text{C}$ . It was observed that the spectra measured at different Ca-doped concentrations are basically the same except for a systematic data shift. The IR spectra showed strong bands at  $660$  and  $465\text{ cm}^{-1}$  which are characteristic M-O (possibly Gd-O and Al-O stretching frequencies) vibrations for the perovskite structure compounds<sup>40</sup>. Additionally, it was noted that the Ca-doped samples showed three new peaks at  $815, 870,$  and  $924\text{ cm}^{-1}$  and the peaks at  $660\text{ cm}^{-1}$  moved to a higher wave number with increasing  $x$ . It has been reported that the size-induced lattice variations and the concentration of oxygen vacancies might lead to a red shift of IR absorption<sup>41,42</sup>. For the  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  systems, since the diameter size of  $\text{Ca}^{2+}$  ion is bigger than that of  $\text{Gd}^{3+}$  ion, it results in the lattice expansion and formation of oxygen vacancies. The Ca-doped  $\text{GdAlO}_3$  point defect reaction could be written as Eq. 2<sup>26</sup>:





**Figure 4.** SEM images of the surfaces of  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrates calcined at  $1500^\circ\text{C}$  for 4 h (A)  $x = 0.05$ , the inset shows the  $x = 0$ , (B)  $x = 0.1$ , (C)  $x = 0.15$ , and (D)  $x = 0.2$ .

Here, with increasing  $x$ , the concentration of mobile oxygen vacancies increased. Moreover, these new IR peaks are originated from the formation of some new chemical bonds by introduction of calcium. The above results suggested that  $\text{Ca}^{2+}$  ions have entered into the perovskite lattice structure.

Figure 4 shows the SEM images of surface of the  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrate calcined at  $1500^\circ\text{C}$  for 4 h. The surface was consisted of microparticles with sizes between 1 and  $5\ \mu\text{m}$ , and no open pore could be seen. The surface morphology of the undoped gadolinium aluminate sample is shown in inset of Fig. 4A. Compared to the undoped sample, it can be seen that there is no significant change in morphology and surface structure for  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrates. Only the average grain sizes increased slightly with the increase of Ca doping concentration.

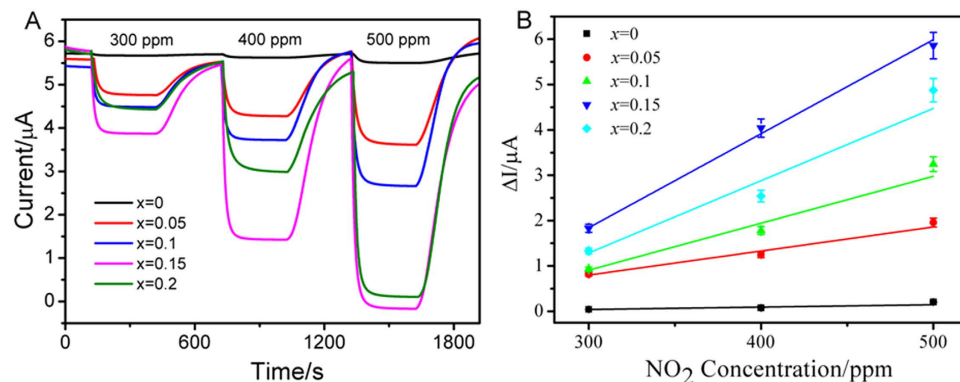
**Sensing performance of the devices.** This sensor based on the solid electrolyte substrates can be shown as the following electrochemical cells in the presence of  $\text{O}_2$  and  $\text{NO}_2$ : (–)  $\text{O}_2 + \text{NO}_2$ ,  $\text{NiO}/\text{GCA}/\text{Pt}$ ,  $\text{NO}_2 + \text{O}_2$  (+). When the sensor was exposed to the sample gas, the response current value changed at the fixed potential of  $-300\ \text{mV}$ . The following electrochemical reactions would occur at the triple-phase boundary (TPB, among gas/sensing electrode/electrolyte) and counter electrode in a series of physisorption and charge exchange reactions, as described by Eq. 3 and Eq. 4.



