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# Fe<sup>3+</sup> Facilitating the Response of NiO towards H<sub>2</sub>S

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Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates have been successfully prepared by a facile method through immersing NiO nanoplates with aqueous Fe(NO<sub>3</sub>)<sub>3</sub> solution and annealing the corresponding as-immersed NiO nanoplates. When studied as sensing materials, the as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates display enhanced response towards H<sub>2</sub>S in comparison with pure NiO nanoplates.

Gas sensing has been widely studied owing to its important applications in the environmental monitoring. Gas-sensing performance usually depends on the as-employed sensing materials. So far, many semiconductors have been explored as important sensing materials, such as Fe<sub>2</sub>O<sub>3</sub>,<sup>1,2</sup> ZnO,<sup>3,4</sup> WO<sub>3</sub>,<sup>5,6</sup> SnO<sub>2</sub>,<sup>7,8</sup> CuO,<sup>9,10</sup> TiO<sub>2</sub>,<sup>11,12</sup> NiO,<sup>13,14</sup> and Co<sub>3</sub>O<sub>4</sub>,<sup>15,16</sup> etc. Moreover, other strategies have also been employed to improve the sensing performance, such as noble metal doping oxides,<sup>17-19</sup> heterogeneous oxides,<sup>20-22</sup> and carbon or polymer/oxides,<sup>23-26</sup> etc.

As one of most important p-type sensing semiconductors, various NiO materials have been studied.<sup>13, 14, 27-30</sup> However, pure NiO usually has relatively poor sensing properties. Much effort has been made to modify NiO nanostructures to achieve excellent gas-sensing properties.<sup>31-35</sup> For example, NiO@ZnO heterostructured nanotubes fabricated by the coelectrospinning method improved H<sub>2</sub>S-sensing properties owing to the change of nanostructure and activity of ZnO and NiO nanocrystals as well as combination of homo- and heterointerfaces.<sup>31</sup> Nguyen et al. reported that the response of the NiO-decorated SnO<sub>2</sub> nanowire sensor to 10 ppm H<sub>2</sub>S at 300 °C reached as high as 1372 owing to the catalytic effect of NiO and the formation of a continuous chain of n-p-n-p junctions.<sup>32</sup> Inspired by these examples, exploring an alternative, facile decorating method is highly desirable.

Fe<sub>2</sub>O<sub>3</sub> is a well-known H<sub>2</sub>S-sensing material.<sup>1, 2, 36-38</sup> Thus, it is expected that loading Fe<sub>2</sub>O<sub>3</sub> on NiO nanoplates could exhibit high response towards H<sub>2</sub>S gas. In this communication, we have prepared the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates through immersing hydrothermally

proceeded NiO nanoplates with aqueous Fe(NO<sub>3</sub>)<sub>3</sub> solution and annealing the corresponding as-immersed NiO nanoplates. The as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates have largely enhanced the response towards H<sub>2</sub>S in comparison with pure NiO nanoplates.

The Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates were prepared by two steps: 1) NiO nanoplates were obtained through annealing hydrothermally proceeded Ni(OH)<sub>2</sub> nanoplates with the assistance of n-butylamine;<sup>38</sup> 2) Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates were produced through annealing immersed NiO nanoplates with aqueous Fe(NO<sub>3</sub>)<sub>3</sub> solution. The phase of NiO and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO was analyzed by X-ray diffraction (XRD). In Fig. 1, one could find that all the peaks in patterns could be attributed to these of the standard card (PDF: 47-1049).<sup>39</sup> There is no diffraction peak of Fe<sub>2</sub>O<sub>3</sub> observed for the XRD pattern of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates, which indicate that the content of Fe<sub>2</sub>O<sub>3</sub> is extremely low. The content of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanocomponents is about 3.9 % by weight, as supported by EDX (Fig. S1).

