In situ reduced MXene/AuNPs composite toward enhanced charging/discharging and specific capacitance

Zixiang ZHENG^{a,†}, Wei WU^{a,†}, Tao YANG^{a,*}, Enhui WANG^a, Zhentao DU^b,
Xinmei HOU^{a,*}, Tongxiang LIANG^c, Hailong WANG^d

^aBeijing Advanced Innovation Center for Materials Genome Engineering, Collaborative Innovation Center of Steel Technology, University of Science and Technology Beijing, Beijing 100083, China

^bMOE Key Laboratory of New Processing Technology for Non-ferrous Metals and Materials, Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, Guangxi University, Nanning 530004, China

^cSchool of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

^dSchool of Materials Science Engineering, Zhengzhou University, Zhengzhou 450001, China

Received: February 4, 2021; Revised: April 28, 2021; Accepted: May 3, 2021

© The Author(s) 2021.

Abstract: In this work, gold nanoparticles (AuNPs) decorated $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets (MXene/AuNPs composite) are fabricated through a self-reduction reaction of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets with HAuCl_4 aqueous solution. The obtained composite is characterized as AuNPs with the diameter of about 23 nm uniformly dispersing on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets without aggregation. The composite (MXene decorated on 4.8 wt% AuNPs) is further employed to construct supercapacitor for the first time with a higher specific capacitance of $278 \text{ F} \cdot \text{g}^{-1}$ at $5 \text{ mV} \cdot \text{s}^{-1}$ than that of pure $\text{Ti}_3\text{C}_2\text{T}_x$ and 95% of cyclic stability after 10,000 cycles. Furthermore, MXene/AuNPs composite symmetric supercapacitor with filter paper as separator and H_2SO_4 as electrolyte, is assembled. The supercapacitor exhibits a high volumetric energy density of $8.82 \text{ Wh} \cdot \text{L}^{-1}$ at a power density of $264.6 \text{ W} \cdot \text{L}^{-1}$ and ultrafast-charging/discharging performance. It exhibits as a promising candidate applied in integrated and flexible supercapacitors.

Keywords: supercapacitors; MXene; gold nanoparticles (AuNPs); self-reduction; composite

1 Introduction

On account of excellent cycle stability, high rate of charge/discharge, and high-power density, supercapacitors

have caught great attention during these years [1]. Now one of the key challenges in making supercapacitors is improving the energy density [2]. Researchers concentrate on exploring and developing the electrode materials with excellent performance, which are key ingredients for high performance supercapacitors [3]. Two-dimensional (2D) materials are among the most promising electrode materials for supercapacitors. Due to their high surface-area-to-volume ratios, 2D materials

[†] Zixiang Zheng and Wei Wu contributed equally to this work.

* Corresponding authors.

E-mail: X. Hou, houxinmeiustb@ustb.edu.cn;

T. Yang, yangtaoustb@ustb.edu.cn

offer an abundance of active surface area for charge storage through electric double layer capacitance (EDLC) or fast surface redox reactions (pseudocapacitance) [4]. During the last decade, due to relatively better chemical stability, higher specific surface area and active surface sites, excellent hydrophilicity, and higher electrical conductivity, transition metal carbides and/or nitrides (MXene) as a novel family of 2D materials have been applied in different areas including energy storage, water desalination, catalysis, electromagnetic interference shielding, and transparent conductive films [5–7]. The general formula of MXenes is $M_{n+1}X_nT_x$ ($n = 1–3$), where M represents a transition metal (such as Sc, Ti, and Zr), X is carbon and/or nitrogen, and T stands for the surface termination (i.e., hydroxyl, oxygen, or fluorine) [5]. The earliest explored and the most widely applied MXene is $Ti_3C_2T_x$ which shows exceptional performances as a potential electrode material for supercapacitors [8].

However, due to the presence of van der Waals force, almost all of 2D materials, including MXene, have the inevitable problems of aggregation and self-restacking [9]. This problem prevents electrolyte penetration into layers, limits the ion transport, and reduces the active site in supercapacitors. Therefore the restacking has become a huge obstacle to ameliorate the performance of MXene [10]. In order to solve the problem, various interlayer spacers are introduced into 2D materials to prevent the stacking of them, which can accelerate electrolyte penetration and ion diffusion [11,12]. These include carbon nanomaterials such as carbon nanotubes (CNTs) [13] and graphene [14,15], conductive polymers such as polypyrrole (PPy) [16], poly(3,4-ethylenedioxythiophene) (PEDOT) [17], polyaniline (PANI) [18], and metal nanoparticles such as silver nanoparticles (AgNPs) [19] and gold nanoparticles (AuNPs) [11]. In particular, since AuNPs is one of the highest conductivity metals with large specific surface area and high stability at the nanoscale level, it can be available for high performance energy storage devices [20]. To the best of our ability, there are still no reports about $Ti_3C_2T_x$ nanosheets modified by AuNPs to improve the electrochemical properties.

In this work, AuNPs decorated $Ti_3C_2T_x$ nanosheets were fabricated through a self-reduction reaction of $Ti_3C_2T_x$ with $HAuCl_4$ aqueous solution. By vacuum filtration of the mixture solution, freestanding composite films were fabricated. Then MXene/AuNPs composite

was used as electrode material of supercapacitors for the first time. MXene/AuNPs electrodes showed significantly enhanced electrochemical property compared to the pure $Ti_3C_2T_x$ electrodes. The integrated device can power a red light emitting diode (LED), demonstrating its energy storage capacity.