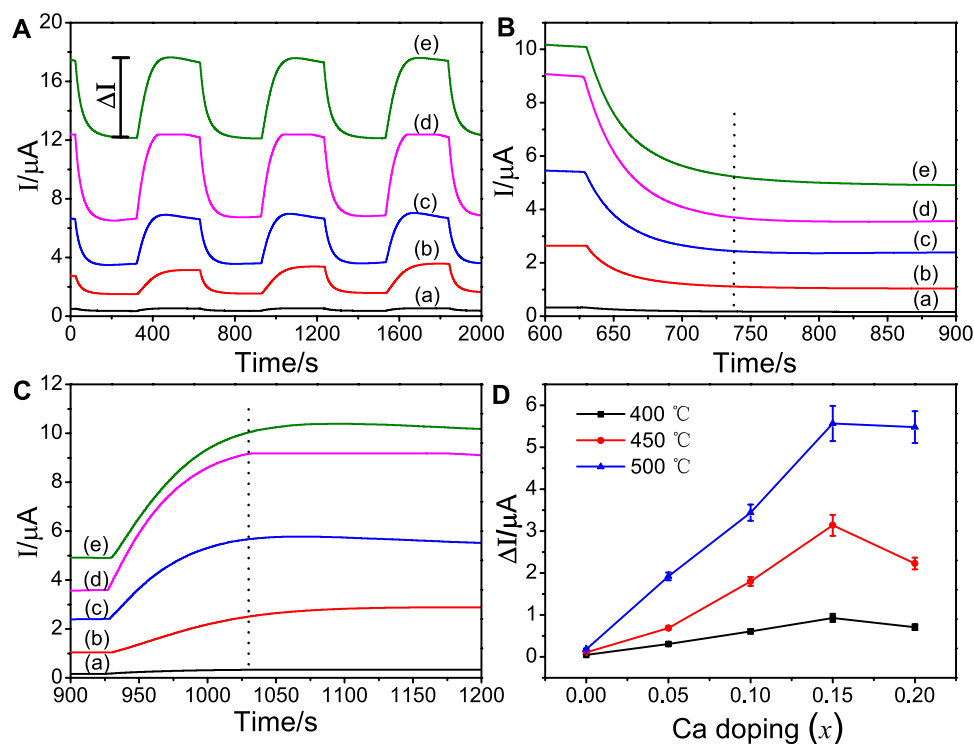
Amperometric response and recovery transients to 500 ppm  $\text{NO}_2$  with a polarized potential of  $-300\ \text{mV}$  at 400, 450, and  $500^\circ\text{C}$  for the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate were shown in Fig. S2. As well known, if you choose the cathode to be positive in the software setup, and a negative voltage of  $-300\ \text{mV}$  is applied in the work, you will obtain a positive current. As seen from Fig. S2, the baseline current increased with increasing temperature due to some reactions of low level impurities at electrode and slight electric conductive contribution, which was in agreement with the result reported by Wang *et al.*<sup>43</sup>

Figure 5A shows the response transients of the sensor based on  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrates at  $500^\circ\text{C}$  under various  $\text{NO}_2$  concentrations in the range between 300 to 500 ppm in the presence of 5 vol. %  $\text{O}_2$ , when the potential of  $-300\ \text{mV}$  was applied. In order to better distinguish the response curve, the base current levels have been shifted. At each  $\text{NO}_2$  concentration, a large increase in response current value was observed in the case of the sensor based on  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrate. For instance, the response current value of the sensor based on  $\text{Gd}_{0.9}\text{Ca}_{0.1}\text{AlO}_{3-\delta}$  substrate was  $0.93\ \mu\text{A}$  for 300 ppm  $\text{NO}_2$  at  $500^\circ\text{C}$ . When the  $\text{NO}_2$  concentration went up to 400 ppm, the response current value inclined to  $1.78\ \mu\text{A}$ . For the  $\text{NO}_2$  sensor in this study, the NiO sensing electrode showed a strong adsorption and catalytic activity for  $\text{NO}_2$ . An increase of the  $\text{NO}_2$  concentration brought enhancement of  $\text{NO}_2$  adsorption on the sensing electrode, which would produce more oxygen ions ( $\text{O}^{2-}$ ) through the cathodic reaction of Eq. 3 and thus the response current of the sensors was improved.

