ARTICLE TYPE

Highly sensitive sensor for the detection of nitrite based on nanoporous Fe$_2$O$_3$/CoO composites

Jinping Wang, Dianyun Zhao, Yu Zhang, Juefei Li, and Caixia Xu*

Nanoporous (NP) Fe$_2$O$_3$/CoO nanoparticle composites are easily fabricated by mild dealloying of FeCoAl ternary alloy in NaOH solution. Electrochemical characterization shows that NP-Fe$_2$O$_3$/CoO composites have high electrochemical sensing activity toward nitrite with a fast response less than 3 s, a wide linear range of 0.2-16.2 mM, and a low detection limit as 0.1 μM. In particular, long-term sensing test 10 demonstrates that NP-Fe$_2$O$_3$/CoO composites have remarkable sensing durability with almost no activity loss upon nitrite detection over 4000 s. The proposed sensor based on NP-Fe$_2$O$_3$/CoO composites is effective for determination of nitrite in sausage samples, thus holding great potential for electrochemical sensing towards nitrite.

1 Introduction

15 Nitrite as a ubiquitous compound has been widespread applied in environmental and food fields as additive and corrosion inhibitor. Due to the toxicity of nitrite the continuous ingestion of these ions can cause serious implications for animal and human health.[1-5] It has been reported that nitrite can damage the nervous 20 system, spleen and kidneys, which has a strong correlation with high cancer levels when its concentration is higher than 4.5 mg mL^{-1}.[6] Consequently, the quantitative analysis of nitrite becomes more significant in environmental protection and public health due to the potential toxicity of nitrite anion. Many efforts have 25 been made to develop some methods to detect nitrite such as colorimetry, chemiluminescence, fluorescence spectroscopy, and isotachophoresis.[7-10] However, these methods often require complicated and expensive instruments. In recent years, electrochemical sensing based on various electrocatalysts has 30 attracted great attention due to it high sensitivity, rapid response, and simplicity.[11-16] Furthermore, electrochemical sensors are especially suitable for detecting nitrite in real time.

For electrochemical sensors, electrocatalyst materials play important roles for the achievement of high and effective nitrite 35 detection. At present, a variety of of electrocatalyst materials have been used for the construction of nitrite sensors, such as carbon nanomaterials, metal nanomaterials, metallic oxides, etc.[17-22] Among various electrocatalysts toward nitrite detection, the metallic oxide nanomaterials have received great interests due 40 to their low cost and broad range of electronic properties.[23] Moreover, transition metal oxides have received an upsurge of interest in recent years, such as Ni$_{0.3}$Co$_{2.7}$O$_4$, Mn$_3$O$_4$-Co$_3$O$_4$, and ZnO-NiO.[24-26] For instance, Cao et al. prepared hollow Fe$_2$O$_3$ by wet chemical route, keeping the mixure of NH$_3$•H$_2$O, ethanol, 45 FeCl$_3$•6H$_2$O, polyvinylpyrrolidone, and N,N-dimethylformamide at 180 °C for 60 h in an autoclave, and found unique nitrite

sensing performance.[27] Feng et al. fabricated β-MnO$_2$ nanorods through keeping KMnO$_4$, NaNO$_2$, and H$_2$SO$_4$ solution in autoclave at 170 °C, washing the precipitates with water and 50 ethanol, and drying the products in vacuum at 60 °C overnight.[28] Fortunately, they found that β-MnO$_2$ nanorods behave high nitrite sensing activity in acidic solution. As stated above, metallic oxides have been successfully applied as electrode materials for nitrite sensing. However, it is noted that these preparation 55 procedures are usually very complicated and often needs multi-step operation. Additionally, it also needs excessive organic agents and high temperature processing with low production yield. In summary, the above shortcomings are not desirable in terms of the ever-demanding concerns for green synthesis, 60 environmental protection, high yields, and a low fabrication cost.

