

The electrochemical performance of Self-doped polyaniline-Molybdenum disulfide nanocomposite for vitamin B2 determination

Lixia Wang¹, Tao Yang², Changming Mao^{1,*} and Fanglin Du^{1,*}

¹ College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

² Key Laboratory of Eco-chemical Engineering (Ministry of Education), College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

Abstract: In this work, the self-doped polyaniline-molybdenum disulfide (SPAN-MoS₂) nanocomposite with outstanding conductivity and synergistic electrochemical activity was prepared by the ultrasonic exfoliating method. In the ultrasonic process, the negatively charged SPAN served as an intercalator to result in few-layers MoS₂ nanosheets exfoliated from bulk MoS₂. The obtained SPAN-MoS₂ nanocomposite owns large conjugated structure and rich negative charge because of the strong π - π^* stacking interaction and electrostatic repulsion, which can enhance the adsorption of some conjugate structured and positively charged biomolecules, such as vitamin B2 (VB2). The results also displayed that the electrochemical responses were further affected by the mass ratio and the ultrasonication time.

Keywords: Self-doped polyaniline; Molybdenum disulfide; vitamin B₂; Synergistic effect.

Introduction

Today, we attach great importance to environmental protection, emphasizing green materials, creating green furniture industries, the most important is the use of environmentally friendly materials. At the meantime, extensive attentions have been focused on some 2D nanomaterials¹, so the low-cost and environmentally friendly method was applied to prepare a kind of material for determination, which including the transition metal dichalcogenides (e.g., MoS₂, etc.) due to their 2D layer structure analogous to graphene. What is different from graphene is that MoS₂ overcomes the shortcomings of the zero band gap of graphene. Owing to its inherent properties, it has attracted extensive attention in the electrochemical field. For example, the individual MoS₂ modified electrode has been employed for the reduction of H₂O₂ with a low detection limit of 2.5 nmol/L². And the electrochemical reduced MoS₂ has been widely used for the determination of dopamine (DA) and ascorbic acid (AA). Besides, MoS₂ has been integrated with other functional materials, such as polyaniline (PANI), self-doped polyaniline^{3, 4} to construct novel nanocomposites for showing the synergetic effect to

improve redox behaviors. MoS₂/PANI nanowires can greatly improve Li⁺-storage properties owing to the hierarchical structure of MoS₂/PANI and the PANI-hybrid structures have been investigated by Schmidt et al. and the optimal admixture (MoS₂ 66.7 % : PANI 33.1 %) exhibited a high charge capacity⁵. Wang et al. prepared PANI/MoS₂ nanocomposite with a large contact surface area⁶, which could be further integrated with gold nanoparticles (AuNPs) for serving as a synergetic electrocatalyst to DA⁷.

As a kind of drug, in the process of production of vitamin B₂, there will be resulting in environmental pollution more or less. To reduce the impact on the environment as much as possible, it is necessary to detect the amount of residue of VB₂. And so far, many methods are supplied for VB₂ determination. TLC-scanning determination, spectrophotometric method, high performance liquid chromatography, fluorescence spectroscopy are the traditional methods. But the special environment of detection and the more tedious process are required, such as treating with physical or chemical ways, which can limit the development of other methods. Peidong Xu et al. prepared a sensitive vitamin B₂ electrochemical sensor based on molecularly

*Corresponding author : Changming Mao, Fanglin Dua
Email address : mcm@qust.edu.cn, dufanglin@qust.edu.cn
DOI : <http://dx.doi.org/10.13171/mjc53/016051019/fanglin>

