Three-Dimensional Graphene–TiO$_2$–SnO$_2$ Ternary Nanocomposites for High-Performance Asymmetric Supercapacitors

Golnoush Zamiri,* A.S. Md. Abdul Haseeb,* Priyanka Jagadish, Mohammad Khalid, Ing Kong, and Syam G. Krishnan*

ABSTRACT: Ternary nanocomposites synergistically combine the material characteristics of three materials, altering the desired charge storage properties such as electrical conductivity, redox states, and surface area. Therefore, to improve the energy synergistic of SnO$_2$, TiO$_2$, and three-dimensional graphene, herein, we report a facile hydrothermal technique to synthesize a ternary nanocomposite of three-dimensional graphene–tin oxide–titanium dioxide (3DG–SnO$_2$–TiO$_2$). The synthesized ternary nanocomposite was characterized using material characterization techniques such as XRD, Raman spectroscopy, FTIR spectroscopy, FESEM, and EDXS. The surface area and porosity of the material were studied using Brunauer–Emmett–Teller (BET) studies. XRD studies showed the crystalline nature of the characteristic peaks of the individual materials, and FESEM studies revealed the deposition of SnO$_2$–TiO$_2$ on 3DG. The BET results show that incorporating 3DG into the SnO$_2$–TiO$_2$ binary nanocomposite increased its surface area compared to the binary composite. A three-electrode system compared the electrochemical performances of both the binary and ternary composites as a battery-type supercapacitor electrode in different molar KOH (1, 3, and 6 M) electrolytes. It was determined that the ternary nanocomposite electrode in 6 M KOH delivered a maximum specific capacitance of 232.7 C g$^{-1}$ at 1 A g$^{-1}$. An asymmetric supercapacitor (ASC) was fabricated based on 3DG–SnO$_2$–TiO$_2$ as a positive electrode and commercial activated carbon as a negative electrode (3DG–SnO$_2$–TiO$_2$|AC). The ASC delivered a maximum energy density of 28.6 Wh kg$^{-1}$ at a power density of 367.7 W kg$^{-1}$. Furthermore, the device delivered a superior cycling stability of $\sim$97% after 5000 cycles, showing its prospects as a commercial ASC electrode.

INTRODUCTION

Transformation of technologies from wired to wireless communication devices and fossil fuel-sourced transportation to electric vehicles require efficient energy storage devices. For a longer duration energy release process (higher energy density), lithium-ion batteries (LIB) are currently preferred. Redox reactions involving electrode–electrolyte surfaces due to the intercalation–deintercalation process of Li ions store charges in LIBs as chemical energy. Although LIBs are accompanied by higher energy densities, their lower power density hinders their high power applications. Supercapacitors, another energy storage subclass, have gained prominence due to their increased power density, rapid charging/discharging, and long cyclic efficiency, along with their increased environmental friendliness and relatively low cost. However, the low energy density limited the use of supercapacitors in many applications. From this perspective, it is critical to increase energy density by developing a hybrid energy storage device, known as an asymmetric supercapacitor (ASC), which combines the characteristics of both supercapacitors and batteries. A typical ASC consists of battery-grade materials (redox-active materials enabling faradaic reaction processes) as a positive electrode (high energy density) and carbonaceous materials such as activated carbon (high power density) as a negative electrode.

Several redox-active metal oxides such as NiO, RuO$_2$, MnO$_2$, TiO$_2$, Co$_3$O$_4$, SnO$_2$, and so forth were utilized for high-performance energy storage devices. Among these metal oxides, TiO$_2$ and SnO$_2$ are excellent candidates for electrode materials due to their low cost and environmental friendliness. Furthermore, these possess negligible volume expansion during the discharge–charge process, resulting in long cycle life and durability. However, pure SnO$_2$ and TiO$_2$ nanostructures have low electronic conductivity, poor electrochemical stability, low rate capability, and relatively low theoretical capacity, limiting their industrial application. Synergistically combining the properties of two or more materials is proven to be one of the effective ways to overcome the obstacles of pure SnO$_2$ and TiO$_2$. A recent research report on the electrospun binary composites of SnO$_2$–TiO$_2$ 3D nanoflowers showed higher...
specific capacitance (500 F g\(^{-1}\)) than nanofibers (350 F g\(^{-1}\)) at 1 A g\(^{-1}\), showing the superiority of the 3D structure.\(^{10}\) However, the rate capability of the SnO\(_2\)–TiO\(_2\) electrode was lower, achieving a lower capacitance at higher current densities.\(^{11}\) The performance of supercapacitors can be enhanced by incorporating the high surface area of carbon-based materials into metal oxide nanostructures.\(^{12}\) Nowadays, the fabrication of three-dimensional graphene (3DG) with high surface area, low density, and high electrical conductivity is increasingly receiving research attention.\(^{13}\) Intercalation of metal oxides with graphene-based materials including 3DG provides more electrochemically active sites for rapid redox processes and conducting networks, as well as the benefit of reducing the risk of large volume changes during a charge–discharge mechanism.\(^{14}\) For example, 3DG–NiO nanocomposite electrodes with a high specific capacitance of 1328 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) have been fabricated by Bao et al.\(^{15}\) The device shows cycling stability with 87% retention of the capacitance after 2000 cycles of galvanostatic charge–discharge. Furthermore, the importance of 3DG was further iterated by Jiang and his group by synthesizing the 3DG–TiO\(_2\) nanocomposite.\(^{16}\) The 3DG–TiO\(_2\) composite electrode obtained a specific capacitance of 235.6 F g\(^{-1}\) at 0.5 A g\(^{-1}\) in 2 M KOH and delivered a rate capability of 87% after 2000 cycles of charge–discharge. Therefore, in general, nanocomposites based on 3DG achieved appreciable specific capacitance, and the rate capability of these devices was improved by adding 3DG to the composites. However, most of the reported composites exhibited poor cyclic stability (less than 80%).