Dealloying more reactive metal from binary or multicomponent alloys is a versatile strategy for facile fabrication of three-dimensional bicontinuous nanoporous materials in terms of simple operation, perfect reproducibility, and good control to 65 structure uniformity.[29-31] In this work, NP-Fe$_2$O$_3$/CoO composites were straightforwardly fabricated by dealloying FeCoAl ternary alloy under free corrosion conditions at room temperature. NP-Fe$_2$O$_3$/CoO composites have been reported to exhibit behave high sensing activity toward H$_2$O$_2$ in previous report,[32] thus it is 70 interesting to investigate applications in details for electrochemical sensing. In present work, nitrite was chosen as model to study the electrocatalytic activities of NP-Fe$_2$O$_3$/CoO composites. Moreover, this novel nitrite sensor was developed and used in the quantitative analysis of nitrite in food samples in 75 order to construct highly sensitive, stable, and reliable electrochemical sensor.

2 Experimental

2.1 Reagents

$Fe_5Co_5Al_{90}$ alloy foils with the thickness at 50 μm were made by refining pure Fe, Co, and Al (99.99 %) in an arc-furnace, followed by melt-spinning under Ar-protected atmosphere. NP-Fe_2O_3/CoO composites were prepared by etching $Fe_5Co_5Al_{90}$ alloy foils in 2 M NaOH for 48 hours at room temperature. $NaNO_2$ (sodium nitrite) was purchased from Sigma-Aldrich (USA). The phosphate buffered saline (PBS, 0.1 M, pH 7.0) solution was prepared using Na_2HPO_4 and KH_2PO_4. All the chemicals were of analytical reagents grade, and used without further purification. Ultra-pure water (18.2 MΩ) was used throughout the whole experiments.

2.2 Apparatus

JSM-6700 field-emission scanning electron microscope (SEM) was employed to obtain the morphology of the sample. All electrochemical measurements were performed using CHI 760D electrochemical workstation (Shanghai CH Instruments Co., China). A conventional three-electrode cell was used with Pt foil as a counter electrode, mercury sulfate electrode as the reference electrode, and glassy carbon electrode (GCE, 3 mm in diameter) as work electrode.

2.3 Preparation of the modified electrodes

Catalyst ink was prepared by mixing 1.5 mg carbon powder, 1.0 mg NP-Fe_2O_3/CoO composites, 200 μL isopropanol, and 200 μL nafion solutions (0.5 wt. %) under sonication for 20 min. The working electrode was made by dropping 2 μL catalyst inks and 4 μL nafion solution on a polished glassy carbon electrode. All potentials presented in this study were reported with respect to the reversible hydrogen electrode (RHE).

3 Results and discussion

3.1 Characterization of NP-Fe_2O_3/CoO composites

In previous report, the component of the source alloy is around $Fe_5Co_5Al_{90}$ as analyzed by EDS which is consistent with the initial designed feeding ratio.[32] Due to the more reactive property, Al can be selectively leached out in mild alkaline solution without the corrosion of Fe and Co. Fig. 1A shows the typical SEM image of the NP-Fe_2O_3/CoO composites after etching FeCoAl ternary source alloy foils in 2 mM NaOH solution. It is obvious to observe that the NP-Fe_2O_3/CoO composites consist of a mount of nanoparticles with the typical diameter around 80 nm. High magnification SEM image allows closer inspection of the nanoparticle structure, and from Fig. 1B further displays the resulted sample possesses nanospongy morphology with uniform size distribution. TEM image (Fig. 1C) provides more details for this structure, and the clear contrast between the dark skeletons and bright pores further demonstrates the formation of nanoporous nanostructure.

3.2 Electrooxidation of nitrite on NP-Fe_2O_3/CoO composites

As an interesting type of particularly desirable bimetallic oxides electrocatalyst with a uniform structure size distribution, NP-Fe_2O_3/CoO composites are favorable for the unlimited transport of medium molecules and the conductivity of electrons due to the 3D bicontinuous nanoprous structure.[33] Hence, it would be of great interest to investigate the electrocatalytic

properties of the NP-Fe_2O_3/CoO composites with open nanospongy structure. Cyclic voltammetric (CV) curves were recorded to understand the electrocatalytic behaviors of NP-Fe_2O_3/CoO composites modified electrode in PBS solutions in the absence and presence of nitrite. As shown in Fig. 2A, the NP-Fe_2O_3/CoO electrode exhibits pronounced electrocatalytic effect for the oxidation of nitrite in comparison to the bare GCE, though there is electrocatalytic activity towards nitrite on bare GCE (as displayed in Fig. 2B). As for the catalytic mechanism, it can be deduced that the Fe_2O_3 first reacts with NO_2^- chemically and gives NO_3^-, then the resulted Fe^{II} and Co^{II} are electrochemically oxidized to renew the Fe^{III} and Co^{III}.[27] In fact, according to the previous reports Fe^{IV} cannot be ruled out as the active species. The catalytic mechanism of the Fe_2O_3/CoO composites to nitrite oxidation may be tentatively explained by the following scheme.