2 Experimental

2.1 Materials

High-purity Ti_3AlC_2 MAX phase powders (99 wt%) were supplied by Kaikai Materials Co., Ltd., China. $HAuCl_4$ was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Xinya Equipment Co., Ltd., China, supplied cellulose membrane with 0.44 μm pore size and $\phi 50$ mm in diameter. The coin cell (CR2032-CASE-304Pt, coating Pt of the thickness of 300–500 Å) was supplied by Hefei Kejing Materials Technology Co., Ltd., China.

2.2 Preparation of MXene/AuNPs composite

In view of the preparation of $Ti_3C_2T_x$, minimally intensive layer delamination (MILD) method was used [21]. Briefly, 12 M HCl of 40 mL solution and LiF of 2 g were mixed with stirring of 30 min. After the powder was completely dissolved, Ti_3AlC_2 powders of 2 g were mixed slowly with the LiF–HCl solution. The as-prepared solution was stirred with 500 rpm for 24 h at 35 °C. The suspension was completely transferred to a centrifuge tube. Then the etched powder was washed using deionized water to ensure the pH value of the solution higher than 6. Each wash process included 2500 rpm for 3 min centrifugation and 2–4 min hand shaking. The as-prepared multilayer $Ti_3C_2T_x$ powder was dispersed in 100 mL deionized water by sonicating for 1 h and centrifuging at 3500 rpm to obtain the $Ti_3C_2T_x$ colloidal solution. Finally, $Ti_3C_2T_x$ film was obtained by vacuum filtered on a cellulose membrane filter.

Based on this, the $Ti_3C_2T_x$ film was dispersed in deionized water to obtain a uniform suspension ($1\text{ mg}\cdot\text{mL}^{-1}$). Then, $HAuCl_4$ (1 wt%) solution with different volumes of 125, 250, and 500 μL was slowly added to 30 mL $Ti_3C_2T_x$ aqueous solution. The corresponding mixture was named as MXene/AuNPs-1 (2.4 wt% AuNPs), MXene/AuNPs-2 (4.8 wt% AuNPs), and MXene/AuNPs-3 (9.6 wt% AuNPs), respectively. After stirring for 20 min, the obtained composite

suspension was filtered on a cellulose membrane filter by vacuum filtration, and dried at room temperature for 24 h. Then, flexible and freestanding MXene/AuNPs composite film (about 30 mg) was obtained.

2.3 Characterization

$\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs samples were characterized by a scanning electron microscope (SEM, FEI, Nova 230, USA), with an energy dispersive spectrometer (EDS, Apollo XLT SDD, Japan), X-ray powder diffraction (XRD, TTRIII, Rigaku, Japan), a transmission electron microscope (TEM, FEI, Tecnai G2 F30, USA), and an X-ray photoelectron spectroscope (XPS, VG Multilab 2009, Al K α , UK). The specific surface area was determined from the nitrogen adsorption–desorption isotherm measured at 77 K using Brunauer–Emmett–Teller model (Micromeritics ASAP 2010, BET, USA). The conductivity of samples was characterized by the precision source/measurement unit (Keysight B2911, USA).

2.4 Electrochemical measurements

CHI 660E electrochemical workstation was used in all electrochemical measurements. In a three-electrode system, electrochemical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs electrode were studied by cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS) in 1 M H_2SO_4 electrolyte. Ag/AgCl was served as reference electrodes, Pt sheet was used as the counter electrode, and $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs were served as the working electrode. A symmetric supercapacitor was sandwiched in a coin cell with MXene/AuNPs composite film ($\Phi 16$ mm in diameter) as electrode, filter paper ($\Phi 20$ mm in diameter) as separator, and 1 M H_2SO_4 as electrolyte.

3 Results and discussion

3.1 Characterization and preparation mechanism

Fabrication of MXene/AuNPs composite film is shown in Fig. 1. By selective etching of Al layer of Ti_3AlCl_2 powders, multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ powders are obtained. Then, multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ powders are sonicated into $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. There are functional groups on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, such as $-\text{F}$, $-\text{O}$, and $-\text{OH}$. These functional groups make $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets

have a dispersability in aqueous solutions. Finally, adding the HAuCl_4 solution into $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet dispersion, the composite material will be formed due to the reduction reaction between AuCl_4^- and the functional groups on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Additionally, this film obtained by vacuum filtration can be easily wrapped around a glass bar and retain its integrity, as showed in Fig. 1, indicating good flexibility.

From Fig. 2, the high diffraction peak at 6.9° for $\text{Ti}_3\text{C}_2\text{T}_x$ corresponds to the (002) facet, suggesting the existing of the $\text{Ti}_3\text{C}_2\text{T}_x$ phase. For the MXene/AuNPs composite film, the (002) peak positions of $\text{Ti}_3\text{C}_2\text{T}_x$ do not vary, implying the presence of MXene and no Au embedded into the lattice of MXene [5]. The four diffraction peaks, as shown in Fig. 2, at 38.1° , 44.4° , 64.5° , and 77.5° , correspond to (111), (200), (220), and (311) planes of AuNPs, respectively. As HAuCl_4 content increasing, the four diffraction peaks become stronger and sharper, implying that the content of AuNPs decorated on $\text{Ti}_3\text{C}_2\text{T}_x$ is increasing.

Fig. 1 Schematic of the synthesis of MXene/AuNPs composite film.