In this work, the response current value was defined as the difference of current value between the sample gas and base gas ( $\Delta I = |I_{\text{gas}} - I_{\text{base}}|$ , where  $I_{\text{gas}}$  and  $I_{\text{base}}$  referred to the current values in the targeted concentration  $C$  ppm and 0 ppm  $\text{NO}_2$ ). Figure 5B shows the relationship between the response current of the sensor based on



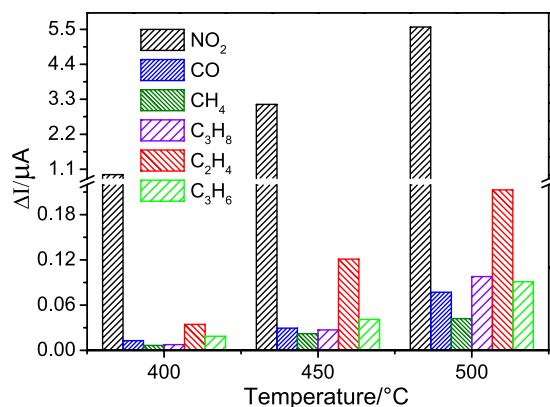
**Figure 5.** (A) Response transients of the sensor based on  $Gd_{1-x}Ca_xAlO_{3-\delta}$  substrates to 300–500 ppm  $NO_2$  at 500 °C in the presence of 5 vol%  $O_2$  (applied potential  $-300$  mV, flow rate  $200$  cm<sup>3</sup>/min); (B) The relationship between the response current values and  $NO_2$  concentrations.



**Figure 6.** (A) Response transients of the sensor based on  $Gd_{1-x}Ca_xAlO_{3-\delta}$  substrates to 500 ppm  $NO_2$  in the presence of 5 vol%  $O_2$  at 500 °C (applied potential  $-300$  mV, flow rate  $200$  cm<sup>3</sup>/min): (a)  $x=0$ , (b)  $x=0.05$ , (c)  $x=0.1$ , (d)  $x=0.15$ , (e)  $x=0.2$ ; (B) and (C) showed the enlarged portions of (A) response transients in the range between 600 to 1200 s; (D) the effect of calcium doping on the response current value of gadolinium aluminate system in 500 ppm  $NO_2$  at 400–500 °C.

$Gd_{1-x}Ca_xAlO_{3-\delta}$  substrate and the  $NO_2$  concentration at a bias potential of  $-300$  mV. It can be seen that the response current value was almost linear to the  $NO_2$  concentration from 300 to 500 ppm for the sensor based on  $Gd_{1-x}Ca_xAlO_{3-\delta}$  substrate at 500 °C. The sensitivity of the sensor is defined as the ratio of response current to  $NO_2$  concentration. For  $x=0.05$ – $0.15$ , the sensitivity of the sensor was enhanced with increasing the Ca doping. For example, the sensitivities of the sensors based on  $Gd_{1-x}Ca_xAlO_{3-\delta}$  substrate with  $x=0.05$ ,  $0.1$  and  $0.15$  were 5.71, 11.58 and 20.15 nA/ppm at 500 °C, respectively. Nevertheless, the sensitivity of the sensor based on the  $Gd_{0.8}Ca_{0.2}AlO_{3-\delta}$  substrate declined to 19.22 nA/ppm because of over-doping. Compared to the response transient of the reference sensor based on YSZ-8 substrate to 500 ppm  $NO_2$  in the presence of 5 vol%  $O_2$  at 500 °C (see Supplementary Fig. S3), the sensor based on  $Gd_{1-x}Ca_xAlO_{3-\delta}$  substrates showed the potential application in motor vehicles.