$$2Fe^{III}\text{-}Co^{II} + N^{III}O_2^- \longrightarrow 2Fe^{II}\text{-}Co^{II} + N^vO_3^-$$
$$Fe^{IV} + N^{III}O_2^- \longrightarrow Fe^{III} + N^vO_3^-$$
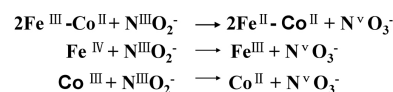$$Co^{III} + N^{III}O_2^- \longrightarrow Co^{II} + N^vO_3^-$$

Fig. 3 displays the CV curves obtained on the Fe_2O_3/CoO composites electrode in PBS solution containing different concentrations of nitrite. In the blank PBS solution, there is no obvious current change during the whole scanning process. As shown in Fig. 3, an obvious oxidation peak around 0.76 V emerges in the presence of 0.002 mM nitrite, indicating a high catalytic activity of Fe_2O_3/CoO even in the lower nitrite concentration. Clearly, the catalytic peak currents occur at ca. 0.76 V and increase with the nitrite concentrations. Meanwhile, the oxidation current dramatically increases accompanied with the oxidation peak. The wide and obvious oxidation current indicates that nitrite can be easily oxidized on these nanostructured composites over a broad potential range from 0.35 to 1.05 V. The relationship between the peak current changes and the concentrations of nitrite has shown in Fig. 3B. The peak current increased linearly by the nitrite concentration in the range of 0.005 to 0.1 mM. The equation of the calibration curve was y = 3.6 + 62.9 x, r = 0.976. These results demonstrate that Fe_2O_3/CoO composites possess a great application potential in nitrite sensing.

The electrocatalytic behavior of Fe_2O_3/CoO composites towards nitrite detection was further investigated by changing the scan rate. As shown in Fig. 4A, the oxidation peak currents gradually intensify with the increasing of the scan rate. It can be observed that the anodic peak currents are linear relative to the scan rate in the range from 20 to 140 mV s^{-1} (Fig. 4B). And the corresponding linear equations for anodic peak currents is I (μA) = 2.05 + 0.126 υ with a linear correlation coefficient of 0.998. These results indicate that the electrochemical oxidation of nitrite on the Fe_2O_3/CoO composites modified electrode is a surface-controlled process.[33]

3.3 Electrochemical sensing of NP-Fe_2O_3/CoO towards nitrite

The high electrocatalytic activity of Fe_2O_3/CoO composites towards nitrite oxidation makes it attractive for the fabrication of corresponding nonenzymatic sensor. Fig. 5A provides the typical steady-state catalytic current response of Fe_2O_3/CoO with successive injection of nitrite (the number of repeats: 81) to a continuously stirred PBS solution. With the addition of nitrite, a

dramatic increase in the response current is observed as illustrated in Fig. 5A. The response to each addition of nitrite is very fast and reaches the maximum steady-state within 3 s. The fast response is mainly attributed to the synergistic effect of Fe_2O_3 and CoO. In addition, the nanoporous 3D bicontinuous structure provides a favorable conductive pathway to the electron transfer of NO_2^-. For clarity, the current responses on the beginning addition of nitrite solution are enlarged as shown in Fig. 5A inset. As displayed in Fig. 5B, the Fe_2O_3/CoO composites exhibit excellent linear response to nitrite concentration up to 16.2 mM (linear equation: y = 6.9×10^{-3} + 5.9×10^{-3} x, R=0.997) with a lower detection limit of 0.1 μM (S/N=3) towards nitrite. These analytical parameters are better than other reported catalysts based nitrite sensors as listed in Table. 1.[34-42] It is concluded that the Fe_2O_3/CoO composites can be used as the sensor for nitrite over a wide range between 0.2 and 16.2 mM. The excellent performance of Fe_2O_3/CoO composites towards the nitrite detection makes them attractive for the construction of nitrite biosensor.

