Highly Sensitive Electrochemical Detection of Folic Acid by Using a Hollow Carbon Nanospheres@molybdenum Disulfide Modified Electrode

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As a nutrient in body functions, folic acid (FA) plays a very important role for human health, and thus developing a highly sensitive method for its determination is of great significance. In the present work, carbon hollow nanospheres decorated with molybdenum disulfide nanosheets (CHN@MoS₂) nanomaterials were produced through a simple method and adopted to modify a glassy carbon electrode for assembling a highly sensitive electrochemical sensor of FA. After characterizing the prepared nanomaterials using scanning-/transmission-electron microscopy and Raman spectra, as well as optimizing various testing conditions, including the pH value of the buffer solution, the accumulation time and amount of nanomaterials on electrode surface, and the electrochemical determination of FA was carried out using a CHN@MoS₂ electrode. Owing to the coordinative advantages from CHN and MoS₂, the results show that CHN@MoS₂ exhibits excellent sensing responses for FA, and it has a wide linear range from 0.08 to 10.0 μM coupled with a low detection limit of 0.02 μM. Finally, the proposed method for FA detection was successfully applied in human urine analysis. The obtained results are satisfactory, revealing that the developed method based on CHN@MoS₂ nanomaterials has important applications for FA determination.

Keywords Folic acid, hollow carbon nanospheres, electrochemical determination, molybdenum disulfide, nanomaterials, sensors

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Introduction

As an indispensable nutrient for the body functions, folic acid (FA), also called vitamin B₉, is very vital during the periods of rapid cell growth and division.^{1,2} It is also crucial to produce red blood cell, to improve brain health and hearing loss and to synthesize and repair DNA/RNA. A lack of FA can arouse various numerous diseases such as megaloblastic anemia, cancer, metabolic syndromes, disorders hypertension and diabetes. For pregnant women, FA is a necessary nutrient to avoid the fetus from causing malformations of a skull, spine and brain.³⁻⁵ Consequently, developing a simple and reliable method for detecting FA is very important.

Presently, several kinds of methods including fluorescence,

ultra-performance liquid chromatography, spectrophotometry, HPLC and electrochemical techniques have been proposed to detect FA.⁶⁻⁸ Among these methods, the electrochemical techniques have attracted a lot of attentions, resulting from their distinctive advantages, such as simple operation, low-cost, high reproducibility and rapid response.⁹⁻¹¹ For instance, Wang and his colleagues¹⁰ prepared ZrO₂/ZnO nanocomposites for sensing FA electrochemically. The related results revealed that a ZrO₂/ZnO modified electrode has a linear range of from 2.0 to 400.0 μM and a detection limit (LOD) of 0.037 μM. In another work, Jost *et al.*¹¹ prepared a carbon nanotubes/nickel hydroxide nanocomposite. They used it to construct an electrochemical sensor of FA. The linear range was from 0.5 to 26.0 μM and had a LOD of 0.095 μM. Although these methods for detecting FA are very important, achieving highly sensitive and reliable detection of FA is still a great challenge.

For achieving efficient and sensitive determination, the employed materials for modifying the electrode are a key factor in electrochemical sensing.¹²⁻¹⁵ Molybdenum disulfide (MoS₂) nanosheet, a 2D transition metal dichalcogenide, exhibits a

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Fig. 1 SEM images of MoS₂ (A), CHN (B), and CHN@MoS₂ (C); TEM images of MoS₂ (D), CHN (E), and CHN@MoS₂ (F).

graphene-like layered nanostructure, and constituted a Mo layer sandwiched between 2 sulfur layers.^{16–19} It possesses many interesting characteristic properties (*e.g.*, excellent catalytic ability, low cost, design flexibility, abundant marginal active sites). Presently MoS₂ nanosheets have received extensive attentions in many fields.^{20–22} Meanwhile, some reports have indicated the advantages of MoS₂ nanosheet enables it to be one of the promising nanomaterials for developing next-generation electrochemical sensors.²³ This makes us believe that MoS₂ can be selected to construct a highly sensitive electrochemical sensor for FA. However, pure MoS₂ nanosheets are easy to stack with each other, and its conductivity is not desirable.^{24–29}

