View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Wang, Z. Wang, X. Xiang, R. Zhang, X. Shi and X. Sun, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC05837G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 17 August 2018. Downloaded on 8/18/2018 2:38:42 AM



Journal Name

COMMUNICATION

MnO₂ nanoarray: an efficient catalyst electrode for nitrite electroreduction toward sensing and NH₃ synthesis applications

Received 00th January 20xx, Accepted 00th January 20xx

Rui Wang,^{¶a} Zao Wang,^{¶a,b} Xiaojiao Xiang,^a Rong Zhang,^b Xifeng Shi^c and Xuping Sun^{a*}

DOI: 10.1039/x0xx00000x

www.rsc.org/

It is highly attractive to develop efficient electrocatalysts for sensitive and selective detection of nitrite. In this communication, we report that MnO_2 nanoarray on titanium mesh (MnO_2 NA/TM) is an efficient catalyst electrode for electroreduction of nitrite. Electrochemical measurements demonstrate that the constructed MnO_2 NA/TM sensor offers superior sensing performances, having a short response time of 3 s, a wide detection range of 1.0 μ M to 5.0 mM, a low detection limit of 1.5 nM (S/N = 3), a response sensitivity of 10301 μ A mM⁻¹ cm⁻², with satisfactory selectivity, specificity, and reproducibility. This electrochemical system is also capable of catalyzing the electrochemical reduction of nitrite to NH₃ with a transformation efficiency of 6%.

As an important necessity for preservatives and fertilizing reagents for food, nitrites are widely presented in environment.¹ The rapid increasing pollution of ground water resources for human consumption by nitrites due to the anthropogenic activities from agriculture (by using nitrogen based fertilizer) and waste water from industry is receiving worldwide attention.² Noticeable, nitrites are an essential precursor for the formation of carcino genic N-nitrosamine.³ Therefore, it is of great importance to accurately monitor nitrite for public health, environmental and food industries. Several analytical techniques have been developed for nitrite determination including fluorescence,⁴ chemiluminescence,^{5,6} capillary electrophoresis,⁷ and chromatography.⁸ However, expensive equipments, tedious detection procedures and often time consuming have limited the further applications of these analytical methods. Compared to these methods, the electrochemical method can provide compact, relatively inexpensive, reliable, sensitive and real-time analysis.9-11

Manganese oxides are very attractive alternative to noble metal catalysts due to their merits, including molecular adsorption, ion-changing, suitably high density and purity, electrochemical and magnetic properties.¹² Previous reports have illustrated that MnO_2 nanostructures are potential catalysts for constructing nitrite sensor, which based on electrochemical oxidation of nitrite.¹³⁻¹⁸ Contrast with anodic oxidation, cathodic catalytic reduction can not only avoid secondary reactions,¹⁹ but could produce NH_3 as fertilizer. To the best of our knowledge, however, their application toward electrochemical nitrite detection based on cathodic catalytic reduction has scarcely reported yet.

In this communication, we report the first use of MnO_2 nanoarray supported on titanium mesh ($MnO_2 NA/TM$) as an efficient catalyst electrode for nitrite reduction under neutral condition. As an electrochemical sensor for nitrite, such MnO_2 NA/TM exhibits superior sensing performance with a rapid response time of 3 s, a wide range of 1.0 µM to 5.0 mM, a low detection limit of 1.5 nM (S/N = 3), a response sensitivity of 10301 µA mM⁻¹ cm⁻², with satisfactory selective specificity and reproducibility. Interestingly, this electrochemical system also offers a nitrite-to-NH₃ transformation efficiency of 6%.