The long-term catalytic activity of the Fe_2O_3/CoO composites is evaluated by studying their steady-state current response. Fig. 6 presents the chronoamperometry data in nitrite solution for 4000 s. At the beginning, the rapid current decay for the catalyst is caused by the formation of double-layer capacitance. Upon short-time operation, the current gradually reaches a quasi-equilibrium steady state and has almost no decay as the time goes on, which indicates that the Fe_2O_3/CoO composites have dramatically catalytic durability toward nitrite detection.

3.4 Real sample detection

Based on the experimental data, it is obvious that the Fe_2O_3/CoO composites based sensor possesses high sensitivity and prominent durability for detecting nitrite in standard nitrite solution. As illustrated in Table 1, compared with other reported sensor, the results indicate that the present sensor shows a wider linear range and lower detection. Furthermore, this detection is carried out in neutral medium, which is greatly preferable to apply in biochemical detection of nitrite. In order to demonstrate the applicability of the proposed sensor for real sample analysis, the analytical utility of the Fe_2O_3/CoO composites-based sensor was demonstrated by measuring the concentration of nitrite in sausage samples. In order to estimate the precision, efficiency, and feasibility of this sensor, Griess Assay is employed for the determination of nitrite in the same samples as the standard for comparisons.[43] Based on the results illustrated in Table 2, it is observed that the detection of nitrite on this sensor is effective, sensitive, and feasible. The data obtained from this method are well consistent with that obtained from spectrophotometric method, indicating the reliability of the Fe_2O_3/CoO composites sensor for the nitrite determination in real samples.
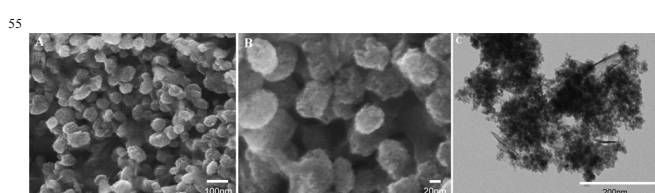

Fig. 1 SEM (A and B) and TEM (C) images of the resulted sample upon dealloying FeCoAl alloy in 2 M NaOH solution at room temperature for 48 h.
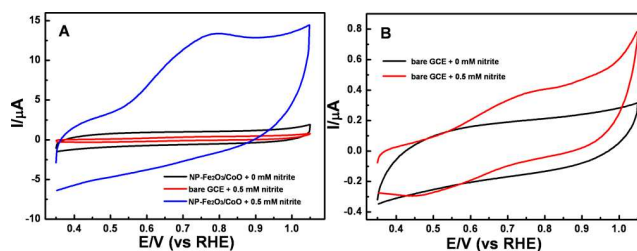

Fig. 2 (A) CV curves of NP-Fe_2O_3/CoO and bare GCE in 0.1 M PBS solution and 0.5 mM nitrite + 0.1 M PBS solution; (B) CV curves of bare GCE in 0.1 M PBS solution and 0.5 mM nitrite + 0.1 M PBS solution, scan rate: 50 mV/s.
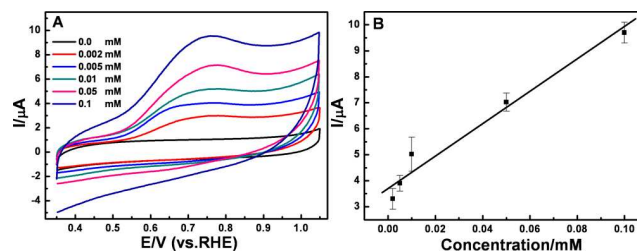