In this research, a novel attempt to improve the charge storage process of SnO\(_2\)–TiO\(_2\) was performed using 3DG. A ternary nanocomposite of SnO\(_2\)–TiO\(_2\) with 3DG (3DG–SnO\(_2\)–TiO\(_2\)) was prepared by the hydrothermal method for the first time, and the electrochemical performance of the 3DG–SnO\(_2\)–TiO\(_2\) ternary nanocomposite using 6 M KOH as an electrolyte was investigated. An increase in surface area of the SnO\(_2\)–TiO\(_2\) composite was observed with the addition of 3DG into it. This addition shall increase the active surface of the binary composite, providing more active sites for the solvated electrolytes to access. Hence, in the three-electrode system, the ternary nanocomposite of 3DG–SnO\(_2\)–TiO\(_2\) exhibited a higher specific capacity compared to the binary nanocomposite of SnO\(_2\)–TiO\(_2\). Finally, an ASC was fabricated based on the 3DG–SnO\(_2\)–TiO\(_2\) ternary nanocomposite for the first time, which showed good electrochemical performance and superior cycling stability.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Graphite flakes were purchased from Asbury Inc. (USA). All the experimental chemicals such as aniline, hydrogen peroxide (H\(_2\)O\(_2\)), ammonium persulfate (APS), poly (vinylidene fluoride) (PVDF), activated carbon (AC), hydrazine, nickel foam, potassium permanganate (KMnO\(_4\)), sulfuric acid (H\(_2\)SO\(_4\)), hydrochloric acid (HCl), potassium hydroxide pellets (KOH), phosphoric acid (H\(_3\)PO\(_4\)), N-methyl-2-pyrrolidone (NMP), tin chloride hydrate, and titanium isopropoxide were supplied by Sigma-Aldrich, USA.

#### 2.2. Preparation of the SnO\(_2\)–TiO\(_2\) Nanocomposite.

To prepare the binary nanocomposite of SnO\(_2\)–TiO\(_2\), 1:1 M mixture of tin chloride hydrate (SnCl\(_2\)·5H\(_2\)O) and titanium isopropoxide (C\(_{12}\)H\(_{26}\)O\(_7\)Ti) was added to the mixture of ethanol and dimethylformamide (DMF). Then, the mixture was stirred vigorously for 24 h at room temperature to form a homogeneous solution. After that, the solution was transferred to a 50 mL Teflon-lined autoclave and heated at 75 °C for 24 h. The autoclave was naturally cooled to room temperature, and the prepared SnO\(_2\)–TiO\(_2\) nanocomposite was washed with distilled water and ethanol.

#### 3. RESULTS AND DISCUSSION

##### 3.1. Structural and Morphological Characteristics of Materials

The FTIR spectra of SnO\(_2\)–TiO\(_2\) and 3DG–SnO\(_2\)–TiO\(_2\) are shown in Figure 1. The broad peak from 3000 to 3600 cm\(^{-1}\) in the FTIR spectra of both SnO\(_2\)–TiO\(_2\) and 3DG–SnO\(_2\)–TiO\(_2\) corresponds to the surface stretching
and (220) planes of SnO$_2$.