Received April 11th, 2016
Accepted May 3rd, 2016
Published May 10th, 2016

imprinted nonconducting polymer of *o*-aminophenol by potentiostat polymerization in the presence of vitamin B2 (VB2) on a glassy carbon electrode, the sensor exhibited good sensitivity, selectivity, and reproducibility to VB2 with the detection limit 2.3851 nmol/L⁸. a self-assembled monolayer of L-cysteine was used for the determination of vitamin B2⁹, Wenying Zhong et al. apply fluorescence resonance energy transfer quenching for determination of vitamin B2¹⁰. However, the process is fussy and produces higher energy consumption. Meanwhile, more highlights are focused on the simultaneous determination of various vitamin B. The three-dimensional fluorescence spectra was used as the method to analysis VB1, VB2, and VB6 in B-vitamins complex tablets.¹¹ The artificial neural networks and partial least squares regression were applied to UV spectral data for quantitative determination of thiamin hydrochloride (VB1), riboflavin phosphate (VB2), pyridoxine hydrochloride (VB6) and nicotinamide (VPP) in pharmaceutical samples¹². A fast, versatile, cheap, and environmentally safe analytical method for quantifying VB2, VB3, VB6 and VB7 in Corn steep liquor (CSL) was developed¹³. The electrochemically synthesized electroactive species-doped PEDOT films with nanostructure were applied as electrochemical sensors for simultaneous determination of VB2, VB6 and VC¹⁴. Application of renewable silver amalgams annular band electrode to the voltammetric determination of vitamins C, B1, and B2¹⁵. As a justified effective preparation method of two-dimensional nanosheets, liquid exfoliation has been widely adopted with the help of some surfactants and polymers through ultrasonication¹⁶⁻¹⁸.

Herein, SPAN was integrated with MoS₂ to construct a specific structured and negatively charged nanocomposite through a simple and low-cost method by ultrasonication accompanying intercalation. The SPAN-MoS₂ nanocomposite owning the special benzene ring structure and the negative charge endow it could easily be attached by some conjugate structured or positively charged biomolecules or aromatic molecules¹⁹. In this paper, SPAN-MoS₂ nanocomposite was prepared, owning the conjugated benzene ring structure and positive charge and showing outstanding conductivity and synergistic electrocatalytic activity of constructed platform, for efficient detection of VB2.

Experimental section

The preparation of SPAN-MoS₂ nanocomposite

0.01 g SPAN and 0.01 g MoS₂ were mixed, and dispersed in ultrapure water, followed by ultrasonication for a certain time, and then a homogenous mixture of SPAN-MoS₂ was formed. Changing the mass ratio between SPAN and MoS₂

or the ultrasonication time, a series of SPAN-MoS₂ hybrid materials were obtained. The ultrasonic process was carried out by KQ-50E signifier (Kunshan ultrasonic instruments Co. Ltd.), and the resulted composite was characterized through scanning electron microscopy (SEM) (JSM-6700F machine, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM) micrographs (JEM 2100 transmission electron microscopy). SPAN was synthesized according to the ref²⁰. Bulk molybdenum disulfide (MoS₂, analytical pure) was provided from BASF Chemical Co, Ltd. (Tianjin, China).

The fabrication of the modified electrode

20 μ L of the above mixture of SPAN-MoS₂ was dropped on the bare carbon paste electrode (CPE) surface and dried in the air naturally. The CPE was prepared by the method reported by Yang²¹. The obtained electrode was named as SPAN-MoS₂/CPE. Similarly, MoS₂/CPE and SPAN/CPE were prepared. The next, we optimized a series of the condition and using the modified electrode for highly sensitive detection of vitamin B2.

Electrochemical measurements

The electrochemical measurements were carried out by Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV), with a CHI 832 (Shanghai CH Instrument Company, China). A platinum wire was used as the auxiliary electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a carbon paste electrode (CPE) or modified electrode was used as the working electrode. All the supporting electrolyte in all experiments were B-R (pH 4.0) containing a certain amount of VB2.

In this process, the reported result for every electrode was the mean value of three parallel measurements.

Results and discussion

Characterization of the SPAN-MoS₂ hybrid

The morphology and structure of nanocomposites are characterized by SEM and TEM, as shown in the Fig.1. The representative SEM and TEM images of MoS₂, SPAN, and SPAN-MoS₂ display an obviously layered structure. MoS₂ flat layer could be observed in Fig.1A and 1B. Fig.1C and 1D reveal the net-like nanostructure of SPAN with the diameter of 70-90 nm and length of several micrometers. The fibrous and layered structure can be simultaneously observed for SPAN-MoS₂ in Fig.1E, F, which demonstrated that the fibrous SPAN has successfully intercalated with the layered MoS₂. This unique structure of the nanocomposites provides the continuous and multiple passageways for highly effective electron conduction and created a higher specific surface.