Fig. 2 XRD patterns of MXene/AuNPs, $\text{Ti}_3\text{C}_2\text{T}_x$, and AuNPs.

In view of the morphology of the pure $\text{Ti}_3\text{C}_2\text{T}_x$ film (Fig. S1 in the Electronic Supplementary Material (ESM)), the surface is crumpled (Fig. S1(a) in the ESM). The $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets have analogous wrinkles and high transparency, which are similar to graphene features (Fig. S1(b) in the ESM). The high resolution TEM (HRTEM) image shows that the fringe spacing of 0.253 nm corresponds to the (002) lattice plane of $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. S1(c) in the ESM). The selected area electron diffraction (SAED) pattern (Fig. S1(d) in the ESM) shows characteristic diffraction rings corresponding to the (002) planes of $\text{Ti}_3\text{C}_2\text{T}_x$, clearly revealing the polycrystal of $\text{Ti}_3\text{C}_2\text{T}_x$. As shown in Figs. 3(a) and 3(b), MXene/AuNPs composite film exhibits similar morphologies of pure $\text{Ti}_3\text{C}_2\text{T}_x$ film, but the surface is relatively rougher. Figures 3(b) and 3(d) reveal a uniform distribution of AuNPs on $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets with the average particle size about 23 nm (Fig. 3(e)). The film exhibits crumpled morphology stacked by layers (Fig. 3(c)). And the intercalation of AuNPs has little effect to the thickness of MXene films. As shown in Fig. S2 in the ESM, the thickness of MXene films with different amounts of AuNPs at the same areal weight loading is almost 6.6 μm . As shown in Fig. 3(e), the HRTEM image shows that the fringe spacings of 0.235 and 0.203 nm correspond to the (111) and (200) lattice planes of Au, respectively. The SAED pattern (Fig. 3(f)) shows characteristic diffraction rings corresponding to the (200) and (220) planes of Au. Figure S3 and Table S1 in the ESM show the EDS of MXene/AuNPs composite, indicating that AuNPs are decorated on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets after HAuCl_4 treatment in the absence of reducing agents

and under the ambient condition. As shown in Fig. S4 in the ESM, the elemental mapping images indicate the even distribution of AuNPs.

The full XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs are shown in Fig. 4(a). The presence of MXene together with $-\text{F}$, $-\text{Cl}$, $-\text{OH}$, and $-\text{O}$ groups can be proved by observing the common peaks of Ti 2p, C 1s, F 1s, Cl 2p, and O 1s from 0 to 800 eV. The C 1s spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs both have four characteristic peaks locating at 288.9, 286.4, 284.8, and 282.1 eV, as shown in Figs. 4(b) and 4(f), which correspond to the groups of $\text{O}-\text{C}=\text{O}$, $\text{C}-\text{OH}$, $\text{C}-\text{C}$, and $\text{C}-\text{Ti}-\text{O}$, respectively [22,23]. As shown in Figs. 4(c) and 4(g), the Ti 2p spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs are both indexed with three characteristic peaks locating at 454.5, 455.9, and 457.4, corresponding to tetravalent $\text{Ti}-\text{C}$, $\text{Ti}-\text{X}$ (TiC_x , $x < 1$), and Ti_xO_y , but there is a characteristic peak locating at 458.8 eV in the Ti 2p spectra of MXene/AuNPs corresponding to TiO_2 , indicating the slight oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ after mixing with HAuCl_4 [24–26]. The O 1s spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs both have four characteristic peaks locating at 529.8, 531.2, 532.0, and 533.8 eV, corresponding to the groups of absorbed O, $\text{C}-\text{Ti}-\text{O}_x$, $\text{C}-\text{Ti}-\text{OH}$, and $\text{C}-\text{OH}$, respectively, as shown in Figs. 4(d) and 4(h). The peak locating at 532.8 eV corresponds to OR, indicating the presence of organic compounds. The content of O of MXene/AuNPs reduces by 27% compared to that of $\text{Ti}_3\text{C}_2\text{T}_x$, as determined by XPS. As shown in Fig. 4(e), Au 4f spectrum of MXene/AuNPs shows two characteristic peaks locating at 84.0 and 87.7 eV where the binding energy difference is 3.7 eV, manifesting the presence of Au^0 .

Fig. 3 (a, b) Different magnification SEM images of MXene/AuNPs composite film, (c) the cross-sectional SEM image of MXene/AuNPs composite film, (d) TEM image of MXene/AuNPs composite, (e) HRTEM image of MXene/AuNPs composite, and (f) SAED pattern of MXene/AuNPs composite.

Fig. 4 (a) XPS full profile of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs samples. High resolution XPS spectra of (b) C 1s for $\text{Ti}_3\text{C}_2\text{T}_x$, (c) Ti 2p for $\text{Ti}_3\text{C}_2\text{T}_x$, (d) O 1s for $\text{Ti}_3\text{C}_2\text{T}_x$, (e) Au 4f for MXene/AuNPs, (f) C 1s for MXene/AuNPs, (g) Ti 2p for MXene/AuNPs, and (h) O 1s for MXene/AuNPs.

From above results, the AuNPs are assembled and decorated on the surfaces of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets evenly. It should be pointed out that no additional reducing agent was added in this work. Cheng *et al.* [27] have demonstrated that MXenes with $-\text{OH}$ terminations can reduce noble metal ions into zero-valent metals. Since the surfaces of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are covered by $-\text{F}$,

$-\text{O}$, and $-\text{OH}$, AuCl_4^- can be directly reduced by $-\text{OH}$ and formed AuNPs [28].

which is consistent with reduction in O content calculated above.