Fig. 3 (A) CV curves of NP-Fe_2O_3/CoO composites in PBS, and PBS + nitrite mixed solution with nitrite concentrations of 0, 0.002, 0.005, 0.01, 0.05, and 0.1 mM, scan rate 50 mV/s. (B) Calibration curve of NP-Fe_2O_3/CoO toward different concentrations of nitrite, Error bar = RSD (n= 5).
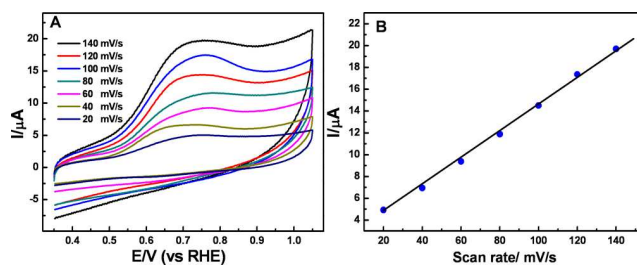

Fig. 4 (A) CV curves of 0.05 mM nitrite on NP-Fe_2O_3/CoO composites at different scan rates 20, 40, 60, 80, 100, 120, and 140 mV/s; (B) peak current vs. scan rate.
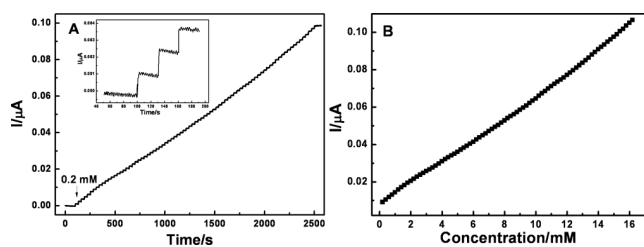
Fig. 5 (A) Amperometric current responses of NP-Fe$_2$O$_3$/CoO electrode on successive addition of 0.2 mM nitrite in PBS solution at 0.85 V, (B) Plots of current vs. nitrite concentration.
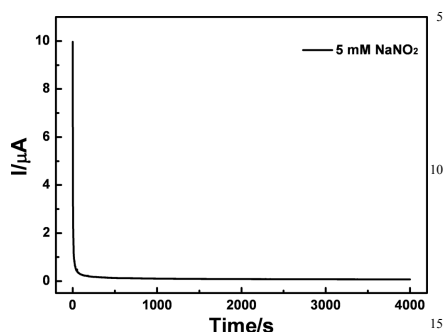

Fig. 6 Chronoamperogram for NP-Fe$_2$O$_3$/CoO composites in stirred 5 mM nitrite + PBS solution at 0.85 V.

Table. 1 A comparison of the performance of some sensor platforms using different electrodes for nitrite detection.

Modified electrode	Linear range (mM)	Detection limit (μM)	Reference
Cu/ZnSOD immobilized on carbon nanotube in polypyrrole matrix	0.0005-2	0.5	34
Silica-cerium mixed oxide carbon	0.03-3.9	2	35
gold nanoparticles /poly(3-methylthiophene) composites	0.005-0.5	2.3	36
Potassium-doped graphene	0.0005-3.9	0.2	37
graphene nanoplatelet-protein composite film	0.05-2.5	10	38
copper calcined layered double hydroxide and gold nanoparticles	0.001-0.191	0.5	39
gas-phase molecular absorption spectrometric	0.021-5	7	40
molecular absorption spectrometry	0.0217-2.17	0.65	41
screen printed graphite band electrodes	0.01-0.7	0.05	42
NP-Fe$_2$O$_3$/CoO	0.2-16.2	0.1	This work

Table. 2 Determination of nitrite content in sausage samples.

Samples	Nitrite content (mg·kg^{-1})	
	UV–vis	This sensor
Sample 1	9.88	9.95
Sample 2	10.12	10.05
Sample 3	11.23	11.15
Sample 4	10.57	10.42

4 Conclusions

NP-Fe$_2$O$_3$/CoO composites are easily prepared by a simple dealloying strategy. This nanoporous structure of oxides exhibits high electrocatalytic activity towards the nitrite detection. NP-Fe$_2$O$_3$/CoO composites-based sensor can be used for sensitive electrochemical detection of nitrite in a wide concentration range from 0.2 to 16.2 mM with a low detection limit about 0.1 μM. Additionally, the NP-Fe$_2$O$_3$/CoO composites have other advantages, such as easy preparation, low cost, green fabricating process, suitable for large-scale preparation, etc. These nanoporous oxide composites with uniform nanoparticles are not only scientifically interesting but also have great potential in electrochemical sensors.

