Short Communication

Ultra Sensitive Voltammetric Determination of Hydrazine with Curcumin - Ordered Mesoporous Carbon Composite as Sensing Material

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With curcumin - ordered mesoporous carbon (CM - OMC) composite as sensing material, an ultra sensitive voltammetric sensor toward hydrous hydrazine determination was developed and evaluated. The morphology of the present CM-OMC showed that after electro-deposition, OMC was partially coated by CM, which may led to an enhanced electro-catalytic ability of CM-OMC compared with CM or OMC. Electrochemical evaluations, including cyclic voltammograms (CVs) and amperometric i-t technique showed that the present sensor displayed excellent electrocatalytic activity towards hydrazine electrochemical oxidation. A linear relationship between the oxidation peak current and hydrazine concentration was obtained in the range of 12.5 to 225 $\mu molL^{-1}$ with a correlation coefficient of 0.998 using the amperometric detection technique. The sensitivity and detection limit were determined to be 10.54 $nA\mu molL^{-1}$ and 0.39 $\mu molL^{-1}$, respectively. The present electro-catalytic method was expected to be widely used due to its simplicity, low cost, high sensitivity, and fast response for the detection of hydrous hydrazine.

1. INTRODUCTION

Hydrazine is a colorless, fuming, flammable and corrosive liquid that is highly toxic and dangerously unstable unless handled in solution [1]. it was now widely applied in many industrially fields [2, 3, 4, 5, 6, 7]. Symptoms of acute exposure to high levels of hydrazine may include irritation of the eyes, nose, and throat, dizziness, headache, and coma in humans. Acute exposure can also damage the liver, kidneys and central nervous system [8]. Because of these side effects, analytical

chemists are make their efforts to develop reliable and sensitive detection techniques for hydrous hydrazine determination.

Various analytical methods have been reported for the separation and determination of hydrazine based on spectrophotometry, titrimetry and fluorimetry etc [9, 10, 11]. However, electrochemical techniques are becoming very important for hydrous hydrazine detection as a result of its rapidity, easy operation, low cost, high sensitivity, low detection limit and wide linear range responses. Since direct electrochemical oxidation of hydrous hydrazine is kinetically slow and generally occurs at a relatively high oxidation potential on common electrodes, a more reliable and sensitive method must be established to overcome this problem. Previously, some effective electrochemical methods have been reported.[3,4] Our group also has fabricated a cerium hexacyanoferrate/OMC based sensor towards the determination of hydrous hydrazine [12].

CM is a principal curcuminoid that can exist in several tautomeric forms, including a 1, 3-diketo form and two equivalent enol forms [13]. It is known to posses biological activities such as anti-angiogenic, antioxidant, wound healing and anti cancer effects. It fights free radical formations in blood and body tissues and helps to prevent various cardio-vascular, viral and other chronic diseases [14]. Because of these biological importances, the redox process and the catalytic activity of CM are becoming increasingly important to analytical chemist. For instance Reza Ojani et. al used Nickel-CM complex modified carbon paste electrode to investigate the electrocatalytic oxidation of amoxicillin [15]. Constantin Mihailciuc et al investigated the electrochemical response of CM and its analogue on activated glassy carbon electrode (GCE) [16].

OMC is known to exhibits excellent electro-catalytic activities due to its well-ordered pore structure, electrical conductivity, and high surface area [17]. Here we combine the advantages of both CM and OMC together to construct a CM-OMC composite based hydrazine sensor and the evaluation results showed that the sensor produces a very good response for both voltammetric and amperometric detection.

2. EXPERIMENTAL PART

2.1 Reagents

OMC was obtained from Aldrich. Hydrous hydrazine was obtained from Tianjin, chemical reagent Co. CM was obtained from Sinopharm Chemical Regent Co., Ltd. Sodium bicarbonate (NaHCO$_3$), sodium dihydrogen phosphate dihydrate (NaH$_2$PO$_4$·2H$_2$O) and disodium hydrogen phosphate dodecahydrate (Na$_2$HPO$_4$·12H$_2$O) were purchased from Beijing chemical reagent Co. Doubly-distilled water was used to prepare and dilute the high concentration of all stock solutions used. The experiments were conducted at room temperature and repeated several times in order to have consistent and satisfactory results.