Fig. 1a shows the X-ray diffraction (XRD) patterns for MnO₂ NA/TM, suggesting the presence of MnO₂ (JCPDS. 44-0141) and metallic titanium. The scanning electron microscopy (SEM) analysis indicates that the entire surface of TM (Fig. S1) is completely covered by MnO₂ nanowires array (Fig. 1b). The transmission electron microscopy (TEM) image (Fig. 1c) also confirms the formation of MnO₂ nanowire. From the high resolution TEM (HRTEM) image presents in Fig. 1d, we can clearly resolve the lattice with an interplanar spacing of 0.236 nm indexed to the (211) plane of MnO₂. Energy-dispersive Xray (EDX) elemental mapping images (Fig. 1e) demonstrate the homogenous distribution of Mn and O elements throughout the entire nanoarray. Fig. 1f shows the X-ray photoelectron spectroscopy (XPS) survey spectrum for MnO₂. The Mn 2p spectrum (Fig. 1g) exhibits binding energies (BEs) at 641.6 and 653.4 eV eV for Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively, consistent with the characteristic peaks of MnO2.20 The BEs located at

^a Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China. E-mail: xpsun@uestc.edu.cn

^b College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China ^c College of Chemistry, Chemical Engineering and Materials Science, Shandona

Normal University, Jinan 250014, Shandong, China † Electronic Supplementary Information (ESI) available: Experimental section and

^{*} Electronic Supplementary Information (ESI) available: Experimental section and supplementary figures. See DOI:

COMMUNICATION

Published on 17 August 2018. Downloaded on 8/18/2018 2:38:42 AM

531.9 and 530.1 eV are assigned to the O 1s region (Fig. 1h). These results demonstrate the successful growth of MnO_2 nanowires array on TM.



within 3 s. The calibration curve for our NaNO₂ sensor is shown in Fig. 3c, which gives a linear dependence on NaNO₂ concentration in the range of 1.0 μ M to 5.0 mM (R² = 0.9938). The detection limit and sensitivity were calculated as 1.5 nM (S/N = 3) and 10301 μ A mM⁻¹ cm⁻², respectively. These values compare favorably to the behaviors of most reported electrochemical NaNO₂ sensors (Table S1). Anti-interference is another important factor for analysis applications.²² The antiinterference properties were assessed by successive additions of 1.0 mM NaNO₂ and 3.0 mM other interferences in 0.1 M Na2SO4. As shown in Fig. 3d, these compounds have no interference on NaNO₂ determination. a -2 b-30 1.0 µM -50 0.04 mM 0.2 mM cm⁻²) 0.5 mMcu, -1.0 Ym) -75 Am) -42



further illustrates that the cathodic peak current density

increases linearly as the rise of NaNO2 concentration, as shown

in Fig. 2c. Although previous work reported that platinum wire

as counter electrode could cause anodic dissolution and

subsequent Pt deposition at the working electrode,²¹ using graphite rod as the counter electrode in our present study

gives consistent experimental result (Fig. S2). It indicates that

NA/TM electrode in 0.1 M Na_2SO_4 with consecutive step changes of $NaNO_2$ concentrations at an applied potential of – 1.75 V. The electrode shows a fast amperometric response toward $NaNO_2$ and can achieve steady state current density

Fig. 3a and 3b present typical current-time plots of MnO₂

platinum wire has no effect on sensing performance.

Fig. 3. (a, b) Amperometric responses and (c) the corresponding calibration curve of MnO_2 NA/TM electrode to successive additions of $NaNO_2$ at -1.75 V in 0.1 M Na_5O_4 . (d) Amperometric responses of MnO_2 NA/TM to the successive addition of 1.0 mM $NaNO_2$, 3.0 mM Na_2O_4 . (a) Mm $NaNO_2$, 3.0 mM Na_2O_4 . (b) mM $NaNO_2$, 3.0 mM Na_2O_4 . (c) mM $NaNO_2$ (c) mM $NaNO_2$ (c) mM $NaNO_2$ (c) mM $NaNO_2$ (c) mM $NaNO_2$.

Furthermore, the reproductivity of this nitrite senor was assessed by detecting 10 mM sample with five prepared electrodes independently, and the relative standard deviation is 1.5%, showing the satisfactory reproducibility. Considering potential practical application, we also conducted stability test. As shown in Fig. S3, the currents percents remains the same after 30 days, indicating a good stability. In addition, chronoamperometry experiments were conducted to evaluate a continuous stability of MnO_2 NA/TM in 0.1 M NaSO₄ containing 5.0 mM NaNO₂ at -1.75 V. As shown in Fig. S4, there is no obviously decrease within at least 13 h, indicating a satisfactory stability.