The characteristic peaks at approximately 27, 36, 42, 46, 52, and 56$^\circ$ in the XRD patterns of SnO$_2$ correspond to (002), (100), and (004) carbon reflections, respectively. The peaks observed at around 28, 36, 42, 46, 52, and 56$^\circ$ in the XRD patterns of SnO$_2$-TiO$_2$ ternary nanocomposites are ascribed to the (110), (101), (111), (210), (211), (220), and (002) planes of the TiO$_2$ rutile phase. The four characteristic peaks at approximately 27, 36, 42, and 56$^\circ$ can be associated to the (110), (200), (211), and (220) planes of SnO$_2$, respectively. The sharp and characteristic peak at around 45 and 49$^\circ$ in the 3DG-SnO$_2$-TiO$_2$ XRD pattern confirms the presence of 3DG in the ternary nanocomposite. However, due to the overlapping (110) planes of TiO$_2$ and SnO$_2$, the characteristic peak of 3DG (002) is not observed in the XRD pattern of the ternary nanocomposite. Hence, the characteristic peaks of all the materials were well assimilated in the ternary composite, proving the formation of the 3DG-SnO$_2$-TiO$_2$ composite.

Figure 3 shows the Raman spectra of 3DG, SnO$_2$-TiO$_2$ binary, and 3DG-SnO$_2$-TiO$_2$ ternary nanocomposites. The Raman spectra of 3DG displayed a D band at 1348 cm$^{-1}$ that represents the sp$^2$ vibrations of C atoms of disordered graphene and a G peak at 1584 cm$^{-1}$ which is related to the in-plane vibration of sp$^2$-bonded carbon atoms. The D and G peak intensity ratio ($I_D/I_G$) indicates the quality of the products. The $I_D/I_G$ intensity ratio increases from 1.13 of 3DG to 1.33 of the 3DG-SnO$_2$-TiO$_2$ ternary nanocomposite, which is related to a decrease in the average size of the sp$^2$ domains upon the reduction of the exfoliated GO, and this indicates the removal of oxygen groups. The peaks appear at 144, 434, and 598 cm$^{-1}$ in the Raman spectra of SnO$_2$-TiO$_2$ binary and 3DG-SnO$_2$-TiO$_2$ ternary nanocomposites corresponding to the system matrices of B$_{1g}$, E$_g$, and A$_{1g}$ of the TiO$_2$ rutile phase, and another characteristic broad compound vibrational peak at 230 cm$^{-1}$ aroused from the multiple phonon scattering processes. In addition, the peaks at 630 and 774 cm$^{-1}$ correspond to A$_{1g}$ and B$_{2g}$ modes of SnO$_2$, which are related to the symmetric and asymmetric stretching of Sn=O bonds, respectively.

The surface morphologies of SnO$_2$-TiO$_2$ and 3DG-SnO$_2$-TiO$_2$ nanocomposites are shown in Figure 4. The FESEM images of SnO$_2$-TiO$_2$ showed irregular-shaped nanoparticles due to the agglomeration of tiny spherical shaped crystals. Figure 4c,d illustrates the FESEM images of 3DG-SnO$_2$-TiO$_2$ nanocomposites at low and high magnifications. The deposition of the SnO$_2$-TiO$_2$ nanocomposite on 3D graphene sheets was clearly visible (Figure 4d).

The EDX elemental mapping of the 3DG-SnO$_2$-TiO$_2$ ternary nanocomposite is shown in Figure 5a–f. The EDX analysis confirmed all the elemental components of the prepared 3DG-SnO$_2$-TiO$_2$ nanocomposite, as indicated in Figure 5a–e. The overall mapping in Figure 5a demonstrates the presence of C, O, Sn, and Ti, proving the elemental composition of the nanocomposite. Figure 5b shows the carbon distribution within the prepared nanocomposite. The presence of oxygen, Sn, and Ti elements in Figure 5c–e corresponds to the presence of the SnO$_2$-TiO$_2$ nanocomposite. From Figure 5d, it is observed that the Sn element was not detected, confirming the presence of SnO$_2$-TiO$_2$ nanocomposite.
Based on the results, the specific capacity of the ternary nanocomposite in the various electrolytes decreases in the order of 6 M KOH > 3 M KOH > 1 M KOH. The enhancement in the specific capacity of the 3DG–SnO$_2$–TiO$_2$ nanocomposite in 6 M KOH can be attributed to the concentration of the ions in the electrolyte. The conductivity of the electrolyte can be increased by increasing its concentration in aqueous solution. Therefore, 6 M KOH provided higher conductivity and more enough OH$^-$ concentration compared to 1 and 3 M solutions, which facilitates the charge transfer in both the bulk electrolyte and electrode. This happens as the number of ions participating in the redox reactions increases. The 6 M KOH electrolyte possesses a high current value, resulting in a higher capacitance.

To compare the electrochemical performance of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite with the SnO$_2$–TiO$_2$ binary nanocomposite, working electrodes based on the SnO$_2$–TiO$_2$ binary nanocomposite and 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite were made, and their electrochemical performances were investigated. CV curves at a lower scan rate (3 mV s$^{-1}$) for the binary and ternary composites are compared in Figure 7a. The CV curves at lower voltages indicate the redox process involving both the charge storage processes. The asymmetry in the CV curve shows that the charge storage process is battery-type. The multiple redox peaks in the ternary composite can be attributed to the faradaic reaction involving the metal oxide and the solvated ions during the charge–discharge process. In general, the redox peaks occurred due to the insertion/de-insertion of the K$^+$ ions in/out of the composite oxides with concomitant oxidation/reduction of the Sn and Ti ions. The 3DG–SnO$_2$–TiO$_2$ CV curves exhibit well-defined redox peaks compared with the SnO$_2$–TiO$_2$ CV curves.