For overcoming the MoS₂ defects and improving its practical performance, integrating MoS₂ nanosheets with carbon materials is considered to be an ideal project, because the formed nanostructures can exhibit specific coordinative properties of each component to avoid MoS₂ stacking and to enhance the electrochemical properties.^{30–34} Hollow carbon nanospheres (CHN) are a desirable candidate to integrate MoS₂ nanosheets due to the high surface area, conductivity and stability. In this work, for achieving a highly sensitive determination of FA, CHN decorated with MoS₂ nanosheets (CHN@MoS₂) nanomaterials was synthesized firstly *via* a simple and green method, and CHN@MoS₂ was then applied to modify a GCE to assemble an electrochemical sensor (CHN@MoS₂/GCE) of FA. The experimental results showed that CHN@MoS₂/GCE exhibits much higher sensing performances than pure CHN or MoS₂ modified GCE resulting from synergetic effects due to MoS₂ and CHN. Importantly, after optimizing various conditions, a wide linear range and low LOD were achieved by CHN@MoS₂/GCE for FA. It is expected that the developed electrochemical method for detecting FA has important applications in the analysis of real samples.

Experimental

Synthesizing CHN@MoS₂

CHN was firstly prepared according to previous work.³⁵ Then, CHN was added into ultrapure water and ultrasonicated for some minutes, and L-cysteine/Na₂MoO₄ was added to CHN dispersion *via* stirring. Next, the formed mixture was moved in

a Teflon-autoclave to be heated for 12 h at 200°C, and the autoclave was left further to cool down. The produced CHN@MoS₂ nanohybrid was collected *via* centrifugation and cleaned with water/ethanol, and was then dried overnight. Finally, the prepared CHN@MoS₂ was annealed in a N₂ atmosphere at high temperature. For a comparison, the pure MoS₂ nanosheets were prepared by similar processes.

Preparing CHN@MoS₂/GCE and electrochemical texts

The GCE surface was carefully polished with 0.05-/0.5-μm alumina, respectively, and then cleaned with ultrapure water, followed by cleaning ultrasonically in acetone and ultra-pure water, respectively. Then 2.0 mg CHN@MoS₂ was added into 4.0 mL of ultrapure water and sonicated for 20 min to form a homogeneous suspension. CHN@MoS₂/GCE was prepared by dropping different amounts of a CHN@MoS₂ suspension on the GCE surface. For a comparison, MoS₂/GCE and CHN/GCE were prepared through similar steps. The electrochemical sensing of CHN@MoS₂/GCE towards FA was carried out following 2 consecutive processes: (i) the pre-concentration of FA to the electrode surface with certain of accumulation time; and (ii) measuring with electrochemical technologies.

Results and Discussion

Characterization of the CHN@MoS₂

Scanning- and transmission-electron microscopy (SEM, TEM) were used to investigate the structures and morphologies of CHN@MoS₂ and related nanomaterials. As depicted in Fig. 1(A), the pure MoS₂ nanosheets tend to agglomerate with each other. Figure 1(B) exhibits a SEM image of pure CHN; it's noted that CHN is distributed uniformly with a hollow structure and a smooth surface. As for CHN@MoS₂ (Fig. 1(C)), it can be found that the MoS₂ nanosheets loosely wrap with the CHN surface, showing flower-like nanostructures. Figures 1(D) to 1(F) show TEM images of MoS₂ (Fig. 1(D)), CHN (Fig. 1(E)) and CHN@MoS₂ (Fig. 1(F)). As shown in Fig. 1(D), the pure MoS₂ tends to stack tightly together with an interlaced nanostructure. For CHN, the hollow structures are observed visibly with a thickness of the 10 nm carbon layer, which could offer a large surface area for loading MoS₂ nanosheets. As for the CHN@MoS₂

Fig. 2 Raman spectra of MoS₂ (a), CHN (b) and CHN@MoS₂ (c).