2.2 Apparatus

All electrochemical experiments were performed using a CHI660C electrochemical work station (CH Instruments, Shanghai Chenhua Instrument Corporation, China) with a conventional three electrode cell. Cyclic voltametry (CV) and amperometric techniques were selected using an Ag/AgCl (saturated with KCl) electrode, glassy carbon electrode and a platinum wire as reference, working and counter electrode, respectively. SEM images were obtained on a FEG leo 1550 (Gemini instrument).

2.3 Preparation of CM-OMC-GCE

First the GCE was polished with 1, 0.3 and 0.05 µm Al_2O_3 on a polish pad until a shiny surface was obtained. The polished electrode was then washed with distilled water and then sonicated in water for 10 seconds and then in 95% absolute ethanol for another 10 seconds using a ultrasonic cleaner. The bare electrode was electrochemically activated in 0.1 $molL^{-1}$ $NaHCO_3$ with continuous potential cycling between - 1.0 and 1.55 V at a scan rate of 100 mVs^{-1} for 32 cycles in order to obtain a convincing stable voltammogram. The other step involved the modification of the GCE surface using OMC to form modified OMC-GCE. To achieve this 2 µl of OMC (0.5 mg/ml in DMF) was applied two times to a freshly prepared electrode surface and dried after each application using an infra red lamp for 15 minutes. Next a freshly prepared electrode was put into a 0.2 $molL^{-1}$ PBS (pH 8.0) containing 0.1 $mmolL^{-1}$ CM for 32 cycles between - 0.2 and 0.5 V at a scan rate of 100 mVs^{-1}. This process led to the formation of CM-GCE modified. And finally the OMC-GCE was further modified using CM to form modified CM-OMC-GCE as working electrode. For this the same procedure was used as that of the CM-GCE modification.

## 3. RESULTS AND DISSCUSSIONS

3.1 Morphology of the CM-OMC-GCE
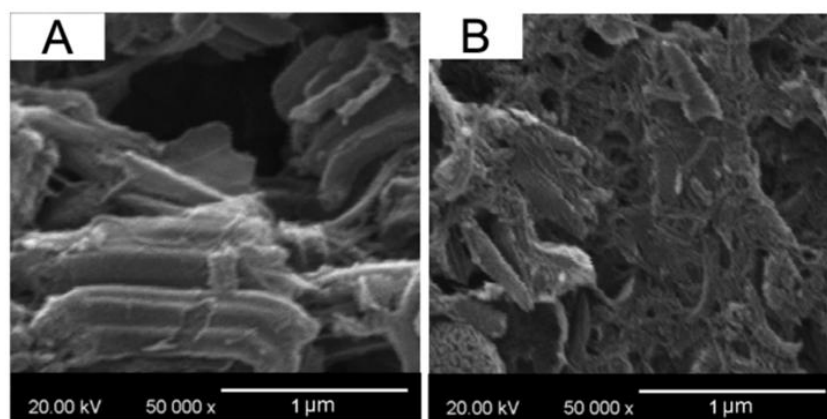
Figure 1. SEM images of A: OMC, B: CM/OMC.

The morphology of the present CM-OMC-GCE was characterized by SEM with OMC-GCE for comparison. Figure 1 revealed the images of OMC/GCE (A) and CM/OMC/GCE (B). It could be clearly seen that the surface of OMC was a well-defined morphology, and the OMC exhibited the form of small bundles and uniform dispersion. After electro-deposition, the OMC was found to be partially coated by CM.

