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Facile In-Situ Synthesis of $Ti_3C_2T_x/TiO_2$ Nanowires Toward Simultaneous Determination of Ascorbic Acid, Dopamine and Uric Acid

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Abstract: The development of electrochemical sensors with high sensitivity for the simultaneous detection of ascorbic acid (AA), dopamine (DA) and uric acid (UA) is urgently desirable in clinical medicine. However, the challenge lies in achieving simultaneous detection due to their closely oxidation potentials. In this work, we present the synthesis of a composite material comprised of in-situ grown TiO_2 nanowires (NWs) on a $Ti_3C_2T_x$ substrate ($Ti_3C_2T_x/TiO_2$ NWs) through a facile alkali process. By modifying a glassy carbon electrode (GCE) with $Ti_3C_2T_x/TiO_2$ NWs ($Ti_3C_2T_x/TiO_2$ NWs/GCE), it showed excellent electrocatalytic activity for the simultaneous detection of AA/DA/UA by regulating the surface functional groups of $Ti_3C_2T_x$. Remarkably, the $Ti_3C_2T_x/TiO_2$ NWs/GCE enabled simultaneous detection of AA in the range of 300-1800 μM, DA in the range of 2-33 μM, and UA in the range of 2-33 μM. The limits of detection (LODs) for AA, DA, and UA were estimated as 66.07 μM, 0.023 μM, and 0.011 μM, respectively. The proposed $Ti_3C_2T_x/TiO_2$ NWs/GCE demonstrated good stability, high selectivity, and reliable reproducibility, making it a promising electrochemical sensor for the detection of AA, DA, and UA. This work offers a new perspective for human health monitoring, paving the way for advancements in this field.

Keywords: $Ti_3C_2T_x$; TiO_2; Ascorbic acid; Dopamine; Uric acid; Electrochemical sensor

1. Introduction

Ascorbic acid (AA), dopamine (DA), and uric acid (UA) coexist in body fluids, with basal concentrations ranging from 100-1400 μM, 0.01-1 μM, and 200-500 μM, respectively. They are three essential biomolecules coexisting in body fluids that play vital roles in regulating various physiological functions [1]. Fluctuations in the levels of these biomolecules have been linked to various common ailments such as skin rashes, Alzheimer's disease, Parkinson's disease, and gout [2, 3]. Therefore, the rapid and accurate simultaneous detection of AA, DA, and UA concentrations in body fluids plays a crucial role in disease diagnosis [4, 5]. In this work, a composite of TiO_2 nanowires grown in situ on $Ti_3C_2T_x$ ($Ti_3C_2T_x/TiO_2$ NWs) was synthesized through a simple alkali treatment. By regulating the surface functional groups and incorporating TiO_2, the $Ti_3C_2T_x/TiO_2$ NWs modified electrode achieved the individual and simultaneous detections of AA, DA, and UA. Furthermore, the proposed $Ti_3C_2T_x/TiO_2$ NWs/GCE exhibited excellent stability, selectivity, reproducibility, and repeatability.

2. Result and Discussion

2.1. Characterization of $Ti_3C_2T_x/TiO_2$ NWs

SEM images in Fig. 1e-g depict the $Ti_3C_2T_x$ treated in a 6 M KOH solution for 10, 20, and 30 hours, respectively. After 10 hours of alkaline treatment, only a few NWs can be observed growing between the $Ti_3C_2T_x$ lamellae (Fig. 1a). Subsequently, after 20 hours of alkali treatment, the number of NWs significantly increases (Fig. 1b). Moreover, as shown in Fig. 1c, the NWs start to clump together after 30 hours of alkali treatment. TEM and high-resolution TEM images in Fig. 1d-f display the $Ti_3C_2T_x$ treated in a 6 M KOH solution for 20 hours. NWs with lengths ranging from 350-450 nm and diameters of 10-35 nm grow on the surfaces and edges of the $Ti_3C_2T_x$ lamellae (Fig. 1d). The lattice fringe spacing of the lamellae is determined to be 0.253 nm, which corresponds to the (002) crystal plane of $Ti_3C_2T_x$ (Fig. 1e). Additionally, the lattice fringe spacing of the NWs is measured to be 0.352 nm, in alignment with the (101) crystal plane of anatase TiO_2 (Fig. 1f) [6].