Fig. 3 EIS plots of the MoS₂/GCE (a), CHN/GCE (b), and CHN@MoS₂/GCE (c) recorded in a Fe(CN)₆^{3-/4-} solution.

hybrids (Fig. 1(F)), CHN as a substratum affords more attachment sites for supporting the formation and impeding the agglomeration of MoS₂ nanosheets; hence, it can be noted that MoS₂ sheets are uniformly dispersed on the CHN surface, of which the result is inconsistent with the former SEM characterization.

Raman spectra were further used to study the prepared CHN@MoS₂ and related nanohybrids (Fig. 2). For pure MoS₂ and the prepared CHN@MoS₂, there are 2 distinct peaks at ~405.0 and 377.0 cm⁻¹ ascribed to the out-of-plane A_{1g} phonon modes and in-plane from MoS₂, respectively. For CHN and CHN@MoS₂ materials, the 2 characteristic peaks presented at ~1590 and 1340 cm⁻¹ correspond to the G and D band, respectively, owing to the presence of carbon. The intensity proportion of the D and G bands (denoted as I_D/I_G) is frequently used to assess the graphitization degree in carbon nanomaterials.³⁶ The figure shows that the relative intensity from the G band is stronger compared to the D band, suggesting that CHN is well graphitized *via* the calcining step. Meanwhile, the I_D/I_G value from CHN@MoS₂ is even smaller than that from CHN, attributed to two-time annealing. These results indicate that CHN@MoS₂ nanomaterials were produced successfully.

Next, the electrochemical impedance technique was adopted to study the electron transfer behaviors in various electrodes. Figure 3 shows the corresponding impedance spectroscopy (EIS) of MoS₂/GCE (a), CHN/GCE (b) and CHN@MoS₂/GCE (c) recorded in a 5.0 mM [Fe(CN)₆]^{3-/4-} solution. Through simulating the EIS data using a Randles equivalent circuit, it can

Fig. 4 CV responses of 25.0 μM FA at (a) GCE, (b) MoS₂/GCE, (c) CHN/GCE, and (d) CHN@MoS₂/GCE in 0.1 M PBS.

be known the charge-transfer resistance (R_{CT}) of MoS₂/GCE (~350.0 Ω) is larger than those from the other electrodes, since the conductivity of pure MoS₂ nanosheet is not desirable, while the R_{CT} value of CHN is considerable small, and it can even be neglected, suggesting that the electron transfer rate in CHN is very high. It is worth noting that CHN@MoS₂/GCE has a much lower R_{CT} value (~130.0 Ω) compared to MoS₂/GCE, indicating the introduction of CHN could obviously improve the conductivity of MoS₂-based nanomaterials.

Electrochemical behaviors of FA

The electrochemical behaviors of FA at CHN@MoS₂/GCE and the related modified electrodes were studied by cyclic voltammetry (CV) technology in a 0.1 M phosphate buffer solution (PBS, pH 7.0). As depicted in Fig. 4, the CV response of FA at GCE shows a weak and broad oxidation peak located at 0.85 V, while MoS₂/GCE shows an apparently increased oxidation peak current, which is much stronger than that at GCE resulting from the high catalytic ability and abundant marginal active sites of MoS₂. Owing to the high surface area and the prominent electrochemical activity of CHN, CHN/GCE also shows a much larger oxidation current than bare GCE. Interestingly, it is noted that the peak current value of FA at CHN@MoS₂/GCE displays a significant increase compared to all of the other modified electrodes, and the oxidation potential was shifted to 0.73 V negatively; specifically, the current value at CHN@MoS₂/GCE is ~16.1, ~3.3 and ~2.6-times higher than those at GCE, MoS₂/GCE and CHN/GCE, respectively. This implies that CHN@MoS₂/GCE can exhibit the coordinative advantages from MoS₂ and CHN for electrochemically detecting FA, which is expected to possess promising applications for constructing a highly sensitive electrochemical sensor of FA.

Optimization of the conditions

As a powerful electrochemical technology, differential pulse voltammetry (DPV), has a higher sensitivity and resolution compared to CV technology. For achieving a highly sensitive determination of FA based on CHN@MoS₂/GCE, various experimental text conditions were optimized by DPV; the related results are exhibited in Fig. 5.