The AuNPs and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are combined

into a structure of conducting network, which depicts the pronounced contributions of AuNPs to the enhancement of conductivity. This structure contributes to the electrolyte penetration, the ion transport, and the active site increase in electrochemical reaction.

3.2 Electrochemical property of MXene/AuNPs electrode

Figure 5(a) shows the CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs electrodes at $5 \text{ mV}\cdot\text{s}^{-1}$ in $1 \text{ M H}_2\text{SO}_4$ solution. Due to the contribution of pseudocapacitance derived from the varied valence of transition metal Ti atoms, CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs film exhibit deformed rectangle shape. According to the CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$, MXene/AuNPs-1, MXene/AuNPs-2, and MXene/AuNPs-3 electrodes, the specific capacitance is calculated as 228, 234, 278, and $250 \text{ F}\cdot\text{g}^{-1}$, respectively. MXene/AuNP-2 composite electrode shows the largest CV area, which is about 1.2 times larger than that of $\text{Ti}_3\text{C}_2\text{T}_x$ electrode, indicating it possesses better electrochemical capacitive performance by wedging AuNPs. Figure 5(b) presents CV curves of MXene/AuNPs-2 varying from 5 to $100 \text{ mV}\cdot\text{s}^{-1}$. The

shape deformation of CV curves becomes heavier with the scan rate increasing. This phenomenon is possibly caused by slow ion response at high rates. GCD measurement was performed to investigate electrochemical performance of MXene/AuNPs-2 at current density ranging from 1 to $10 \text{ A}\cdot\text{g}^{-1}$ as shown in Fig. 5(c). GCD curves of MXene/AuNPs are almost symmetric and linear triangles, indicating that MXene/AuNPs has reversible charge/discharge process and good capacitance behavior. The inset of Fig. 5(c) is the coulombic efficiency (CE) calculated from different current densities. The calculated results of $1, 2, 5,$ and $10 \text{ A}\cdot\text{g}^{-1}$ are $72.8\%, 86.5\%, 97.4\%$, and 99.5% , respectively, showing that MXene/AuNPs has a high coulombic efficiency. In view of the rate capability as shown in Fig. 5(d), the specific capacitance of $5, 10, 20, 50,$ and 100 mV/s is $278, 251, 225, 198,$ and $181 \text{ F}\cdot\text{g}^{-1}$, respectively, indicating that MXene/AuNPs-2 retains about 65% of the initial capacitance. The good rate capability is attributed to the 2D structure and good conductivity of MXene/AuNPs, which allows rapid ion transport. It should be noted that the AuNPs have no capacitive contribution. Therefore, the specific

Fig. 5 (a) CV curves of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs electrodes; (b) CV curves of MXene/AuNPs-2 electrode with different scan rates; (c) GCDs of MXene/AuNPs-2 electrode with different current density, the inset is the CE calculated from different current density; (d) the specific capacitance of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs electrode vs. the scan rate; (e) Nyquist plots of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs electrode, the insets are the magnified high-frequency region and the equivalent circuit diagram of the electrochemical system; and (f) cycling performance of MXene/AuNPs-2 after 10,000 cycles.

capacitance decreases with the excessive addition of HAuCl_4 solution. The Nyquist plots shown in Fig. 5(e) are composed of two regions with a semicircle at the high-frequency part and an inclined line at the low-frequency part. The intercept of the x -axis represents the equivalent series resistance, which is related to the resistance of the electrode [29,30]. The equivalent series resistance of the MXene/AuNPs-2 (1.4Ω) shows the lowest resistance value compared to those of the $\text{Ti}_3\text{C}_2\text{T}_x$ (2.5Ω), MXene/AuNPs-1 (1.5Ω), and MXene/AuNPs-3 (1.4Ω) electrodes. The semicircle represents the charge transfer resistance (R_{ct}) at the electrode–electrolyte interface, which is 0.008, 0.007, 0.006, and 0.008Ω for $\text{Ti}_3\text{C}_2\text{T}_x$, MXene/AuNPs-1, MXene/AuNPs-2, and MXene/AuNPs-3, respectively. The Warburg impedance stemming from the slope of the curve reflects the ion diffusion of the electrode [31], which is 8.7, 8.5, 11.1, and $8.3 \text{ S}^{1/2}$ for $\text{Ti}_3\text{C}_2\text{T}_x$, MXene/AuNPs-1, MXene/AuNPs-2, and MXene/AuNPs-3, respectively. Among them, the MXene/AuNPs-2 electrode has the smallest R_{ct} and the highest Warburg impedance, indicating excellent ion diffusion capabilities. The mechanism of MXene/AuNPs-2 with the best electrochemical performance can be mainly attributed to the following points: i) Compared with MXene/AuNPs-1 (AuNPs of $\sim 18 \text{ nm}$ in diameter and 0.43 at%), MXene/AuNPs-2 (AuNPs of $\sim 23 \text{ nm}$ in diameter and 0.95 at%) with larger spacing of MXene nanosheets possesses higher conductivity for electronic, better diffusion for electrolyte and ions, and larger specific surface area for active sites (Fig. S5 and Table S1 in the ESM); ii) compared with MXene/AuNPs-3, as the increasing of content of Au (1.74 at%), AuNPs will aggregate and grow up ($\sim 50 \text{ nm}$), which making the spacing of MXene nanosheets too large. This is harmful to

the conductivity of MXene film (Fig. S5(d) in the ESM) [32]. Therefore, compared with MXene/AuNPs-1 and MXene/AuNPs-3, MXene/AuNPs-2 has the best electrochemical performance. The cyclic stability of MXene/AuNPs-2 electrodes is shown in Fig. 5(f). Notably, at $50 \text{ mV}\cdot\text{s}^{-1}$, it exhibits excellent stability and the specific capacitance of MXene/AuNPs-2 still remains 95.0% after 10,000 cycles.