Figure 6A shows the response transients of the sensor to 500 ppm  $NO_2$  at 500 °C and a bias potential of  $-300$  mV. In order to better distinguish the response curve, the base current levels have been also shifted. It was



**Figure 7.** Selectivity of the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate in 500 ppm various gases at 400, 450 and 500 °C, respectively (applied potential – 300 mV, flow rate 200  $\text{cm}^3/\text{min}$ ).

observed that the response current values increased steadily from the base level upon switching from the base gas to the sample gas. The current quickly recovered to the original level when the sensor was exposed to the base gas. The response and recovery times are important parameters used to characterize a sensor. The response time is defined as the time that the resistance of the sensor reaches to 90% of the saturation value when the sensor was exposed to  $\text{NO}_2$  and the recovery time is defined as the time required for recovering 90% of the original resistance<sup>44</sup>. The response transients in the ranges of 600–900 and 900–1200 s are shown in Fig. 6B and C, respectively. The response and recovery time initially cut down along with the Ca doping. The response time for  $x = 0.05, 0.1$ , and  $0.15$  was 136, 121 and 119 s at 500 °C, respectively. For  $x = 0.2$ , the response time was extended to 178 s at 500 °C. Clearly, the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate is the optimal device for sensing  $\text{NO}_2$  owing to the shortest response (119 s) and recovery (92 s) time.

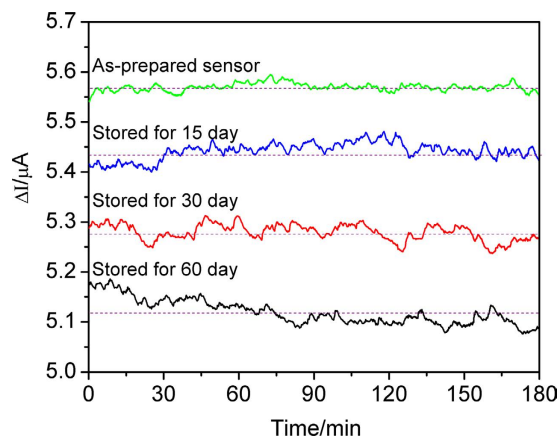
Figure 6D shows the effect of calcium doping on the response current values ( $\Delta I$ ) of the sensor based on the gadolinium aluminate system substrates at different temperatures. The current values of the undoped sample were  $0.049 \mu\text{A}$  at 400 °C. With increase of Ca doping,  $\Delta I$  reached 0.31, 0.61 and  $0.93 \mu\text{A}$  for  $x = 0.05, 0.1$ , and  $0.15$  at 400 °C, respectively. However,  $\Delta I$  of  $x = 0.2$  dropped to  $0.7 \mu\text{A}$ , suggesting that  $\Delta I$  greatly increased by doping Ca. As seen from Fig. 6D,  $\Delta I$  was enhanced with increasing the operating temperature. The sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate exhibited the highest  $\Delta I$  value of  $5.57 \mu\text{A}$  at 500 °C. The response currents of the Ca-doped  $\text{GdAlO}_3$  sensors were one order magnitude higher than that of the undoped  $\text{GdAlO}_3$ . The increase in current value may be attributed to the increased conductivity of the Ca-doped  $\text{GdAlO}_3$  substrates. For the perovskite-type oxides, tolerance factor  $t$ , can be used for describing the relationship between symmetry and ionic radii (Eq. 5):

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (5)$$

Here,  $r_A$  is the ionic radii of  $\text{Gd}^{3+}$ ,  $r_B$  is the ionic radii of  $\text{Al}^{3+}$ , and  $r_O$  is the ionic radii of  $\text{O}^{2-}$ . Theoretically, when  $t$  is equal to 1, the orthorhombic structure of perovskite-typed  $\text{GdAlO}_3$  will be altered to a cubic structure with a higher symmetry. The Ca doping made  $t$  approach to 1, as result of the larger ionic radius of  $\text{Ca}^{2+}$  (0.134 nm) than that of  $\text{Gd}^{3+}$  (0.127 nm) of  $\text{GdAlO}_3$  for coordination number 12<sup>26</sup>, consequently enhancing the conductivity of  $\text{GdAlO}_3$ . Furthermore, by the Ca doping, the cell volume of the perovskite will increase and the concentration of mobile oxygen vacancies that assist the mobility of oxygen ion will increase. In brief, for  $x = 0.05\text{--}0.15$ , the Ca doping  $\text{GdAlO}_3$  solid electrolyte is favorable for conductive properties of the sensor, whereas for  $x = 0.2$ , the conductivity begins to decrease due to the formation of impurity phase.