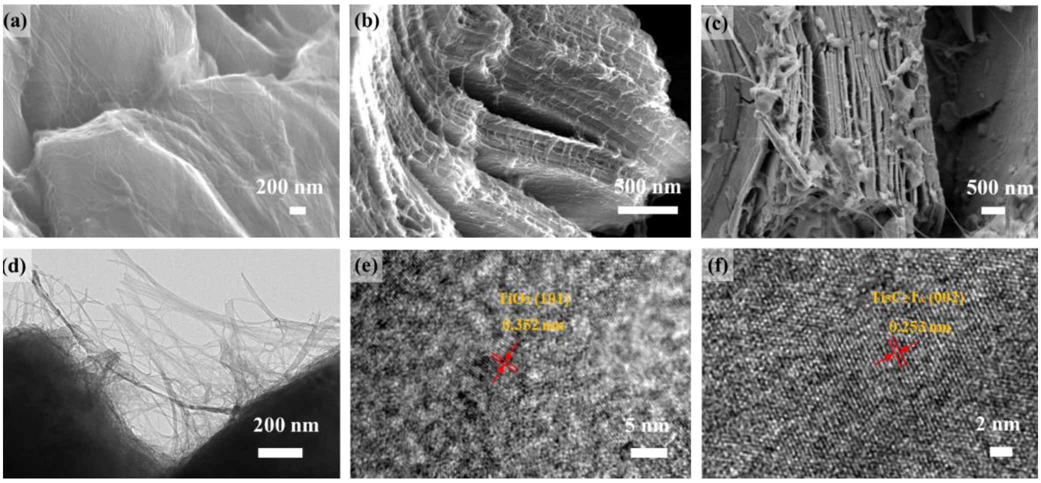

Figure 1. $Ti_3C_2T_x$, $Ti_3C_2T_x$ treated at 6 M KOH for (a) 10 h, (b) 20 h, (c) 30 h; 20h-$Ti_3C_2T_x/TiO_2$ NWs (d) TEM images, (e-f) HR-TEM images.

2.1. Simultaneous measurement of AA, DA, and UA by DPV

Fig. 2 demonstrates the simultaneous detection of AA, DA, and UA by DPV on the $Ti_3C_2T_x/TiO_2$ NWs/GCE, with a scan rate of 50 mV s^{-1}. Fig. 2a exhibits distinct oxidation peak potentials for AA, DA, and UA, measuring 0.18 V, 0.32 V, and 0.59 V respectively. A linear relationship between the peak currents and concentrations is observed in the range of 300-1800 μM for AA, yielding an R^2 value of 0.9953 (Fig. 2b). Similarly, for DA, multiple linear segments are observed within the concentration ranges of 2-9 μM and 9-33 μM, resulting in R^2 values of 0.9930 and 0.9943, respectively (Fig. 2c). For UA, multiple linear segments are observed within the concentration ranges of 2-7 μM and 7-33 μM, yielding R^2 values of 0.9860 and 0.9977, respectively (Fig. 2d). The LODs for AA, DA, and UA are estimated to be 66.07 μM, 0.023 μM, and 0.011 μM, respectively.