The high stability and good electrochemical performance of MXene/AuNPs composite electrode could be mainly derived from three aspects: (1) The intrinsic properties of MXene and gold. MXene possesses both excellent EDLC and pseudo-capacitance. Gold has excellent stability and conductivity. (2) As shown in Fig. 6(a), the AuNPs as the spacer prevents self-stacking between $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and lead to more space between the tightly stacked nanosheets, which significantly enlarge specific surface area of the composite material [33]. The BET results of $\text{Ti}_3\text{C}_2\text{T}_x$ and MXene/AuNPs, as shown Fig. 6(b), reveal that the specific surface area of MXene/AuNPs is about 1.8 times larger than that of $\text{Ti}_3\text{C}_2\text{T}_x$. The larger specific surface area provides more active sites, improving the electrochemical performance. (3) The AuNPs as the spacer prevents self-stacking of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets, which is beneficial for electrolyte penetration and the transport of ions [11]. As shown in Fig. 5(e), the smaller solution resistance (R_s) of MXene/AuNPs implies MXene/AuNPs have faster ion response and lower inherent resistance. (4) The conductivity of MXene/AuNPs composite is significantly improved due to AuNPs' excellent conductivity and the structure of conducting network between the AuNPs and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets [33]. As shown in Fig. S6 in the ESM, the conductivity of MXene/AuNPs is 1.67 times higher than that of $\text{Ti}_3\text{C}_2\text{T}_x$.

Fig. 6 (a) Schematic illustration of $\text{Ti}_3\text{C}_2\text{T}_x$ film and MXene/AuNPs film and (b) N_2 adsorption–desorption curves of $\text{Ti}_3\text{C}_2\text{T}_x$ film and MXene/AuNPs film.

Compared with the performances of the various MXene-based supercapacitors in Table 1, the specific capacitance of MXene/AuNPs with an electrolyte of 1 M H_2SO_4 in this work is calculated to be $278 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$). This value is 1.2 times higher than that of MXene (i.e., $238 \text{ F}\cdot\text{g}^{-1}$) and is better than that of $\text{Ti}_3\text{C}_2\text{T}_x\text{-Cl}$ [34], $\text{Ti}_3\text{C}_2\text{T}_x$ clay [35], and $\text{Ti}_3\text{C}_2\text{T}_x\text{-N}_2\text{H}_4$ [36].

Table 1 Key parameters of various MXene-based supercapacitors

Material	Electrolyte	Specific capacitance	Ref.
$\text{Ti}_3\text{C}_2\text{T}_x\text{-Cl}$	1 M H_2SO_4	$180 \text{ F}\cdot\text{g}^{-1}$ ($2 \text{ mV}\cdot\text{s}^{-1}$)	[34]
$\text{Ti}_3\text{C}_2\text{T}_x$ clay	1 M H_2SO_4	$245 \text{ F}\cdot\text{g}^{-1}$ ($2 \text{ mV}\cdot\text{s}^{-1}$)	[35]
$\text{Ti}_3\text{C}_2\text{T}_x\text{-N}_2\text{H}_4$	1 M H_2SO_4	$250 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[36]
$\text{Ti}_3\text{C}_2\text{T}_x$	1 M H_2SO_4	$238 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[37]
$\text{N-Ti}_3\text{C}_2\text{T}_x$	1 M H_2SO_4	$192 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[38]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$	1 M MgSO_4	$117 \text{ F}\cdot\text{g}^{-1}$ ($2 \text{ mV}\cdot\text{s}^{-1}$)	[39]
$\text{PANI-Ti}_3\text{C}_2\text{T}_x$	1 M Na_2SO_4	$164 \text{ F}\cdot\text{g}^{-1}$ ($2 \text{ mV}\cdot\text{s}^{-1}$)	[40]
d- $\text{Ti}_3\text{C}_2\text{T}_x$ film	1 M KOH	$140 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[41]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{RGO}$	1 M H_2SO_4	$140 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[42]
$\text{MnO}_2@/\text{Ti}_3\text{C}_2\text{T}_x/\text{CNT}$	1 M Na_2SO_4	$181.8 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	[43]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{AuNPs}$	1 M H_2SO_4	$278 \text{ F}\cdot\text{g}^{-1}$ ($5 \text{ mV}\cdot\text{s}^{-1}$)	This work