3.2 Kinetic characteristics of CM-OMC
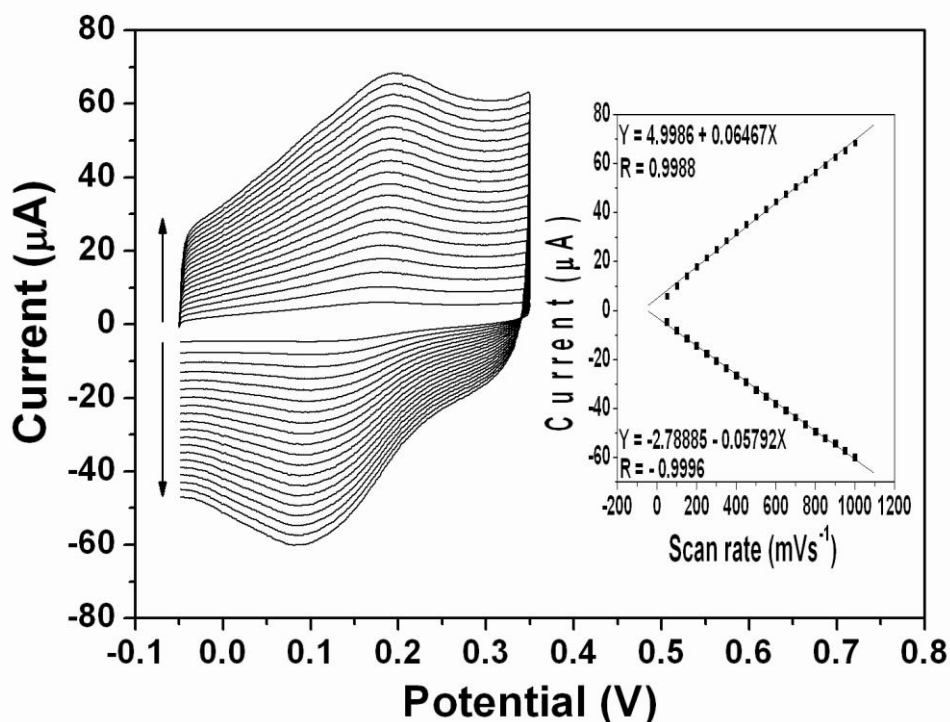
Figure 2. cyclic voltammograms of CM-OMC-GCE in 0.2 molL^{-1} PBS (pH 8.0) from 50 to 1000 mVs^{-1} at intervals of 50 mVs^{-1} (from inner to outer). Inset graph, Plot of peak current against scan rate.

The kinetic characteristics of CM-OMC were investigated using CV. As can be seen from the cyclic voltammograms (CVs) (Figure 2.), the redox behavior of the CM-OMC, including both the peak current (I_p) and the peak separation (E_p), was enhanced with the increase of scan rate. For further analysis of the CV results, it was found that when the scan rate various from 50 to 1000 mVs^{-1}, I_p was proportional to the scan rate (inset of figure 2. a plot of I_p against the corresponding scan rates gives a very good linear correlation of about 0.9988 for the oxidation peak currents and 0.9996 for the reduction peak currents) as predicted theoretically for adsorbed species [18], which was a quasi-reversible surface waves.

3.3 Electrocatalytic oxidation of hydrazine on CM-OMC
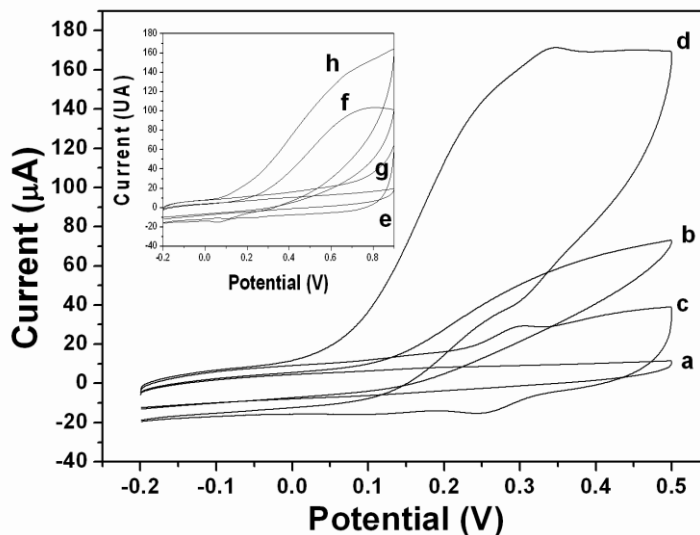
Figure 3. CVs of bare activated GCE, (e, f), OMC-GCE, (g, h), CM-GCE (a, b), CM-OMC-GCE (c, d) in 0.2 molL^{-1} PBS of pH 8.0 in the absence (a, c, e and g) and presence (b, d, f, and g) of 2 mmolL^{-1} hydrazine, respectively.

