In this work, a composite of Ti$_3$C$_2$T$_x$/TiO$_2$ NWs was synthesized through a simple alkali treatment. By regulating the growth conditions of Ti$_3$C$_2$T$_x$/TiO$_2$ NWs on a TiC$_x$T$_x$ substrate, the electrochemical properties of the resulting composite were characterized. The Ti$_3$C$_2$T$_x$/TiO$_2$ NWs/GCE exhibited excellent stability, selectivity, and 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$_3$C$_2$T$_x$, 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 essential biomolecules 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 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 TiC$_x$T$_x$/TiO$_2$ NWs was synthesized through a simple alkali treatment. By regulating the surface functional groups and incorporating TiO$_2$, the Ti$_3$C$_2$T$_x$/TiO$_2$ NWs modified electrode achieved the individual and simultaneous detections of AA, DA, and UA. Furthermore, the proposed Ti$_3$C$_2$T$_x$/TiO$_2$ NWs/GCE exhibited excellent stability, selectivity, reproducibility, and repeatability.

2. Result and Discussion

2.1. Characterization of Ti$_3$C$_2$T$_x$/TiO$_2$ NWs

SEM images in Fig. 1e-g depict the TiC$_x$T$_x$ 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 TiC$_x$T$_x$ lamellae (Fig. 1a). Subsequently, after 20 hours of treatment, the growth of NWs on the substrate becomes noticeable (Fig. 1b). After 30 hours of treatment, the growth of NWs becomes more pronounced, with well-defined nanowires visible on the substrate (Fig. 1c). The grown NWs exhibit a uniform diameter and distribution, indicating a successful alkali treatment process.

Fig. 1a-c show the typical SEM images of TiC$_x$T$_x$ nanowires grown in situ on TiC$_x$T$_x$/TiO$_2$ NWs/GCE after 10, 20, and 30 hours of alkaline treatment, respectively.

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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 TiC$_2$T$_x$ 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 TiC$_2$T$_x$ 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 TiC$_2$T$_x$ (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. TiC$_2$T$_x$, TiC$_2$T$_x$ treated at 6 M KOH for (a) 10 h, (b) 20 h, (c) 30 h; 20h-TiC$_2$T$_x$/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 TiC$_2$T$_x$/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.
3. Conclusion

In summary, the Ti$_3$C$_2$Tx/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$_3$C$_2$Tx exhibited neutral properties due to the substitution of hydroxyl groups with fluorine groups after alkali treatment. Moreover, the active surface area of the Ti$_3$C$_2$Tx/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$_3$C$_2$Tx. 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$_3$C$_2$Tx and TiO$_2$. Overall, the electrochemical sensor based on Ti$_3$C$_2$Tx/TiO$_2$ NWs exhibits exceptional anti-interference ability, stability, and reliable reproducibility.

Reference