Firstly, the influence from the pH value of PBS was studied over pH values from 4.0 to 9.0 (Fig. 5(A), accumulation time of 50 s; amount of CHN@MoS₂ 10.0 μL). It is noted from the figure that the oxidation current of FA keeps increasing along with the increase of the pH value from 4.0 to 7.0, while it begins

Fig. 5 Influence of the pH value (A), amount of CHN@MoS₂ (B) and accumulation time (C) on the DPV peak current of 5.0 μM FA at CHN@MoS₂/GCE.

to reduce when the pH value increases further to 9.0 since protons are involved in FA oxidation. For achieving high sensitivity, a pH of 7.0 was selected in following experiments. Next, the influence from the amount of CHN@MoS₂ nanomaterials on the electrode surface was also studied (Fig. 5(B)), it can be found that the oxidation current from FA obviously increases along with the increase of the CHN@MoS₂ suspension amount (0.5 mg mL⁻¹) from 2.0 to 1.0 μL. As for the amount from 10.0 to 14.0 μL, the peak current shows only weak increases. Hence, 10.0 μL as the optimum amount was applied throughout the work. There is no doubt that the sensing sensitivity is affected by the accumulation time; thus, the influence from the accumulation time was also investigated. As shown in Fig. 5(C), the oxidation current of FA increases with the increase of the accumulation time, obtaining a maximum at 50 s; hence, this time was used as the optimal value time in the study.

Fig. 6 (A) DPV responses of CHN@MoS₂/GCE in 0.1 M PBS containing various concentrations of FA from 0.08 to 10.0 μM. (B) Corresponding standard curve of FA.

Table 1 Comparison of the proposed CHN@MoS₂/GCE with the reported electrochemical sensors in previous literature for detecting FA

Materials used	Linear range/μM	LOD/μM	Ref.
Co ₃ O ₄ /rGO/CTAB	500.0 – 3200.0	95.0	2
Polyortho-methoxyaniline/carbon nanodots	0.5 – 68.0	0.113	3
Molecularly imprinted poly(<i>p</i> -aminobenzene-sulphonic acid)/carbon nanodots	0.0049 – 0.0698	0.0045	4
Au nanoclusters/graphene/carbon nanodots	10.0 – 170.0	0.1	9
ZrO ₂ /ZnO	2.0 – 400.0	0.037	10
Carbon nanotubes/nickel hydroxide	0.5 – 26.0	0.095	11
CHN@MoS ₂	0.08 – 10.0	0.02	This work

Analytical performance of CHN@MoS₂/GCE

Under the above optimal conditions, the analytical performance of CHN@MoS₂/GCE toward FA was evaluated by plotting the related calibration curve containing the changes from the DPV peak currents upon the increase from the FA concentration, it is found that the peak current of FA linearly increases with the FA concentration, ranging from 0.08 to 10 μM (Fig. 6). The corresponding linear regression equation is defined as $I_p(\mu A) = 1.215 + 1.017C(\mu M)$, coupled with the correlation coefficient of $R^2 = 0.9964$; the LOD is calculated to be 0.02 μM ($S/N = 3$). In addition, the proposed detection method for FA in the work is compared with previous studies (Table 1). The comparative

Table 2 Detection of FA in real urine samples

Sample	Added/ μ M	Found/ μ M	RSD, %	Recovery, %
1	0.5	0.53	3.55	106.0
2	2.0	1.92	4.36	96.0
3	5.0	5.25	5.72	105.0
4	8.0	7.88	3.83	98.5

results indicate that CHN@MoS₂/GCE has lower LOD and wider linear range than most of the previous studies, meanwhile it possesses wide linear resulting from abundant marginal active sites and large surface of CHN@MoS₂, suggesting that it can be used in a highly sensitive determination for FA. It should also be pointed out that the preparation method for CHN@MoS₂ is simple, low cost and green.