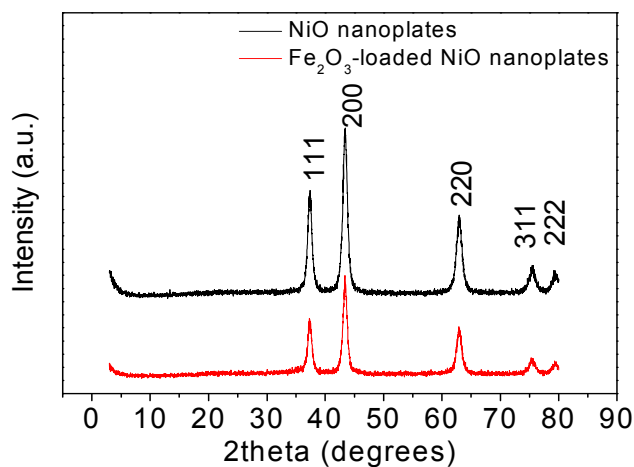
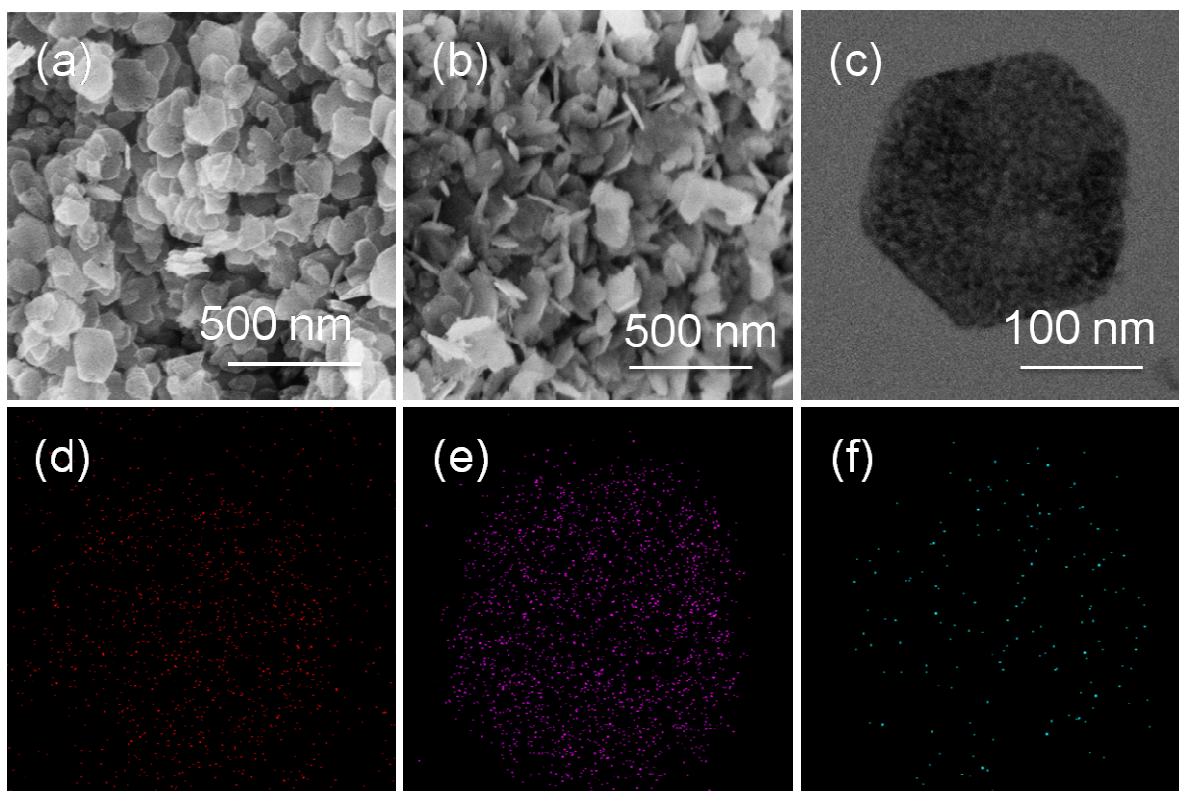
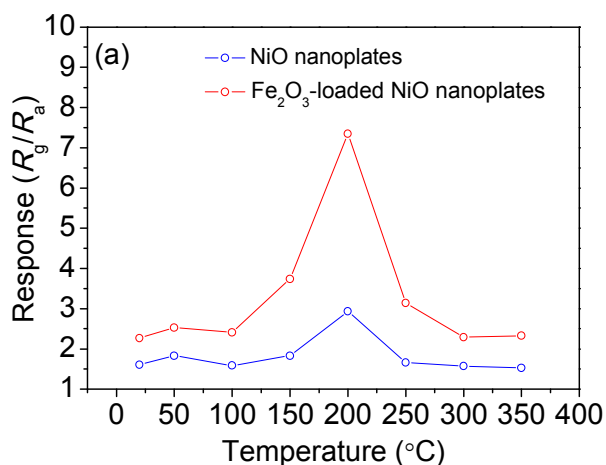