Acknowledgements

Notes and references

Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China
Fax: +86-531-82765969; Tel: +86-531-89736103
Email: chm_xucx@ujn.edu.cn

1 K. Kim, K. L. Kima and K. S. Shin, *Analyst*, 2012, **137**, 3836.
2 Z. W. Xue, Z. S. Wu and S. F. Han, *Anal. Methods*, 2012, **4**, 2021.
3 M. Irandoust, M. Shariati-Rad and M. Haghighi, *Anal. Methods*, 2013, **5**, 5977.
4 Y. Wang, E. Laborda and R. G. Compton, *J. Electroanal. Chem*, 2012, **670**, 56.
5 C. M. Rushworth, Y. Yogarajah, Y. Zhao, H. Morgan and C. Vallance, *Anal. Methods*, 2013, **5**, 239.
6 S. A. Kyrtopoulos, *Cancer Surv.*, 1989, **8,** 423.
7 J. Zhang, C. Yang, C. X. Chen and X. R. Yang, *Analyst*, 2013, **138**, 2398.
8 B. Wang, R. Q. Meng, L. X. Xu, L. X. Wu and L. H. Bi, *Anal. Methods*, 2013, **5**, 885.
9 C. Liu, X. Y. Qiu, J. zhao and Y. L. Yang, *Anal. Methods,* 2014, **6**, 463.
10 J. E. Prest, S. J. Baldock, M. S. Beardah, S. P. Doyle, P. R. Fielden, N. J. Goddard and B. J. T. Brown, *Analyst*, 2011, **136**, 3170.
11 K. Fan and J. Wu, *Anal. Methods*, 2013, **5**, 5146.
12 N. Zhu, Q. Xu, S. Li and H. Gao, *Electrochem. Commun.*, 2009, **11**, 2308.
13 J. Y. Wang, P. Diao and Q. Zhang, *Analyst*, 2012, **137**, 145.
14 A. Kaushik, R. Khan, P. R. Solanki, P. Pandey, J. Alam, S. Ahmad and B. D. Malhotra, *Biosens. Bioelectron.*, 2008, **24**, 676.
15 P. K. Rastogi, V. Ganesan and S. Krishnamoorthi, *J. Mater. Chem. A*, 2014, **2**, 933.
16 Z. P. Chen, Z. Y. Zhang, C. L. Qu, D. W. Pan and L. X. Chen, *Analyst*, 2012, **137**, 5197.
17 S. L. Yang, X. Y. Liu, X. D. Zeng, B. Y. Xia, J. P. Gu, S. L. Luo, N. N. Mai and W. Z. Wei, *Sens. Actuators B: Chem.*, 2010, **145**, 762.
18 G. C. Yang, Y. S. Yang, Y. Z. Wang, L. B. Yu, D. F. Zhou and J. B. Jia, *Electrochim. Acta*, 2012, **78**, 200.
19 A. J. Lin, Y. Wen, L. J. Zhang, B. Lu, Y. Li, Y. Z. Jiao and H. F. Yang, *Electrochim. Acta*, 2011, **56**, 1030.
20 C. Wang, R. Yuan, Y. Q. Chai, F. X. Hu, *Anal. Methods*, 2007, **587**, 240.
21 B. Agboola and T. Nyokong, *Anal. Chim. Acta*, 2007, **587**, 116.
22 C. Wang, X. C. Zou, Q. Wang, K. Y. Shi, J. Tan, X. Zhao, Y. Q. chai and R. Yuan, *Anal. Methods*, DOI: 10.1039/c3ay41550c.

23 X. Cao, N. Wang and L. Guo, *Sens. Actuators B: Chem.*, 2009, **137**, 710.

24 H. B. Wu, H. Pang, and X. W. Lou, *Energy Environ. Sci.*, 2013, **6**, 3619.

5 25 H. Pang, J. W. Deng, J. M. Du, S. J. Li, J. Li, Y. H. Ma, J. S. Zhang, and J. Chen, *Dalton Trans.*, 2012, **41**, 10175.