Reproducibility, stability and selectivity

For evaluating the CHN@MoS₂/GCE reproducibility, which is expressed via the relative standard deviation (RSD), six parallel-made CHN@MoS₂/GCE, were used to measure 5.0 μ M FA by DPV. The RSD value of the peak current response was found to be 4.36%. On other hand, the long-term stability of CHN@MoS₂/GCE was evaluated via testing the peak current response of FA for thirty days with an interval of six days. The results show that CHN@MoS₂/GCE maintained 95.6% of the initial current response. These results demonstrated that CHN@MoS₂/GCE has an acceptable reproducibility and store stability.

The selectivity of CHN@MoS₂/GCE for FA was evaluated by comparing current responses in the presence of potential interfering organic molecules. The results reveal that no evident interference was presented for the following molecules including methotrexate, ascorbic acid, folic acid, tetrahydrofolic acid, uric acid, 5-methyltetrahydrofolic acid, dopamine and pyridoxine (10 times of FA concentration), suggesting that the CHN@MoS₂/GCE has a satisfactory selectivity for FA analysis.

Real samples analysis

For evaluating the feasibility of CHN@MoS₂/GCE in practical applications, FA in human urine was determined by the developed method. First, the urine samples were centrifuged, extracted and diluted with PBS, and sequentially the original content of FA in the urine sample was measured by the proposed method. The results show that there was no FA detected. Next, the samples were spiked with various concentrations of FA and the peak current of FA was recorded by CHN@MoS₂/GCE; the recoveries were applied to evaluate the feasibility in real samples (Table 2). As depicted in Table 2, the obtained recoveries are found in the range from 96.0 to 106.0% and the RSD values are below 6.0%, indicating that the proposed CHN@MoS₂/GCE sensor can detect FA successfully in real samples.

Conclusions

In summary, a novel electrochemical sensor for the highly sensitive detection of FA was successfully developed by preparing CHN@MoS₂ as electrode nanomaterials. The final results demonstrated that CHN@MoS₂ could exhibit the coordinative advantages from MoS₂ and CHN for FA analysis, and the prepared CHN@MoS₂/GCE shows excellent sensing performances with a wide linear range and a low LOD. Meanwhile, the developed CHN@MoS₂/GCE exhibits high reproducibility and stability, as well as excellent selectivity and

practicability. Furthermore, the proposed method for FA analysis is simple, low cost and green. It is confirmed that the developed method for FA detection based on CHN@MoS₂ will have important potentials in real sample analysis.