3.3 Electrochemical performance of MXene/AuNPs symmetric supercapacitor

To evaluate the performance of MXene/AuNPs-2 as supercapacitor, the CV, GCD, and EIS were studied. In the working potential window of 0.0–0.6 V with the scan rates ranging from 5 to $100 \text{ mV}\cdot\text{s}^{-1}$, as shown in Fig. 7(a), CV curves are almost rectangular, demonstrating its ideal characteristic of electrical double-layer capacitor and excellent rate capability. At current density ranging from 1 to $10 \text{ A}\cdot\text{g}^{-1}$, the GCD curves demonstrate a good capacitive performance due to its good linear potential-time profiles as well as nearly symmetrical with their discharging counterpart (Fig. 7(b)). There is no obvious semicircular in the high-frequency Nyquist diagram (Fig. 7(c)), indicating the low R_{ct} and the good electrical conductivity of the composite. The cyclic stability of MXene/AuNPs-2 electrodes is shown in Fig. 7(d). The specific capacitance of symmetric supercapacitor remains 95.0% after 10,000 cycles at $50 \text{ mV}\cdot\text{s}^{-1}$, which exhibits excellent stability. As shown in Fig. S3 in the ESM with the increase of the scanning rate, the gravimetric capacitance obviously decreases, which is due to slow ion transport rate. By calculation, the gravimetric capacitance is 213.8,

Fig. 7 (a) CV curves of MXene/AuNPs-2 symmetric supercapacitor; (b) GCDs of the supercapacitor; (c) Nyquist plots of the supercapacitor, the inset is the equivalent circuit diagram of the electrochemical system; (d) cycling performance of MXene/AuNPs-2 symmetric supercapacitor after 10,000 cycles; (e) volumetric energy and power density for the supercapacitors compared with those in other literature; and (f) schematic diagram of structure of symmetric supercapacitor.

196.1, 186.4, 160.9, and 141.1 $\text{F}\cdot\text{g}^{-1}$ from 100 to 5 $\text{mV}\cdot\text{s}^{-1}$, which can be also found in Fig. S7 in the ESM. Figure 7(e) shows the comparison of the volumetric energy density and power density of MXene/AuNPs with other supercapacitors reported in the literature [44–47]. Calculated from the data in Fig. 7(a), the volumetric power density and energy density at 5, 10, 20, 50, and 100 $\text{mV}\cdot\text{s}^{-1}$ are calculated to be 264.6, 485.3, 922.7, 1991.1, and 3492.2 $\text{W}\cdot\text{L}^{-1}$, and 8.82, 8.09, 7.69, 6.64, and 5.82 $\text{Wh}\cdot\text{L}^{-1}$, respectively. Compared with MXene-based supercapacitor reported in the literature, i.e., rGO/MXene (8.6 $\text{Wh}\cdot\text{L}^{-1}$, 200 $\text{W}\cdot\text{L}^{-1}$) [44], Ni-dMXNC/MXene (10.4 $\text{Wh}\cdot\text{L}^{-1}$, 220 $\text{W}\cdot\text{L}^{-1}$) [45], MP-MX_{1.5} (20.7 $\text{Wh}\cdot\text{L}^{-1}$, 184.8 $\text{W}\cdot\text{L}^{-1}$) [46], and $\text{Ti}_3\text{C}_2\text{T}_x$ paper (18.5 $\text{Wh}\cdot\text{L}^{-1}$, 240 $\text{W}\cdot\text{L}^{-1}$) [47], the energy density of MXene/AuNPs in this work is comparable to these MXene-based symmetric or asymmetric supercapacitor devices while the power density is higher than those. (Table S2 in the ESM). As shown in Fig. S8 in the ESM, the time constant is calculated as 5 s. Leakage current of the supercapacitor has been recorded at 0.6 V. Leakage current diminishes significantly to 0.049 mA within few seconds and then it further reduces to its low value of 0.023 mA. We performed self-discharge test of the supercapacitor for 2 h. Figure S9 in the ESM displays the good capability of 0.32 V after 2 h self-discharge test. In addition, a red LED (1 W, 2.6–2.8 V, 350 mA) is successfully powered by three prepared symmetric supercapacitors in series, as shown in Fig. 7(f), convincingly demonstrating the energy storage capacity of MXene/AuNPs symmetric supercapacitor.

4 Conclusions

In summary, MXene/AuNPs composite is fabricated with AuNPs evenly distributed on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The obtained AuNPs are directly reduced from AuCl_4^- by the groups of $-\text{OH}$ on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. The AuNPs and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are combined into a structure of conducting network, which contributes to rapid electron transfer in electrochemical reactions. Composite electrodes (MXene decorated on 4.8 wt% AuNPs) show enhanced charge storage ability with a capacitance of 278 $\text{F}\cdot\text{g}^{-1}$ at 5 $\text{mV}\cdot\text{s}^{-1}$. The cyclic stability reaches 95.0% after 10,000 cycles. Furthermore, a MXene/AuNPs symmetric supercapacitor with filter paper as separator and H_2SO_4

as electrolyte, exhibits a high volumetric energy density of 8.82 $\text{Wh}\cdot\text{L}^{-1}$ at a power density of 264.6 $\text{W}\cdot\text{L}^{-1}$. The integrated device can power a red LED demonstrating its energy storage capacity.

Acknowledgements

This work is supported by the National Science Fund for Distinguished Young Scholars (No. 52025041), the National Natural Science Foundation of China (Nos. 51974021, 51902020, and 51904021), the Fundamental Research Funds for the Central Universities (Nos. FRF-TP-18-045A1 and FRF-TP-19-004B2Z), the National Postdoctoral Program for Innovative Talents (No. BX20180034), China Postdoctoral Science Foundation (No. 2018M641192), and the Open Foundation of Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, Guangxi University (No. 2021GXYSOF12).