9938). .5 nM values borted ence is e antiditions 0.1 M ve no 1100 ^o 1100 ^o 960 0 960





Fig. 2. (a) LSV curves of blank TM (curves 1 and 2) and MnO₂ NA/TM (curves 3 and 4) in 0.1 M Na₂SO₄ (pH: 7.0) with the absence (curves 1 and 3) and presence (curves 2 and 4) of 4.0 mM NaNO₂ (scan rate: 30 mV s⁻¹). (b) LSV curves for MnO₂/TM in 0.1 M Na₂SO₄ with the presence of varied NaNO₂ concentrations: 0, 2, 4, 6, 8, 10, and 12 mM (from inner to outer) at a scan rate of 30 mV s⁻¹. (c)

The electrocatalytic properties of MnO₂ NA/TM electrode for NaNO_2 reduction were tested with platinum wire as counter electrode and Ag/AgCl as reference electrode. Fig. 2a shows linear sweep cycle voltammetry (LSV) curves of MnO₂ NA/TM and blank TM in 0.1 M Na₂SO₄ with the absence (curve 1, 3) and presence (curve 2, 4) of 4.0 mM NaNO₂ at a scan rate of 30 mV s⁻¹ within the potential rang of 0.0 to -2.0 V. Obviously, blank TM only shows very small increase in cathodic current after introducing 4.0 mM NaNO₂. In sharp contrast, MnO₂ NA/TM offers greatly enhanced cathodic current in the presence of 4.0 mM NaNO₂. These results confirm that MnO₂ is efficient for NaNO₂ electro-reduction. Fig. 2b shows the LSV curves of MnO₂ NA/TM toward different concentrations of NaNO2 in 0.1 M Na2SO4. Clearly, the current densities of reduction peak increase with increased NaNO₂ concentration in a range of 0 to 12 mM. The corresponding calibration curve

This journal is © The Royal Society of Chemistry 20xx

ChemComm Accepted Manuscript

Journal Name

To assess its practicability, $MnO_2 NA/TM$ was applied to detect $NaNO_2$ in river water and tap water. As observed, the reduction peak current densities increased as the successive addition of $NaNO_2$ into the river water and tap water (Fig. S5a and S5c). And the derived calibration curve indicated that the peak current densities increase linearly as the increased $NaNO_2$ concentration in a range of 0.0 to 5.0 mM (Fig. S5b and S5d). These observation strongly demonstrate that the MnO_2 NA/TM electrode is a good candidate for practical samples analysis.

NH₃ is an essential building block for manufacturing synthetic chemicals like fertilizers, medicaments, dyes, explosives, and resins, 23,24 and electrocatalytic N₂ reduction is regarded as a promising environmentally-benign process for sustainable NH₃ production.²⁵ It is very interesting to have found that MnO₂ NA/TM is also capable of catalyzing the electrochemical reduction of nitrite to NH₃. The generated NH₃ was spectrophotometrically determined by the indophenol blue method.²⁶ After the current-time test at different potentials (Fig. 4a), the electrolytes were colored with indophenol indicator before collecting UV-Vis absorption spectra (Fig. 4b). Fig. 4c shows the NH₃ transformation efficiency determined by the calibration curves (Fig. S6). At a nagetive potential of -1.75 V, MnO₂ NA/TM shows the largest NH₃ transformation efficiency of 6%. Also note that during the cycling test (Fig. 4d), the losses of the NH₃ transformation efficiency are negligible.



NA₃ transformation quantity at a series of potential. (d) Cycle test of MinO₂ NA/TM at -1.75 V in 0.1 M Na₂SO₄. In summary, MnO₂ NA/TM is proposed as an efficient

catalyst electrode for nitrite electroreduction under moderate condition. Such $MnO_2 NA/TM$ not only shows superior sensing performances for nitrite detection, but it is also effective to convert nitrite to NH_3 with a transformation efficiency of 6%. This work would open up an exciting new avenue to explore the use of transition metal oxides as an attractive catalyst materials for electroreduction of nitrite toward sensing and NH_3 synthesis applications.