26 H. Pang, Y. H. Ma, G. C. Li, J. Chen, J. S. Zhang, H. H. Zheng And W. M. Du, *Dalton Trans.*, 2012, **41**, 13284.

27 X. Cao, Y. J. Xu and N. Wang, *Electrochim. Acta*, 2012, **59**, 81.

10 28 J. J. Feng, P. P. Zhang, A. J. Wang, Y. Zhang, W. J. Dong and J. R. Chen, *J. Colloid Interf. Sci.*, 2011, **359**, 1.

29 C. X. Xu, Y. Q. Liu, J. P. Wang, H. R. Geng and H. J. Qiu, *J. Power Sources*, 2012, **199**, 124.

30 Z. Qi, Y. Z. Gong, C. Zhang, J. L. Xu, X. G. Wang, C. C. Zhao, H. Ji 15 and Z. H. Zhang, *J. Mater. Chem.*, 2011, **21**, 9716.

31 A. Elisavet, T. Eleni, T. Lazaros, K. Foteini, *Talanta*, 2011, **85**, 2385.

32 J. P. Wang, H. Gao, F. L. Sun, Q. Hao and C. X. Xu, *Biosens. Bioelectron.*, 2013, **42**, 550.

33 V. Kumar, M. Banerjee and A. Chatterjee, *Talanta*, 2012, **99**, 610.

20 34 S. Rajesh, A. K. Kanugula and K. Bhargava, *Biosens. Bioelectron.*, 2010, **26**, 689.

35 G. Silveira, A. Morais, P. C. M. Villis, C. M. Maroneze, Y. Gushikem, A. M. S. Lucho and F. L. Pissetti, *J. Colloid Interf. Sci.*, 2012, **369**, 302.

25 36 X. Huang, Y. X. Li, Y. L. Chen and L. Wang, *Sens. Actuators B : Chem.*, 2008, **134**, 780.

37 X. R. Li, J. Liu, F. Y. Kong, X. C. Liu, J. J. Xu and H. Y. Chen, *Electrochem. Commun.*, 2012, **20**, 109.

38 R. Yue, Q. Lu and Y. K. Zhou, *Biosen. Bioelectron.*, 2011, **26**, 4436.

30 39 L. Cui, X. M. Meng, M. R. Xu, K. Shang, S. Y. Ai and Y. P. Liu, *Electrochim. Acta*, 2011, **56**, 9769.

40 M. Zhang, Z. Zhang, D. X. Yuan, S. C. Feng and B. C. Liu, *Talanta*, 2011, **84**, 443.

41 G. C. Brandao, D. C. Lima and S. L. C. Ferreira, *Talanta*, 2012, **98**, 35 231.

42 J. P. Metters, R. O. Kadara, and C. E. Banks, *Sens. Actuators B : Chem.,* 2012, **169**, 136.

43 X. W. Chen, F. Wang and Z. L. Chen, *Anal. Chim. Acta*, 2008, **623**, 213.
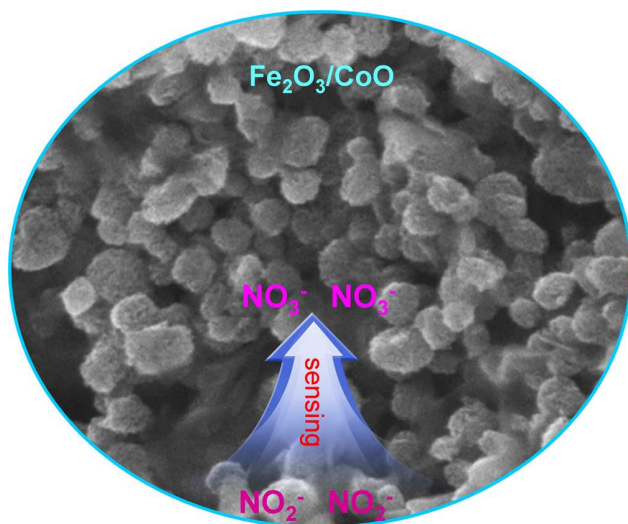
40

45

50

55

60

65

70

TOC graphic

Nanoporous NP-Fe_2O_3/CoO composites, characterized by open three-dimensional bicontinuous nanoparticle architecture, were easily fabricated by selectively dealloying FeCoAl source alloy, which exhibit greatly sensing performance, structure stability, and analytical utility towards nitrite compared.