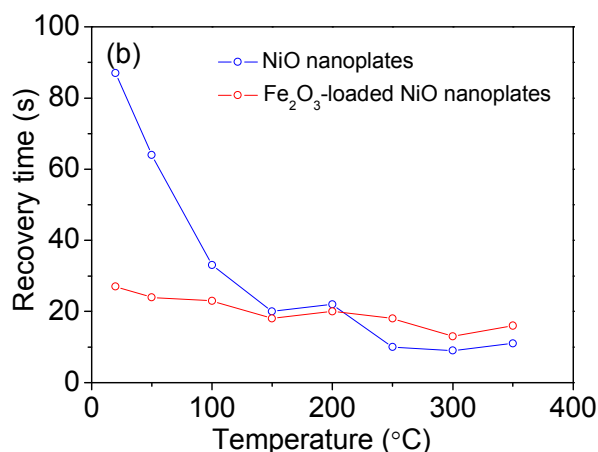
Fig. 1 XRD pattern for NiO nanoplates and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates.



**Fig. 2** (a and b) SEM images of NiO nanoplates and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates, respectively; STEM-EDS elemental maps of as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates: (c) HAADF-STEM image, (d) O elemental map, (e) Ni elemental map, and (f) Fe elemental map.

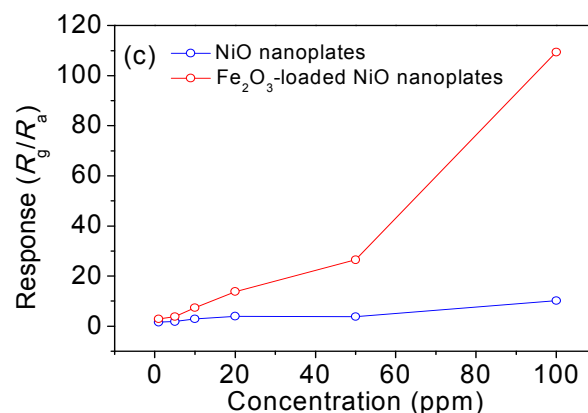
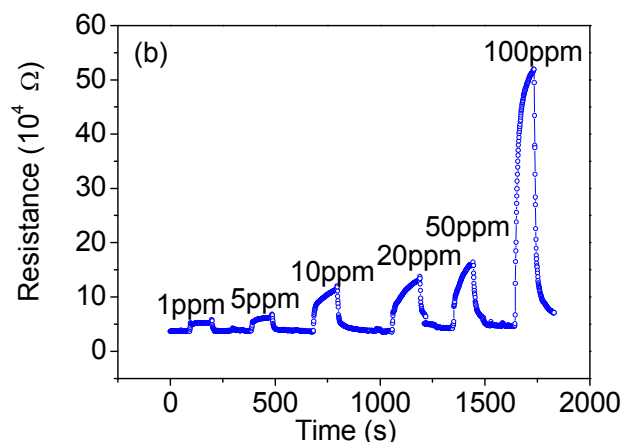
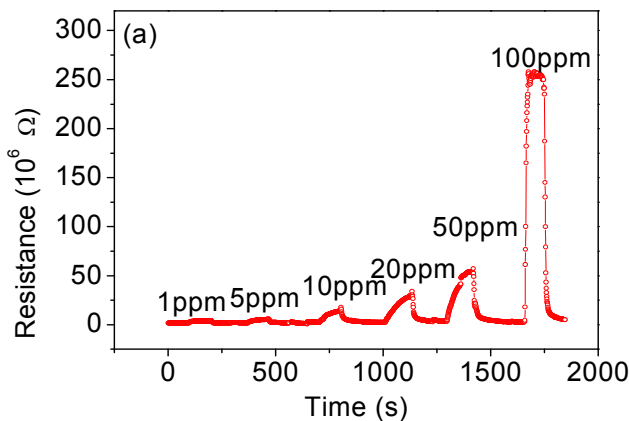
5 The morphology, composition and elemental distribution of the as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates were further mapped through TEM and EDS by displaying the integrated intensity of oxygen, nickel and iron signals as a function of the beam position when operating the TEM in scanning mode  
10 (STEM). The SEM image of NiO without Fe<sub>2</sub>O<sub>3</sub> loading (Fig. 2a) shows the hexagonal nanoplates, similar to our previous report.<sup>39</sup> The as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO sample (Fig. 2b) is composed of hexagonal nanoplates, which is similar to the unloaded NiO nanoplates. Fig. 2c shows an HAADF-STEM  
15 image of the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate. The results shown in Fig. 2d-reveal that the three elements of O, Ni, and Fe are distributed very homogeneously in the nanoplate. Moreover, the Fe/Ni ratio measured from the nanoplates with EDS analysis show an average ratio of 72.03: 2.63. The mapping  
20 data indicates that our as-employed method is effective for us to prepare Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates.