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <https://doi.org/10.1007/s40145-021-0491-0>.

References

- [1] Wang BX, Zhou AG, Liu FF, *et al.* Carbon dioxide adsorption of two-dimensional carbide MXenes. *J Adv Ceram* 2018, **7**: 237–245.
- [2] Yang CH, Tang Y, Tian YP, *et al.* Flexible nitrogen-doped 2D titanium carbides (MXene) films constructed by an *ex situ* solvothermal method with extraordinary volumetric capacitance. *Adv Energy Mater* 2018, **8**: 1802087.
- [3] Gao YP, Wang LB, Li ZY, *et al.* Electrochemical performance of Ti_3C_2 supercapacitors in KOH electrolyte. *J Adv Ceram* 2015, **4**: 130–134.
- [4] Tan CL, Cao XH, Wu XJ, *et al.* Recent advances in ultrathin two-dimensional nanomaterials. *Chem Rev* 2017, **117**: 6225–6331.
- [5] Naguib M, Mochalin VN, Barsoum MW, *et al.* 25th anniversary article: MXenes new family of two-dimensional materials. *Adv Mater* 2014, **26**: 992–1005.
- [6] Liang X, Garsuch A, Nazar LF. Sulfur cathodes based on conductive MXene nanosheets for high-performance lithium–sulfur batteries. *Angewandte Chemie Int Ed* 2015, **54**: 3907–3911.
- [7] Berdiyrov GR, Madjet ME, Mahmoud KA. Ionic sieving through $\text{Ti}_3\text{C}_2(\text{OH})_2$ MXene: First-principles calculations. *Appl Phys Lett* 2016, **108**: 113110.
- [8] Naguib M, Kurtoglu M, Presser V, *et al.* Two-dimensional

- nanocrystals produced by exfoliation of Ti_3AlC_2 . *Adv Mater* 2011, **23**: 4248–4253.
- [9] Liu YT, Zhu XD, Pan L. Hybrid architectures based on 2D MXenes and low-dimensional inorganic nanostructures: Methods, synergies, and energy-related applications. *Small* 2018, **14**: 1803632.
- [10] Xu YX, Lin ZY, Huang XQ, *et al.* Functionalized graphene hydrogel-based high-performance supercapacitors. *Adv Mater* 2013, **25**: 5779–5784.
- [11] Yu HT, Xu PC, Lee DW, *et al.* Porous-layered stack of functionalized AuNP-rGO (gold nanoparticles-reduced graphene oxide) nanosheets as a sensing material for the micro-gravimetric detection of chemical vapor. *J Mater Chem A* 2013, **1**: 4444.
- [12] Zhao MQ, Ren CE, Ling Z, *et al.* Flexible MXene/carbon nanotube composite paper with high volumetric capacitance. *Adv Mater* 2015, **27**: 339–345.
- [13] Yan J, Ren CE, Maleski K, *et al.* Flexible MXene/graphene films for ultrafast supercapacitors with outstanding volumetric capacitance. *Adv Funct Mater* 2017, **27**: 1701264.
- [14] Xu SK, Wei GD, Li JZ, *et al.* Flexible MXene–graphene electrodes with high volumetric capacitance for integrated co-cathode energy conversion/storage devices. *J Mater Chem A* 2017, **5**: 17442–17451.
- [15] Boota M, Anasori B, Voigt C, *et al.* Pseudocapacitive electrodes produced by oxidant-free polymerization of pyrrole between the layers of 2D titanium carbide (MXene). *Adv Mater* 2016, **28**: 1517–1522.
- [16] Chen C, Boota M, Xie XQ, *et al.* Charge transfer induced polymerization of EDOT confined between 2D titanium carbide layers. *J Mater Chem A* 2017, **5**: 5260–5265.
- [17] VahidMohammadi A, Moncada J, Chen HZ, *et al.* Thick and freestanding MXene/PANI pseudocapacitive electrodes with ultrahigh specific capacitance. *J Mater Chem A* 2018, **6**: 22123–22133.
- [18] Khamlich S, Khamliche T, Dhlamini MS, *et al.* Rapid microwave-assisted growth of silver nanoparticles on 3D graphene networks for supercapacitor application. *J Colloid Interface Sci* 2017, **493**: 130–137.
- [19] Dong XC, Huang W, Chen P. *In situ* synthesis of reduced graphene oxide and gold nanocomposites for nanoelectronics and biosensing. *Nanoscale Res Lett* 2010, **6**: 1–6.
- [20] Yan Y, Wang TY, Li XR, *et al.* Noble metal-based materials in high-performance supercapacitors. *Inorg Chem Front* 2017, **4**: 33–51.
- [21] Alhabeb M, Maleski K, Anasori B, *et al.* Guidelines for synthesis and processing of two-dimensional titanium carbide ($\text{Ti}_3\text{C}_2\text{T}_x$ MXene). *Chem Mater* 2017, **29**: 7633–7644.
- [22] Zhang LB, Chen GY, Hedhili MN, *et al.* Three-dimensional assemblies of graphene prepared by a novel chemical reduction-induced self-assembly method. *Nanoscale* 2012, **4**: 7038.
- [23] Tang Y, Zhu JF, Yang CH, *et al.* Enhanced capacitive performance based on diverse layered structure of two-dimensional Ti_3C_2 MXene with long etching time. *J Electrochem Soc* 2016, **163**: A1975–A1982.
- [24] Rakhi RB, Ahmed B, Hedhili MN, *et al.* Effect of postetch annealing gas composition on the structural and electrochemical properties of Ti_2CT_x MXene electrodes for supercapacitor applications. *Chem Mater* 2015, **27**: 5314–5323.
- [25] Peng C, Yang XF, Li YH, *et al.* Hybrids of two-dimensional Ti_3C_2 and TiO_2 exposing {001} facets toward enhanced photocatalytic activity. *ACS Appl Mater Interfaces* 2016, **8**: 6051–6060.
- [26] Halim J, Cook KM, Naguib M, *et al.* X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). *Appl Surf Sci* 2016, **362**: 406–417.
- [27] Cheng RF, Hu T, Hu MM, *et al.* MXenes induce epitaxial growth of size-controlled noble nanometals: A case study for surface enhanced Raman scattering (SERS). *J Mater Sci Technol* 2020, **40**: 119–127.
- [28] Zhou XZ, Huang X, Qi XY, *et al.* *In situ* synthesis of metal nanoparticles on single-layer graphene oxide and reduced graphene oxide surfaces. *J Phys Chem C* 2009, **113**: 10842–10846.
- [29] Li HY, Hou Y, Wang FX, *et al.* Flexible all-solid-state supercapacitors with high volumetric capacitances boosted by solution processable MXene and electrochemically exfoliated graphene. *Adv Energy Mater* 2017, **7**: 1601847.
- [30] Singh SK, Dhavale VM, Boukherroub R, *et al.* N-doped porous reduced graphene oxide as an efficient electrode material for high performance flexible solid-state supercapacitor. *Appl Mater Today* 2017, **8**: 141–149.
- [31] Tang J, Mathis TS, Kurra N, *et al.* Tuning the electrochemical performance of titanium carbide MXene by controllable *in situ* anodic oxidation. *Angewandte Chemie* 2019, **131**: 18013–18019.
- [32] Zhang B, Chen JD, Zhu H, *et al.* Facile and green fabrication of size-controlled AuNPs/CNFs hybrids for the highly sensitive simultaneous detection of heavy metal ions. *Electrochimica Acta* 2016, **196**: 422–430.
- [33] Atar N, Eren TJ, Yola ML, *et al.* Fe@Ag nanoparticles decorated reduced graphene oxide as ultrahigh capacity anode material for lithium-ion battery. *Ionics* 2015, **21**: 3185–3192.
- [34] Ghidui M, Kota S, Halim J, *et al.* Alkylammonium cation intercalation into Ti_3C_2 (MXene): Effects on properties and ion-exchange capacity estimation. *Chem Mater* 2017, **29**: 1099–1106.
- [35] Ghidui M, Lukatskaya MR, Zhao MQ, *et al.* Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. *Nature* 2014, **516**: 78–81.
- [36] Mashtalir O, Lukatskaya MR, Kolesnikov AI, *et al.* The effect of hydrazine intercalation on the structure and capacitance of 2D titanium carbide (MXene). *Nanoscale* 2016, **8**: 9128–9133.
- [37] Boota M, Anasori B, Voigt C, *et al.* Pseudocapacitive electrodes produced by oxidant-free polymerization of pyrrole between the layers of 2D titanium carbide (MXene).