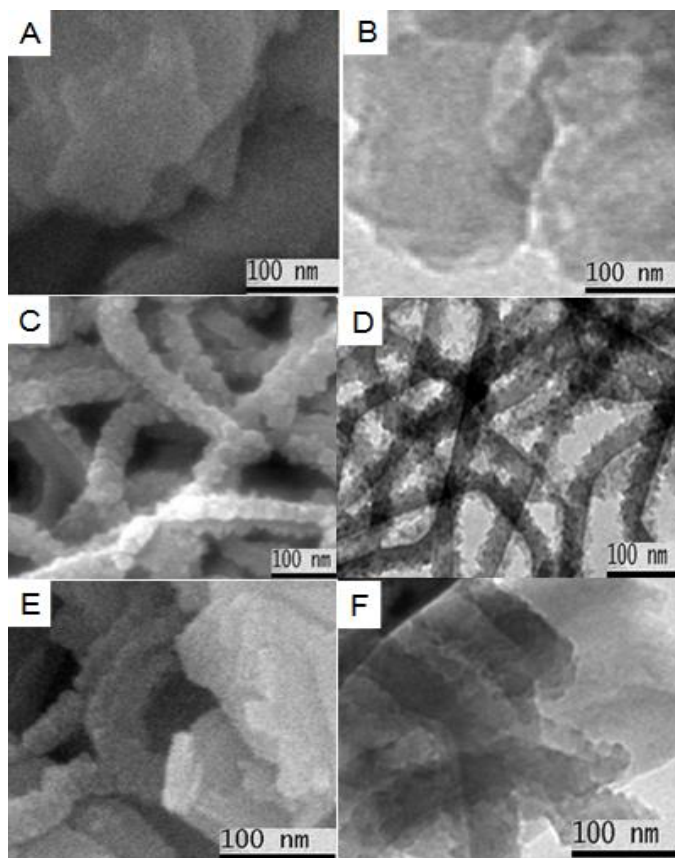


Figure 1. SEM images of the MoS₂ (A), SPAN (C), SPAN-MoS₂ (E) and TEM images of the MoS₂ (B), SPAN (D), SPAN-MoS₂ (F)

Electrochemical reduction behavior of VB₂

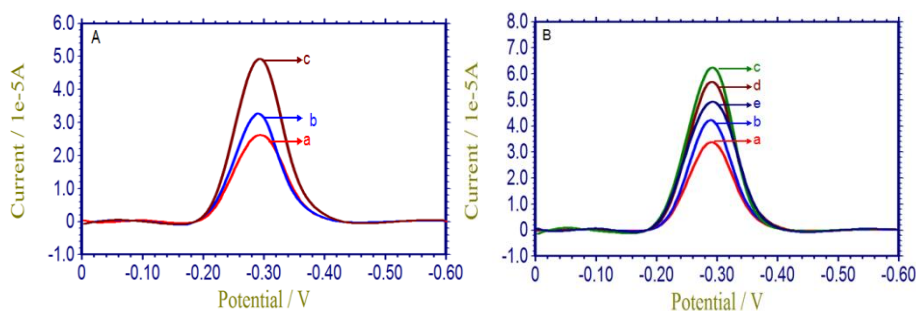


Figure 2. (A)DPVs of 1.0×10^{-3} mol/L VB₂ at (a) MoS₂/CPE; (b) SPAN/CPE; (c) SPAN-MoS₂ (1:3)/CPE ; (B) DPVs of 1.0×10^{-3} M VB₂ at (a) SPAN-MoS₂ (1:1)/CPE; (b) SPAN-MoS₂ (1:2)/CPE; (c) SPAN-MoS₂(1:3)/CPE; (d) SPAN-MoS₂ (1:4)/CPE; (e) SPAN-MoS₂ (1:5)/CPE.