The selectivity is defined as the response discrepancy of an indicated gas from a mixed gas. Here, the selectivity factor is defined as  $S = I_A/I_B$ , where  $I_A$  and  $I_B$  are the responses of a sensor to a target gas A and an interference gas B, respectively<sup>45</sup>. To evaluate the selectivity, the responses of the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate to  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  were examined. Figure 7 shows the responses of different gases with a concentration of 500 ppm. It was observed that the sensor exhibited a high sensitivity and selectivity towards  $\text{NO}_2$  gas compared to the other gases. The  $\Delta I$  value of interference gases was fairly small in comparison with that of the sensor responding to  $\text{NO}_2$  gas. For example, the  $\Delta I$  values of  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  were  $5.57, 7.7 \times 10^{-2}, 4.20 \times 10^{-2}, 9.80 \times 10^{-2}, 2.13 \times 10^{-1}$ , and  $8.97 \times 10^{-2} \mu\text{A}$  at 500 °C, respectively. And the selectivity factors to  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_3\text{H}_6$  were 72.34, 132.62, 56.84, 26.15 and 62.10, respectively. The influence of  $\text{O}_2$  flow on the selectivity of sensor was negligible (see Supplementary Fig. S4).

The stability of the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate was measured for 3 h upon exposure to 500 ppm  $\text{NO}_2$  gas with 5 vol. %  $\text{O}_2$  at 450 °C (Fig. 8). The horizontal shows the centerline of the response current ripple. The as-prepared sensor shows a response current ( $\Delta I$ ) of  $5.57 \mu\text{A}$ . Furthermore, after the sensor was stored for half a month, a month, and two months, the response signal decreased slightly by 2.5%, 5.0% and 7.3%, respectively. The response current decreased by about  $0.43 \mu\text{A}$  after the sensor was stored in ambient atmosphere for two months, compared to the as-prepared sensor. These results suggested that the sensor had a good stability.



**Figure 8.** Stability test for the sensor based on  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  substrate at  $500^\circ\text{C}$  in the presence of  $500\text{ ppm NO}_2$  (applied potential  $-300\text{ mV}$ , flow rate  $200\text{ cm}^3/\text{min}$ ).

## Conclusions

In summary, an amperometric sensor based on  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  substrates was developed. It showed excellent sensitivity to  $\text{NO}_x$  gas at mild temperatures. The response current values of the sensor enhanced with increase of operating temperature. Furthermore, the sensitivity and response current values initially increased and then decreased with increasing the Ca doping. The  $\text{Gd}_{0.85}\text{Ca}_{0.15}\text{AlO}_{3-\delta}$  sensor gave the highest  $\text{NO}_2$  sensitivity of  $20.15\text{ nA/ppm}$  and the highest response current value of  $5.57\text{ }\mu\text{A}$  at  $500^\circ\text{C}$ . Moreover, the sensor also exhibited a great selectivity and excellent stability.

## Methods

**Synthesis and analysis of GCA electrolytes.** The Ca-doped  $\text{GdAlO}_3$  powder was prepared through a citrate gel route<sup>26,39</sup>.  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.99% purity),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (AR Grade), and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (AR Grade) were used as starting materials for preparation of  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  (GCA) samples, where  $x = 0, 0.05, 0.1, 0.15,$  and  $0.2$ , respectively. The starting materials were taken with composition  $(\text{Gd}_{1-x}\text{Ca}_x):\text{Al} = 1:1$  molar ratio. For all the compositions, the molar ratio of total metal ion to citrate ion was kept 1. The gadolinium nitrate, aluminium nitrate and calcium nitrate were first dissolved in  $250\text{ mL}$  distilled water at room temperature. Then citric acid as complex agent was added to the reaction solutions. Further, the mixed solution was slowly evaporated at  $80^\circ\text{C}$  under stirring to form white transparent gel. The gel was further dried at  $120^\circ\text{C}$  in an oven for  $10\text{ h}$  to form precursor powder. After that, the powder was calcined at  $1000^\circ\text{C}$  for  $4\text{ h}$ .