**Fig. 3** (a) Response and (b) Recovery time of NiO nanoplate and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensors to 10 ppm H<sub>2</sub>S gas at different working temperature.

To understand the gas-sensing properties of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates, we compared the response characteristics of NiO nanoplates and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates-based gas sensor, respectively. Fig. 3a and b display that the typical response and recovery time of two sensors to 10 ppm H<sub>2</sub>S at different temperature. From Fig. 3a, it could be found that the response of the two sensors have the same change trend, the response increases with the increase of operating temperature at the beginning, and approaches a maximum value at 200 °C (named as the optimum operating temperature), however, gradually decreases with further increasing operating temperature. The response of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates is constantly higher than that of NiO nanoplates at different temperatures. Moreover, the recovery time of NiO nanoplates and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates were also studied, as shown in Fig. 3b. The recovery time vary from 27 to 13 s (from 25 to 350 °C) for Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates, which did not change much when changing the operating temperature. However, the recovery time of NiO nanoplates dropped dramatically with the temperature increasing from 25 to 250 °C. Analyzed from the data of their response and recovery time, we chose 200 °C as the working temperature.



**Fig. 4** (a and b) The real-time response curve of the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate and NiO nanoplate sensors to H<sub>2</sub>S gas with increased concentration at a working temperature of 200 °C, respectively; (c) The relationship between the response and H<sub>2</sub>S concentration.

To understand the sensing characteristics of two sensors, the real-time response curves of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO sensor and NiO sensor to H<sub>2</sub>S gas with increased concentration ranging from 1 to 100 ppm at a working temperature of 200 °C were investigated, as shown in Fig. 4a and b, respectively. In Fig. 4a and b, one could find that gas responses increase with the increase of H<sub>2</sub>S concentration. As shown in Fig. 4c, the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensor shows the response of approximately 2.89, 3.8, 7.35, 13.8, 26.48, and 109.4 for the corresponding 1, 5, 10, 20, 50, and 100 ppm H<sub>2</sub>S gas, respectively. In comparison, the NiO nanoplates based sensor shows response of approximately 1.64, 1.82, 2.94, 3.95, 3.83, and 10.19 for the corresponding 1, 5, 10, 20, 50, and 100 ppm H<sub>2</sub>S gas, respectively. It is clearly found that the response of NiO nanoplates towards H<sub>2</sub>S gas after loading Fe<sub>2</sub>O<sub>3</sub> is improved dramatically. The response is compared with those results reported by some literatures.<sup>1, 2</sup> However, the sensing mechanism of NiO and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO sensor towards H<sub>2</sub>S gas is different from those reported literatures involved Fe<sub>2</sub>O<sub>3</sub>.<sup>1, 2</sup> The gas-sensing behavior of the p-type NiO semiconductor towards H<sub>2</sub>S gas can be explained by the decrease in the hole concentration due to the increased formation of negatively charged oxygen upon exposure to the oxidizing gas (H<sub>2</sub>S). After injection of H<sub>2</sub>S gas, H<sub>2</sub>S molecules were adsorbed on the surface, providing electrons

to the surface of NiO nanoplates. During this process the potential barrier increased and hence the resistance of the oxide was enhanced. Moreover, owing to extrahigh molar ratio of NiO to Fe<sub>2</sub>O<sub>3</sub>, the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates show the gas-sensing behavior of p-type semiconductors towards H<sub>2</sub>S gas. The NO<sub>2</sub>-sensing performance of Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates are largely improved owing to the change of nanostructure and activity of NiO and Fe<sub>2</sub>O<sub>3</sub> as well as combination of homo- and heterointerfaces.<sup>31</sup>