The electrochemical behaviors of 1.0×10^{-3} mol/L VB₂ at different modified electrodes were investigated in B-R (pH 4.0), which are shown in Fig. 2A. Compared with MoS₂/CPE (curve a) and SPAN/CPE (curve b), SPAN-MoS₂/CPE (curve c) displays a highest reduction peak current. This implied that SPAN-MoS₂ could promote the electron exchange between the electrode surface and the VB₂, which is ascribed to the special benzene ring structure and the negative charge of SPAN-MoS₂ could easily absorb some conjugate structured or positively charged VB₂ and show the synergistic

effect. Furthermore, the mass ratio of the mixture can affect the electrochemical behavior of VB₂. Fig. 2B shows the reduction peak current of VB₂ being influenced by the hybrid materials with the different mass ratio from 1:1 to 1:5. From the results, we can discover that the current response of VB₂ at SPAN-MoS₂ (1:3)/CPE (curve c) is higher than the other modified electrodes. Therefore, the mass ratio of 1:3 was selected as the optimum for the subsequent experiments. In addition, the ultrasonication time and pH was optimized in Fig. S1. When the hybrids being ultrasonicated for 4 h and the pH is 4.0, it shows the best performance.

Detection of VB₂ with different concentrations

Based on the optimum results above, the response of VB₂ with different concentrations was detected. Fig. 3A shows the determination of a series of concentrations of VB₂ with the range of 1~100 μmol/L. When the concentrations of VB₂ increased, the peaks current increased (Fig. 3A). The

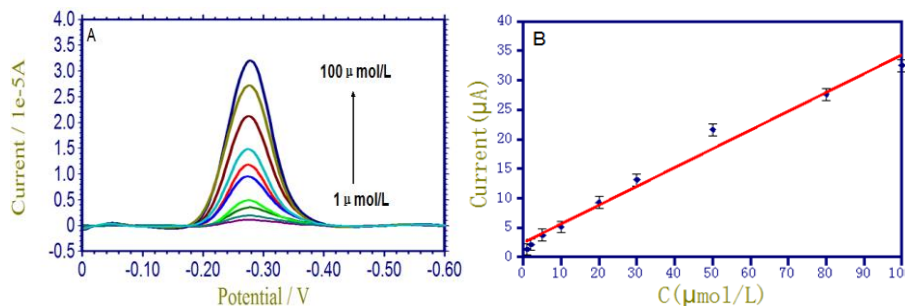


Figure 3. (A) Representative DPVs for the determination of VB₂ in B-Rat SPAN-MoS₂ (1:3)/CPE with VB₂ concentrations ranging from 1~100 μmol/L
(B) Calibration plots of the reduced peak current versus different concentrations of VB₂

Stability and reproducibility of the modified electrode

The most important factor on the practical application of the sensor is the stability and reproducibility. To confirm the long-term stability of the electrochemical sensor, the modified electrode was put off 15 days at room temperature. During the period, the modified electrode was used to test the same concentration of VB₂. The analytical result did not show an obvious decline (relative standard deviation (RSD) ≤ 5%), which demonstrates that the electrodes had good stability. The reproducibility of the modified electrode was estimated by 1.0×10^{-3} mol/L VB₂ with ten modified electrodes made by the same method, and the RSD was found to be 3.62% for reduction peak current of VB₂. This indicated satisfying reproducibility of the fabrication protocol.

Conclusion

In summary, a simple and low-cost technique was applied to prepare SPAN-MoS₂ nanocomposites in the paper. Through ultrasonication of the mixed dispersion of bulk MoS₂ with SPAN co-existing, the negatively charged SPAN ceaselessly diffused and intercalated into the MoS₂ layers to form a homogenous and three-dimensional interconnected structure. Compared with the sole MoS₂ or SPAN, SPAN-MoS₂ interface with the mass ratio of 1:3 (SPAN/MoS₂) and ultrasonication time of 4h have the highest peak currents, displaying remarkable synergistic effect for the reduction of VB₂. The developed sensing platform displays acceptable reproducibility, long-term stability, high sensitivity, and low detection limit, which shows a broad prospect for further application in biosensor and medicine fields.