The electrocatalytic oxidation of hydrazine was investigated using CV in a 0.2 molL^{-1} PBS (pH 8.0). Figure 3. highlights the CVs at the surface of activated bare GCE，OMC-GCE，CM-GCE，and CM-OMC-GCE in the absence and presence of 2 mmolL^{-1} hydrazine. When the activated bare GCE was placed in the PBS there was no observable response (curve e) but upon the addition of 2 mmolL^{-1} hydrazine there was a response between 0.2 and 0.9 V and an oxidation peak potential observed at about 0.76 V (curve f). For the OMC-GCE just like the activated bare GCE there was also no observable response in PBS solution (curve g). But when 2 mmolL^{-1} hydrazine solution was added there was a clear response between 0.1 and 0.9 V and an oxidation peak potential was observed at about 0.68 V (curve h) indicating an electro-catalytic activity between OMC-GCE and hydrazine in the electrolyte. Under the same experimental conditions，a response between 0.1 and 0.5 V was clearly seen on CM-GCE (curve b) in the presence of 2 mmolL^{-1} hydrazine. For CM-OMC-GCE in PBS there was an oxidation peak at about 0.3 V (curve c). This is due to the possible pair of redox peaks pertaining to the Q/QH$_2$ (quinone/hydroquinone) redox couple of CM derivative (CM-Q/CM-QH$_2$). That is CM was first oxidized to a corresponding o-quinone derivative and then underwent the normal Q/QH$_2$ electrochemistry through a two electron and two proton transfer process [19, 20]. As a result of adding 2 mmolL^{-1} hydrazine solution into the PBS the anodic current increased sharply between 0 and 0.5 V and the oxidation peak potential was at about 0.34 V (curve d). The above results indicated that the highest current response and the lowest potential response can be obtained at CM-OMC-GCE among the four present electrodes.

The CV responses (figure not given) of CM-OMC-GCE in 0.2 molL^{-1} PBS (pH 8.0) in the presence of different concentrations of hydrazine revealed that as the hydrazine concentration was increased the oxidation current also increased and the reduction peak current decreased, which indicate a strong electro-catalytic activity of CM-OMC-GCE toward the oxidation of hydrazine. The observable increase of anodic current and the almost disappeared cathodic current indicate that the anodic catalytic current was mainly obtained from the hydrazine concentration in the solution.[4] A plot (not given) of the oxidation currents (collected at 0.34 V) versus the corresponding concentration of hydrazine shows a linear correlation coefficient of 0.998 from 1.0 to 6.0 mmolL^{-1}.

3.4 Amperometric determination of hydrazine

The voltammetric result obtained was used to study the electrochemical sensing of hydrazine at the CM/OMC/GCE. As the amperometric current-time response was recorded, the detection limit and the calibration curve for hydrazine solution at the CM-OMC-GCE were estimated.
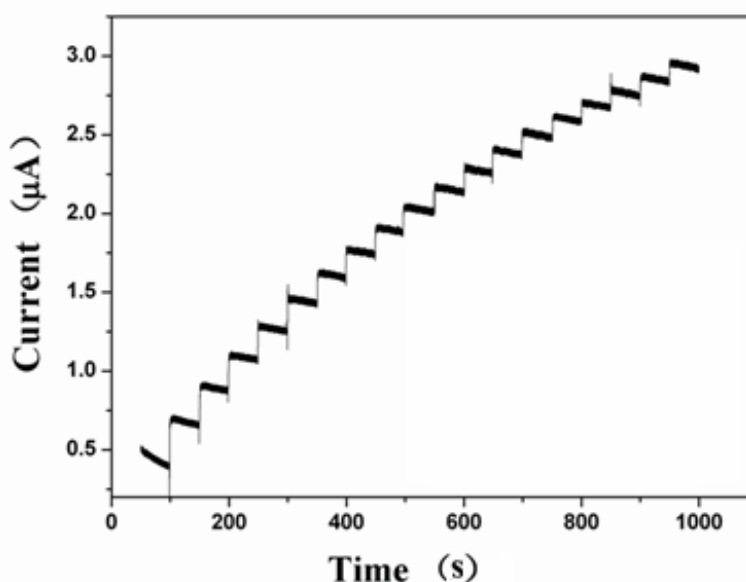
Figure 4. The amperometric response of CM-OMC-GCE in 0.2 molL^{-1} PBS (pH 8) observed during the successive addition of 2.5 µL of 0.05 mmolL^{-1} hydrazine. Applied potential is 0.34 V.