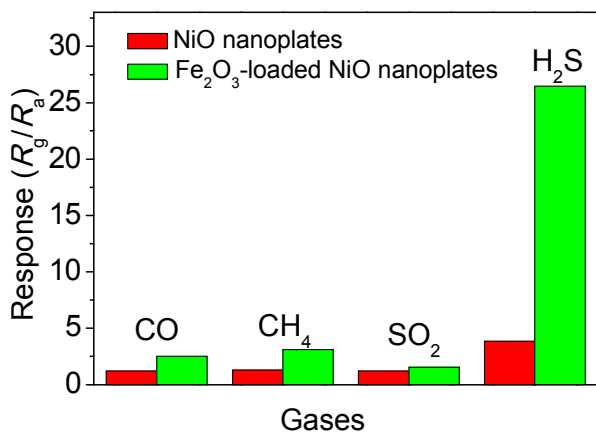


Fig. 5 Sensor response to various gases with 50 ppm at 200 °C.

To further confirm the versatility of as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensors, the selective test towards to 50 ppm CO, CH<sub>4</sub>, SO<sub>2</sub> and H<sub>2</sub>S was conducted at 200 °C, respectively. Fig. 5 indicates that both of NiO nanoplate and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensors show excellent selectivity to H<sub>2</sub>S gas. This indicates that the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensor has a quite wonderful selectivity to H<sub>2</sub>S gas.

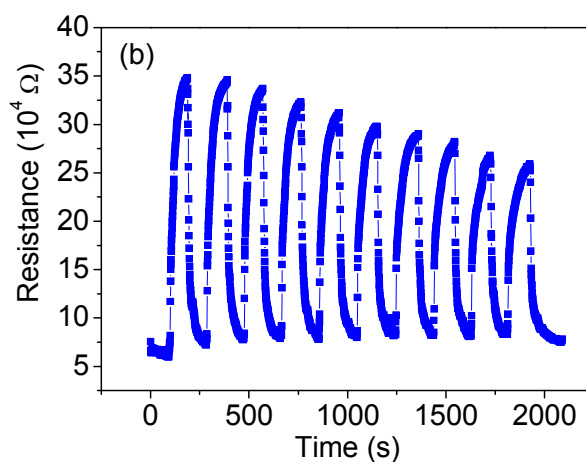
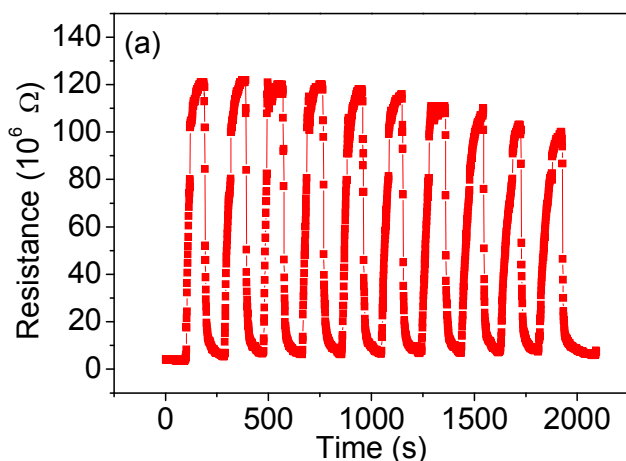


Fig. 6 (a and b) The reproducibility and stability of the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates and NiO nanoplates sensors to 50 ppm H<sub>2</sub>S gas at 200 °C.

In Fig. 6a and b, the reproducibility and stability of the NiO nanoplate and Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensors were also investigated. The results indicate that the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensor maintains 82.7% of its initial response amplitude after ten successive sensing tests to 50 ppm H<sub>2</sub>S gas at 200 °C, which is better than that the NiO nanoplates (74.4%). These results demonstrate that the Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplate sensor has better reproducibility and stability to H<sub>2</sub>S gas than the NiO nanoplates sensor.

In summary, we have developed a synthetic route to prepare Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates with high response, excellent selectivity towards H<sub>2</sub>S gas. Our as-employed method to immerse NiO nanoplates with aqueous Fe(NO<sub>3</sub>)<sub>3</sub> solution and anneal the corresponding as-immersed NiO nanoplates is proven to be effective to synthesize Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates. The as-fabricated Fe<sub>2</sub>O<sub>3</sub>-loaded NiO nanoplates are promising H<sub>2</sub>S-sensing materials due to its response as high as 26.48 and excellent selectivity towards 50 ppm H<sub>2</sub>S gas.

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## Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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