relationship of DPVs and concentrations of 1~100 μmol/L are shown in Fig. 3A. The linear relationships between the reduction peak current values (I_p) and the concentrations of VB₂ are displayed. In the concentrations range (1~100 μmol/L), the linear equation is $I_p = 0.319C + 2.348$, (R²=0.9828) (Fig. 3B). The limit of detection (S/N = 3) is 3.5×10^{-7} mol/L.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 21275084, 41476083, 51272115, 51272113), A Project of Shandong Province Higher Educational Science and Technology Program (J15LA12), National Natural Science Foundation of Shandong Province (No.ZR2012EMM001), and Scientific and Technical Development Project of Qingdao (No. 12-1-4-3-(23) -jch, 15-9-1-65-jch).

References

- (a) J.N. Coleman, M. Lotya, A. O'Neill, et al., *Science* **2011**, 331, 568.
 - (b) K.G. Zhou, N.N. Mao, H.X. Wang, Y. Peng, H.L. Zhang, *Angew. Chem, Int. Ed.* 2011, 50, 10839.
 - (c) C.N.R. Rao, A. Nag, *J.I. Eur. Chem.* **2010**, 4244.
 - (d) M. Osada, T.J. Sasaki, *Mater. Chem.* **2009**, 19, 2503.
 - (e) Z. Zeng, T. Sun, J. Zhu, X. Huang, Z. Yin, G. Lu, Z. Fan, Q. Yan, H.H. Hng, H. Zhang, *Angew. Chem, Int. Ed.* **2012**, 15, 9052.
 - (f) X. Huang, Z. Zeng, H. Zhang, *Chem. Soc. Rev.* **2013**, 42, 1934.
 - (g) M. Chhowalla, H.S. Shin, G. Eda, L.J. Li, K. Loh, H. Zhang, *Nat. Chem.* **2013**, 5, 263.
 - (h) Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nat. Nanotech.* **2012**, 27, 699.
- (a) T.Y. Wang, H.C. Zhu, J.Q. Zhuo, Z.W. Zhu, P. Papakonstantinou, G. Lubarsky, J. Lin, and M.X. Li, *Biosensor Based on Ultrasmall MoS₂ Nanoparticles for Electrochemical Detection of*