This work was supported by the National Natural Science Foundation of China (No. 21575137). We also appreciate Hui Wang from the Analytical & Testing Centre of Sichuan University for her helping with SEM characterization.

Conflicts of interest

There are no conflicts to declare.

References

- R. S. Braman and S. A. Hendrix, Anal. Chem., 1989, 61, 2715– 2718.
- 2 M. Noroozifar, M. Khorasani-Motlagh, A. Taheri and M. Homayoonfard, *Talanta*, 2007, **71**, 359–364.
- 3 Z. Lin, W. Xue, H. Chen and J. M. Lin, *Anal. Chem.*, 2011, **83**, 8245–8251.
- 4 F. Gao, L. Zhang, L. Wang, S. She and C. Zhu, Anal. Chim. Acta, 2005, 533, 25–29.
- 5 R. D. Cox, Anal. Chem., 1980, 52, 332-335.
- 6 P. Mikuska, Z. Vecera and Z. Zdrahal, Anal. Chim. Acta, 1995, **316**, 261–268.
- 7 A. A. Okemgbo, H. H. Hill, W. F. Siems and S. G. Metcalf, *Anal. Chem.*, 1999, **71**, 2725–2731.
- 8 S. B. Butt, M. Riaz and M. Z. Iqbal, *Talanta*, 2001, 55, 789– 797.
- 9 G. Mirri, S. D. Bull, P. N. Horton, T. D. James, L. Male and J. H. R. Tucker, J. Am. Chem. Soc., 2010, 132, 8903–8905.
- 10 Y. Lin, K. Liu, P. Yu, L. Xiang, X. Li and L. Mao, *Anal. Chem.*, 2007, **79**, 9577–9583.
- 11 T. Chen, D. Liu, W. Lu, K. Wang, G. Du, A. M. Asiri and X. Sun, Anal. Chem., 2016, 88, 7885–7889.
- 12 D. K. Walanda, G. A. Lawrance and S. W. Donne, J. Power Sources, 2005, 139, 325–341.
- 13 C. E. Langley, Scaron, B. Ljukic, C. E. Banks and R. G. Compton, *Anal. Sci.*, 2007, **23**, 165–170.
- 14 Š. Biljana and C. R. G., *Electroanal.*, 2007, **19**, 1275–1280.
- 15 C. Xia, W. Ning and G. Lin, Sens. Actuators B-Chem., 2009, 137, 710–714.
- 16 J. J. Feng, P. P. Zhang, A. J. Wang, Y. Zhang, W. J. Dong and J. R. Chen, J. Colloid Interface Sci., 2011, 359, 1–8.
- 17 N. Jaiswal, I. Tiwari, C. W. Foster and C. E. Banks, *Electrochim. Acta*, 2017, **227**, 255–266.
- 18 B. R. Sljukic, R. O. Kadara and C. E. Banks, Anal. Methods, 2011, 3, 105–109.
- 19 M. Kobya, O. T. Can and M. Bayramoglu, J. Hazard. Mater., 2003, 100, 163–178.
- 20 Z. S. Wu, W. Ren, D. W. Wang, F. Li, B. Liu and H. M. Cheng, ACS Nano, 2010, 4, 5835–5842.
- 21 J. Wang, F. Xu, H. Jin, Y. Chen and Y. Wang, *Adv Mater.*, 2017, **29**, 1605838.
- 22 Z. Wang, X. Cao, D. Liu, S. Hao, G. Du, A. M. Asiri and X. Sun, Chem. Commun., 2016, 52, 14438–14441.
- 23 V. Smil, Nature, 1999, 400, 415.
- 24 R. Schlögl, Angew. Chem., Int. Ed., 2003, 42, 2004-2008.
- 25 L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.
- 26 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–841.

, 2010, **37** 1999, **400** *w. Chem.,* X. Ren, Y. Id X. Sun, J. R. E. Rut 841.

This journal is © The Royal Society of Chemistry 20xx