- Adv Mater* 2016, **28**: 1517–1522.
- [38] Wen YY, Rufford TE, Chen XZ, *et al.* Nitrogen-doped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrodes for high-performance supercapacitors. *Nano Energy* 2017, **38**: 368–376.
- [39] Zhao MQ, Ren CG, Ling Z, *et al.* Flexible MXene/carbon nanotube composite paper with high volumetric capacitance. *Adv Mater* 2015, **27**: 339–345.
- [40] Ren YY, Zhu JF, Wang L, *et al.* Synthesis of polyaniline nanoparticles deposited on two-dimensional titanium carbide for high-performance supercapacitors. *Mater Lett* 2018, **214**: 84–87.
- [41] Xu SK, Wei GD, Li JZ, *et al.* Binder-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXene electrode film for supercapacitor produced by electrophoretic deposition method. *Chem Eng J* 2017, **317**: 1026–1036.
- [42] Zhou YH, Maleski K, Anasori B, *et al.* $\text{Ti}_3\text{C}_2\text{T}_x$ MXene-reduced graphene oxide composite electrodes for stretchable supercapacitors. *ACS Nano* 2020, **14**: 3576–3586.
- [43] Liu Q, Yang JJ, Luo XG, *et al.* Fabrication of a fibrous $\text{MnO}_2@\text{MXene}/\text{CNT}$ electrode for high-performance flexible supercapacitor. *Ceram Int* 2020, **46**: 11874–11881.
- [44] Couly C, Alhabeib M, van Aken KL, *et al.* Asymmetric flexible MXene-reduced graphene oxide micro-supercapacitor. *Adv Electron Mater* 2018, **4**: 1700339.
- [45] Xia QX, Fu JJ, Yun JM, *et al.* High volumetric energy density annealed-MXene-nickel oxide/MXene asymmetric supercapacitor. *RSC Adv* 2017, **7**: 11000–11011.
- [46] Lukatskaya MR, Mashtalir O, Ren CE, *et al.* Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* 2013, **341**: 1502–1505.
- [47] Fan ZM, Wang YS, Xie ZM, *et al.* A nanoporous MXene film enables flexible supercapacitors with high energy storage. *Nanoscale* 2018, **10**: 9642–9652.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.