Shown in figure 4 is the direct amperometric response upon the successive addition of 2.5 µL of 0.05 mmolL^{-1} hydrazine under continuous stirring into 10 mL of 0.2 molL^{-1} PBS (pH 8.0). A potential of 0.34 V was constantly used for 1000 seconds. The introduction of hydrazine started after 150 seconds and other subsequent additions were made after every 50 seconds. It was observed that for every addition of 2.5 µL of hydrazine there was an increase in current and the response occurred within 3 seconds. The staircase-like curve obtained indicating a very good electro-catalytic ability of CM-OMC-GCE toward the electrochemical oxidation of hydrazine. The current-hydrazine

concentration curve gives a linear correlation coefficient of 0.998 from 12.5 to 225 $\mu molL^{-1}$. The sensitivity and detection limit were determined to be 10.54 $nA\mu molL^{-1}$ and 0.39 $\mu molL^{-1}$ respectively, which were more lower than the existing report (22.9 $nA\mu molL^{-1}$ and 1.4 $\mu molL^{-1}$) [3].

Table 1. i-t current responses of 20 $\mu molL^{-1}$ hydrazine, 50 $\mu molL^{-1}$ sodium sulfate, potassium nitrate, glucose, ammonium chloride, calcium chloride, sodium nitrite, sodium citrate, zinc nitrate, uric acid and 20 $\mu molL^{-1}$ dopamine in 0.2 $molL^{-1}$ PBS (pH 8.0).

compound	concentration	Target(T) /Interferer(I)	Stable current response value	Interfere or not (Y/N)
hydrazine	20 $\mu molL^{-1}$	T	2.25×10^{-7}A	—
sodium sulfate	50 $\mu molL^{-1}$	I	2.25×10^{-7}A	N
potassium nitrate	50 $\mu molL^{-1}$	I	2.24×10^{-7}A	N
glucose	50 $\mu molL^{-1}$	I	2.26×10^{-7}A	N
ammonium chloride	50 $\mu molL^{-1}$	I	2.26×10^{-7}A	N
calcium chloride	50 $\mu molL^{-1}$	I	2.28×10^{-7}A	N
sodium nitrite	50 $\mu molL^{-1}$	I	2.27×10^{-7}A	N
sodium citrate	50 $\mu molL^{-1}$	I	2.28×10^{-7}A	N
zinc nitrate	50 $\mu molL^{-1}$	I	2.28×10^{-7}A	N
uric acid	50 $\mu molL^{-1}$	I	2.29×10^{-7}A	N
dopamine	20 $\mu molL^{-1}$	I	3.89×10^{-7}A	Y

In real sample analysis, some compounds may coexist with hydrous hydrazine and may interfere with the analyzing result. Here 10 compounds were chosen to test the anti-interfer ability of the present sensor using i-t technique: after reached a stable response, 20 $\mu molL^{-1}$ hydrazine, 50 $\mu molL^{-1}$ sodium sulfate, potassium nitrate, glucose, ammonium chloride, calcium chloride, sodium nitrite, sodium citrate, zinc nitrate, uric acid and 20 $\mu molL^{-1}$ dopamine were added into 0.2 $molL^{-1}$ PBS (pH 8.0) one by one and the currents response were recorded. As shown in table 1, only dopamine exhibit some interference. Herein, some pretreatments are necessary to reduce the interference of dopamine.