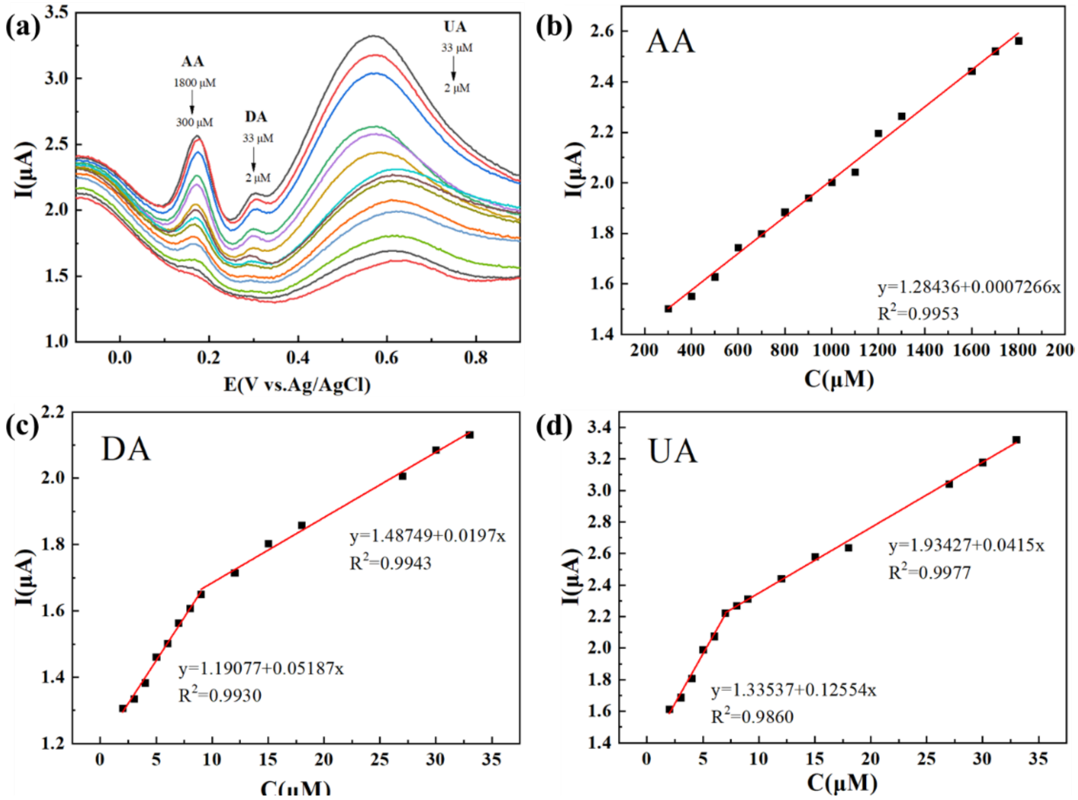

Figure 2. (a) DPVs recorded for different concentrations of AA, DA and UA at the $Ti_3C_2T_x$/TiO_2 NWs/GCE in 0.1 M PBS (pH 7.4) upon successive additions from 300 to 1800 μM for AA, 2 to 33 μM for DA and 2 to 33 μM for UA,.

3. Conclusion

In summary, the $Ti_3C_2T_x$/TiO_2 NWs modified GCE demonstrated the simultaneous detection of AA (300-1800 μM), DA (2-33 μM), and UA (2-33 μM) with LODs of 66.07 μM (AA), 0.023 μM (DA), and 0.011 μM (UA). The surface of $Ti_3C_2T_x$ exhibited neutral properties due to the substitution of hydroxyl groups with fluorine groups after alkali treatment. Moreover, the active surface area of the $Ti_3C_2T_x$/TiO_2 NWs/GCE (0.39 cm^2) was approximately five times larger than that of the bare GCE (0.08 cm^2) due to the in-situ generation of TiO_2 NWs on $Ti_3C_2T_x$. The distinct separation of the detection peaks for AA, DA, and UA can be attributed to the enhanced transition of charge carriers at the heterojunctions of $Ti_3C_2T_x$ and TiO_2. Overall, the electrochemical sensor based on $Ti_3C_2T_x$/TiO_2 NWs exhibits exceptional anti-interference ability, stability, and reliable reproducibility.

Reference

[1] W. Zhang, L. Liu, Y. Li, D. Wang, H. Ma, H. Ren, *et al.*, Electrochemical sensing platform based on the biomass-derived microporous carbons for simultaneous determination of ascorbic acid, dopamine, and uric acid, Biosens Bioelectron, 121(2018) 96-103. http://doi.org/10.1016/j.bios.2018.08.043

[2] N.G. Shang, P. Papakonstantinou, M. McMullan, M. Chu, A. Stamboulis, A. Potenza, *et al.*, Catalyst-Free Efficient Growth, Orientation and Biosensing Properties of Multilayer Graphene Nanoflake Films with Sharp Edge Planes, Adv Funct Mater, 18(2008) 3506-14. http://doi.org/10.1002/adfm.200800951

[3] B. Habibi, M.H. Pournaghi-Azar, Simultaneous determination of ascorbic acid, dopamine and uric acid by use of a MWCNT modified carbon-ceramic electrode and differential pulse voltammetry, Electrochim Acta, 55(2010) 5492-8. http://doi.org/10.1016/j.electacta.2010.04.052

[4] J. Yan, S. Liu, Z. Zhang, G. He, P. Zhou, H. Liang, *et al.*, Simultaneous electrochemical detection of ascorbic acid, dopamine and uric acid based on graphene anchored with Pd-Pt nanoparticles, Colloids Surf B, 111(2013) 392-7.

http://doi.org/10.1016/j.colsurfb.2013.06.030

[5] H.C. Lee, T.H. Chen, W.L. Tseng, C.H. Lin, Novel core etching technique of gold nanoparticles for colorimetric dopamine detection, Analyst, 137(2012) 5352-7. http://doi.org/10.1039/c2an35586h

[6] M. Cao, F. Wang, L. Wang, W. Wu, W. Lv, J. Zhu, Room Temperature Oxidation of Ti_3C_2MXene for Supercapacitor Electrodes, J Electrochem Soc, 164(2017) A3933-A42. http://doi.org/10.1149/2.1541714jes