- H₂O₂ Released by Cells at the Nanomolar Level, *Anal. Chem.* **2013**, 85, 10289-10295.
- 3- T. Yang, H. Chen, R. Yang, Y. Jiang, W. Li, K. Jiao, A glassy carbon electrode modified with a nanocomposite consisting of molybdenum disulfide intercalated into self-doped polyaniline for the detection of bisphenol A, *Microchimica Acta*, **2015**, 182, 2623-2628.
 - 4- R. Yang, J. Zhao, M. Chen, T. Yang, S. Luo, K. Jiao, Electrochemical determination of chloramphenicol based on molybdenum disulfide nanosheets and self-doped polyaniline, *Talanta*, **2015**, 131, 619-623.
 - 5- L.C. Yang, S.N. Wang, J.J. Mao, J.W. Deng, Q.S. Ga, Y. Tang, and O.G. Schmidt, Hierarchical MoS₂/Polyaniline Nanowires with Excellent Electrochemical Performance for Lithium-Ion Batteries, *Adv. Mater.* **2013**, 25, 1180-1184.
 - 6- K.J. Huang, L. Wang, Y.J. Liu, H.B. Wang, Y.M. Liu, L.L. Wang, Synthesis of polyaniline/2-dimensional graphene analog MoS₂ composites for high-performance supercapacitor, *Electrochim. Acta.* **2013**, 109, 587-594.
 - 7- K.J. Huang, J.Z. Zhang, Y.J. Liu, L.L. Wang, Novel electrochemical sensing platform based on molybdenum disulfide nanosheets-polyaniline composites and Au nanoparticles, *Sensors and Actuators B.* **2014**, 194, 303-310.
 - 8- P.D. Xu, C.S. Qiao, S. F. Yang, L.J. Liu, M.W. Wang, J.K. Zhang, Fast Determination of Vitamin B₂ Based on Molecularly Imprinted Electrochemical Sensor, *Engineering.* **2012**, 10B, 129-134.
 - 9- W. Qijin, Y. Nianjun, Z. Haili, Z. Xinpin, X. Bin, Voltammetric behavior of vitamin B₂ on the gold electrode modified with a self-assembled monolayer of l-cysteine and its application for the determination of vitamin B₂ using linear sweep stripping voltammetry, *Talanta*, **2001**, 55, 459-467.
 - 10- W.Y. Zhong, B. Huang, L. Chen and C. Shu, Fluorescence resonance energy transfer quenching for determination of vitamin B₂, *中国药科大学学报*, **2011**, 42, 527-533.
 - 11- J. Chen, B. Q. Li, Y. Q. Cui, E. Yu and H. L. Zhai, A fast and effective method of quantitative analysis of VB₁, VB₂ and VB₆ in B-vitamins complex tablets based on three-dimensional fluorescence spectra, *Journal of Food Composition and Analysis*, **2015**, 41, 122-128.
 - 12- C. Rosângela, Barthus, H. Luiz, Mazo, J. Ronei, Poppi, UV Spectrophotometry and Chemometrics Methods for Simultaneous Determinations of Riboflavin (VB₂), Thiamine (VB₁), Pyridoxine (VB₆) and Nicotinamide (VPP). *Química Nova*, **2007**, 7, 1638-1643.
 - 13- X. Xiao, Y.Y. Hou, J. Du, D. Sun, G. Bai, G. Luo, Determination of vitamins B₂, B₃, B₆ and B₇ in corn steep liquor by NIR and PLSR, *Transactions of Tianjin University.* **2012**, 5, 372.
 - 14- T. Nie, J.K. Xu, L.M. Lu, K.X. Zhang, L. Bai, Y.P. Wen, Electroactive species-doped poly(3,4-ethylenedioxythiophene) films: Enhanced sensitivity for electrochemical simultaneous determination of vitamins B₂, B₆ and C. *Biosens Bioelectron.* **2013**, 50, 244-250.
 - 15- B. Bas, M. Jakubowska, U. Górski, Application of renewable silver amalgam annular band electrode to voltammetric determination of vitamins C, B₁ and B₂, *Talanta.* **2011**, 4, 1032-1037.
 - 16- K. G. Zhou, N.N. Mao, H.X. Wang, Y. Peng, H.L. Zhang, A Mixed-Solvent Strategy for Efficient Exfoliation of Inorganic Graphene Analogues, *Angew. Chem. Int. Ed.* **2011**, 50, 10839 -10842.
 - 17- R.J. Smith, P.J. King, M. Lotya, et al., Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions, *Adv. Mater.* **2011**, 23, 3944-3948.
 - 18- J.N. Coleman, M. Lotya, A. O'Neill, et al., Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials, *Science* **2011**, 331, 568-571.
 - 19- T. Yang, Q. Guan, Q.H. Li, L. Meng, L.L. Wang, C.X. Liu and K. Jiao, Large-area three-dimensional interconnected graphene oxide intercalated with self-doped polyaniline nanofibers as a free-standing electrocatalytic platform for adenine and guanine, *J. Mater. Chem. B.* **2013**, 1, 2926 - 2933.
 - 20- Y.W. Hu, T. Yang, Q.H. Li, Q. Guan, K. Jiao, Conjugated self-doped polyaniline-DNA hybrid as trigger for highly sensitive reagentless and electrochemical self-signal amplifying DNA hybridization sensing. *Analyst*, **2013**, 138, 1067-1074.
 - 21- T. Yang, Q. Guan, X.H. Guo, L. Meng, M. Du, K. Jiao, Direct and freely switchable detection of target genes engineered by reduced graphene oxide-poly(m-aminobenzenesulfonic acid) nanocomposite via synchronous pulse-electrosynthesis. *Anal. Chem.* **2013**, 85, 1358-1366.