The XRD data were first recorded on a Panalytical X'Pert Pro diffractometer at  $40\text{ kV}$  and  $40\text{ mA}$  using  $\text{Co K}\alpha_1$  ( $\lambda = 0.178\ 901\text{ nm}$ ), then revised by  $\text{Cu K}\alpha_1$  ( $\lambda = 0.154\ 056\text{ nm}$ ). The samples were scanned over a  $2\theta$  range from  $10^\circ$  to  $100^\circ$  with a step size of  $0.0167^\circ$  at a scanning rate of  $10^\circ \cdot \text{min}^{-1}$ . The infrared spectra in the range of  $1200\text{--}400\text{ cm}^{-1}$  were recorded on a Thermo Fisher Scientific Nicolet 6700 FTIR device. The samples were prepared as KBr pellets.

**Sensor fabrication and characterization.** A  $\text{NO}_2$  sensor was fabricated using NiO as sensing electrode (NiO-SE), which was synthesized by using the sol-gel method, perovskite-type oxide  $\text{Gd}_{1-x}\text{Ca}_x\text{AlO}_{3-\delta}$  as electrolyte, and a noble metal Pt as reference electrode (Pt-RE). Pellets with  $8\text{ mm}$  in diameter and  $3\text{ mm}$  thickness were produced by applying  $150\text{ Mpa}$  pressure to the calcined powders, and then sintered at  $1500^\circ\text{C}$  for  $4\text{ h}$  in the air. The NiO-SE was made from NiO paste, and a Pt wire ( $0.2\text{ mm}$  diameter) was attached to the NiO layer as a current collector. In addition, the Pt-RE was formed by using platinum paste, which was painted onto polished surface of GCA pellet which was on the other side, and then a Pt wire ( $0.2\text{ mm}$  diameter) was attached to the Pt surfaces. Subsequently, the sample was fired at  $1000^\circ\text{C}$  for  $1\text{ h}$  in air to get the NiO/GCA/Pt sensor.

Scanning electron microscopy (SEM, HitachiS4800 instrument) was applied for observing the morphology of the samples.

**Evaluation of sensing properties.** The fabricated sensor was assembled in a quartz tube and the sensing properties were evaluated in a conventional gas-flow apparatus equipped with a furnace operating at temperatures in range of  $400\text{--}500^\circ\text{C}$  (see Supplementary Fig. S5). The gas environment consisted of a changing concentration of  $\text{NO}_2$  ( $0\text{--}500\text{ ppm}$ ) with base gases ( $\text{O}_2 + \text{N}_2$  balance) at a total flow rate of  $200\text{ cm}^3/\text{min}$ .

The amperometric responses of the sensors were carried out using a potentiostatic method at  $-300\text{ mV}$ . The fore-mentioned electrochemical measurements were carried out by the Electrochemical Workstation (Instrument corporation of Shanghai, China, CHI600E).

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## Acknowledgements

This work was financially supported by National Science Foundation of China (Grants No. 21403035), Natural Science Foundation of Fujian Province, China (Grants No. 2015J01051), and Fujian Provincial Department of Education of Manufacturing, Education and Research project of China (Grants No. JA12023).

## Author Contributions

Yihong Xiao and Fulan Zhong conceptualized the idea and device design. Dongmei Wang and Fulan Zhong performed the experiments and the data analysis. Dongmei Wang wrote the main manuscript text. Guohui Cai and Yong Zheng involved in correction of the manuscript. All the authors discussed the results and reviewed the manuscript.

## Additional Information

**Supplementary information** accompanies this paper at <http://www.nature.com/srep>

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Xiao, Y. *et al.* A GdAlO<sub>3</sub> Perovskite Oxide Electrolyte-Based NO<sub>x</sub> Solid-State Sensor. *Sci. Rep.* **6**, 37795; doi: 10.1038/srep37795 (2016).

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