For the reproducibility investigation, the current response of 1 $mmolL^{-1}$ hydrazine on CM-OMC-GCE was recorded. The results showed that for 10 parallel experiments, the relative standard deviation (RSD) is 2.56%, which revealed good reproducibility. The stability of CM-OMC-GCE was examined during a period of one month. The modified electrode was stored at 4℃ in a refrigerator and tested every day for the first 10 days and every five day over the next 20 days. With the mean current response (n=3) on the first day was set to 100%, the current response at the modified electrode in 1 $mmolL^{-1}$ hydrazine solution remained 88.5% after one month, which suggest good stability of CM-OMC-GCE.

4. CONCLUSIONS

CM was electro-deposited on the OMC-GCE surface to form an effective modified working electrode and this fabricated electrode was used as the hydrazine sensor. The evaluation results of this sensor showed that it exhibit a very good electro-catalytic ability towards the oxidation of hydrazine thus leading to an increase in peak current and decrease in peak potential. This CM-OMC modified electrode is expected to become a very useful tool for hydrazine analysis due to its properties of high sensitivity, good reproducibility, good stability and easy handling.

References

1. M. A. Aziz and A. N. Kawde, *Talanta*, 115 (2013) 214
2. S. P. Kim and H. C. Choi, *Sens. Actuators B*, 207 (2015) 424
3. L. Zheng and J. F. Song, *Sens. Actuators B*, 135 (2009) 650
4. S. M. Golabi and H. R. Zare, *J. Electroanal. Chem*, 465 (1999) 168
5. M. Shamsipur, Z. Karimi, M. A. Tabrizi and A. Shamsipur, *Electroanalisis,* 26 (2014) 1994
6. B. Fang, C. H. Zhang, W. Zhang and G. F. Wang, *Electrochim. Acta*, 55 (2009) 178
7. G. Z. Hu, Z. P. Zhou, Y. Guo, H. Q. Hou and S. J. Shao, *Electrochem. Commun*, 12 (2010) 422
8. E. Gionfriddo, A. Naccarato, Sindona and A. Tagarelli, *Anal. Chim. Acta*, 835 (2014) 47
9. M. George, K. S. Nagaraja and N. Balasubramanian, *Talanta,* 75 (2008) 27
10. J. S. Budkuley, *Mikrochim. Acta*, 108 (1992) 103
11. A.Safavi and A. A. Ensafi, *Anal. Chim. Acta*, 300 (1995) 307
12. H. J. Yang, B. P. Lu, L. P. Guo and B. Qi, *J. Electroanal. Chem*, 650 (2011) 171
13. T. M. Kolev, E. A. Velcheva, B. A. Stamboliyska and M. Spiteller, *Int. J. Quantum. Chem*, 102 (2005) 1069
14. R. K. Maheshwari, A. K. Singh, J. Gaddipati and R. C. Srimal, *Life Sci*, 78 (2006) 2081
15. R. Ojani, J. B. Raoof and S. Zamani, *Bioelectrochemistry*, 85 (2012) 44
16. A. Lungu, I. Sandu, C. Boscornea, S. Tomas and C. Mihailciuc*, Rev. Roum. Chim*, 55 (2010) 109
17. X. L. Zhai, Y. Song, J. Q. Liu, P. Li, M. Zhong, C. Ma, H. Q. Wang, Q. G. Guo and L. J. Zhi, *J. Electrochem. Soc*, 159 (2012) 177
18. A. Salimi, L. Miranzadeh and R. Hallaj, *Talanta*, 75 (2008) 147
19. A. Ciszewski and G. Milczarek, *Anal. Chem*, 71 (1999) 1055
20. F. Pariente, F. Tobalina, M. Darder, E. Lorenzo and H. D. Abruna, *Anal. Chem*, 68 (1996) 3135