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References

1. S. Akbar, A. Anwar, and Q. Kanwal, *Anal. Biochem.*, **2016**, 510, 98.
2. M. Venu, *Int. J. Electrochem. Sci.*, **2018**, 11702.
3. H. Rajabi, and M. Noroozifar, *Mater. Sci. and Eng. C*, **2017**, 75, 791.
4. S. Güney, *J. Electroanal. Chem.*, **2019**, 854, 113518.
5. F. Chekin, F. Teodorescu, Y. Coffinier, G.-H. Pan, A. Barras, R. Boukherroub, and S. Szunerits, *Biosens. Bioelectron.*, **2016**, 85, 807.
6. W. Ren, Y. Fang, and E. Wang, *ACS Nano*, **2011**, 5, 6425.
7. S. Ulusoy, H. Acidereli, S. Erdoğan, and H. İbrahim Ulusoy, *RSC Adv.*, **2016**, 6, 40115.
8. X. Li and L. Chen, *ACS appl. mater. interfaces*, **2016**, 8, 31832.
9. A. A. Abdelwahab and Y. Shim, *Sens. Actuators*, **2015**, 221, 659.
10. Q. Wang, H. Si, L. Zhang, L. Li, X. Wang, and S. Wang, *Anal. Chim. Acta*, **2020**, 1104, 69.
11. J. P. Winiarski, R. Rampanelli, J. C. Bassani, D. Z. Mezalira, and C. L. Jost, *J. Food Compos. Anal.*, **2020**, 92, 103511.
12. Y. Yi, D. Zhang, Y. Ma, X. Wu, and G. Zhu, *Anal. Chem.*, **2019**, 91, 2908.
13. J. Hu, K. T. Ho, X. U. Zou, W. H. Smyrl, A. Stein, and P. Buhlmann, *Anal. Chem.*, **2015**, 87, 2981.
14. K. Hsieh, B. S. Ferguson, M. Eisenstein, K. W. Plaxco, and H. T. Soh, *Acc. Chem. Res.*, **2015**, 48, 911.
15. A. Kotani, M. Kaneko, K. Machida, K. Yamamoto, and H. Hakamata, *Anal. Sci.*, **2020**, 10.2116/analsci.2120p2049.
16. O. Parlak, A. Incel, L. Uzun, A. P. F. Turner, and A. Tiwari, *Biosens. Bioelectron.*, **2017**, 89, 545.
17. A. Sinha, Dhanjai, B. Tan, Y. Huang, H. Zhao, X. Dang, J. Chen, and R. Jain, *TrAC, Trends Anal. Chem.*, **2018**, 102, 75.
18. M. Sharifuzzaman, S. C. Barman, M. A. Zahed, N. J. San, and J. Y. Park, *J. Electrochem. Soc.*, **2019**, 166, B249.
19. D. Zhang, Y. Ma, O. J. Kingsford, J. Qian, and Y. Yi, *J. Electrochem. Soc.*, **2019**, 166, B1392.
20. B. Mao, B. Wang, F. Yu, K. Zhang, Z. Zhang, J. Hao, J. Zhong, Y. Liu, and W. Shi, *Int. J. Hydrogen Energy*, **2018**, 43, 11038.
21. L. Xing and Z. Ma, *Microchim. Acta*, **2015**, 183, 257.
22. Y. Wang, G. Ning, H. Bi, Y. Wu, G. Liu, and Y. Zhao, *Electrochim. Acta*, **2018**, 285, 120.
23. S. K. Tuteja, T. Duffield, and S. Neethirajan, *Nanoscale*, **2017**, 9, 10886.
24. S. Wang, B. Y. Guan, L. Yu, and X. W. D. Lou, *Adv. Mater.*, **2017**, 29.
25. L. Song, X. Wang, F. Wen, L. Niu, X. Shi, and J. Yan, *Int.*

- J. Hydrogen Energy*, **2016**, *41*, 18942.
26. P. Jing, H. Yi, S. Xue, Y. Chai, R. Yuan, and W. Xu, *Anal. Chim. Acta*, **2015**, *853*, 234.
27. A. Ambrosi, Z. Sofer, and M. Pumera, *Small*, **2014**, *11*, 605.
28. A. S. Subramanian, J. N. Tey, L. Zhang, B. H. Ng, S. Roy, J. Wei, and X. M. Hu, *Polymer*, **2016**, *82*, 285.
29. D. Geng, X. Bo, and L. Guo, *Sens. Actuators, B*, **2017**, *244*, 131.
30. S. Y. Park, Y. H. Kim, S. Y. Lee, W. Sohn, J. E. Lee, D. H. Kim, Y.-S. Shim, K. C. Kwon, K. S. Choi, H. J. Yoo, J. M. Suh, M. Ko, J.-H. Lee, M. J. Lee, S. Y. Kim, M. H. Lee, and H. W. Jang, *J Mater. Chem. A*, **2018**, *6*, 5016.
31. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, and H. Dai, *J. Am. Chem. Soc.*, **2011**, *133*, 7296.
32. H. Song, Y. Ni, and S. Kokot, *Biosens. Bioelectron.*, **2014**, *56*, 137.
33. E. B. Bahadır and M. K. Sezgintürk, *TrAC, Trends Anal. Chem.*, **2016**, *76*, 1.
34. R. He, J. Hua, A. Zhang, C. Wang, J. Peng, W. Chen, and J. Zeng, *Nano lett.*, **2017**, *17*, 4311.
35. L. Li, W. Zhang, X. Wang, S. Zhang, Y. Liu, M. Li, G. Zhu, Y. Zheng, Q. Zhang, T. Zhou, W. K. Pang, W. Luo, Z. Guo, and J. Yang, *ACS Nano*, **2019**, *13*, 7939.
36. Y. Chen, W. C. Peng, and X. Y. Li, *Nanotechnology*, **2017**, *28*, 205.
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