The specific capacity of the electrode material from the CV curves was estimated using eq 1 and summarized in Table 1:

$$Q_S = \frac{\int i(E) dE}{vm}$$  \hspace{1cm} (1)

3.2. Electrochemical Measurement. CV and GCD curves were recorded in a three-electrode system to evaluate the electrochemical performance of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite and are shown in Figure 7. The energy storage properties of the prepared ternary nanocomposite using KOH as an electrolyte with various molarities (1, 3, and 6 M) were also investigated and indicated in Figures S1–S4.
where $Q_s$ is the specific capacity ($C \cdot g^{-1}$) of the electrode material, $i(E)$ is the current, $\nu$ is the scan rate ($V \cdot s^{-1}$), and $m$ is the mass loading ($g$) of the active material coated on the electrode.

Based on the calculated values, the ternary nanocomposite of 3DG−SnO$_2$−TiO$_2$ has a higher specific capacity at different scan rates when compared to the binary nanocomposite of SnO$_2$−TiO$_2$. Due to the inability of the solvated ions to access the active sites at higher current rates, the specific capacity of both electrode materials decreased as the scan rate increased (Table 1). At a lower scan rate, the solvated ion can access both the outer and inner pores of the electrode materials, increasing the intercalation reaction. The higher specific capacitance of the 3DG−SnO$_2$−TiO$_2$ ternary nanocomposite...
electrode materials compared with the SnO$_2$–TiO$_2$ binary nanocomposite can be attributed to both the faradaic contribution due to the charge-transfer process with the surface atoms (SnO$_2$ and TiO$_2$) and the nonfaradaic contribution from the double-layer effect (arising from 3DG). The faradaic reactions of the SnO$_2$–TiO$_2$ nanocomposite are related to the following reversible process:

$$\text{TiO}_2 + C^+ + e^- \leftrightarrow \text{TiOO}^C$$  \hspace{2cm} (2)

$$\text{SnO}_2 + C^+ + e^- \leftrightarrow \text{SnOO}^C$$  \hspace{2cm} (3)

where C$^+$ are the protons and alkali metal cations (K$^+$) in the electrolyte (KOH). Based on the above reactions, it is suggested that both the protons and alkali metal cations are involved in the redox process. Furthermore, the presence of 3DG in the nanocomposite provides a support matrix for the growth of the electroactive species at the nanoscale, which results in a larger specific surface area and thus enhances the electrochemical performance.

The origin of capacitance in the material is determined from the CV curves by analyzing the dependence between the anodic peak current (i) and scan rate ($\nu$). A straight line was obtained from ($\nu$)$^{1/2}$ and the anodic peak current (i), proving the domination of diffusion or intercalation reaction for both the binary and ternary composite electrodes (Figure S2) in 6 M KOH. The diffusion coefficient of all the electrodes will be obtained from the slope of the i versus $\nu^{1/2}$ graph, proving the domination of diffusion or intercalation reaction for both the binary and ternary composite electrodes (Figure S2) in 6 M KOH. The diffusion coefficient of all the electrodes will be obtained from the slope of the i versus $\nu^{1/2}$ graph, as detailed in our earlier research. It was observed that the slope determined from the i versus $\nu^{1/2}$ graph for the 3DG–SnO$_2$–TiO$_2$ electrode was an order higher (0.07) than the slope of the SnO$_2$–TiO$_2$ electrode (0.008). This proved that the introduction of 3DG to the secondary composite improved the solvated ion diffusion and hence the charge storage process.

GCD curves were used to investigate the specific capacity of the prepared electrode materials (Figure 7b). The charge–discharge curves of the ternary composite electrode at 1 A g$^{-1}$ were more symmetric compared to the binary composite electrode, demonstrating the superior charge storage of 3DG–SnO$_2$–TiO$_2$ electrodes. The electrode based on the SnO$_2$–TiO$_2$ binary nanocomposite shows a decrease in charging and discharging time with increasing current density, indicating that capacity decreases with increasing current density. The specific capacity (C g$^{-1}$) obtained from the slope of the i versus $\nu^{1/2}$ graph for the 3DG–SnO$_2$–TiO$_2$ electrode was an order higher (0.07) than the slope of the SnO$_2$–TiO$_2$ electrode (0.008). This proved that the introduction of 3DG to the secondary composite improved the solvated ion diffusion and hence the charge storage process.

Table 1. Specific Capacity of the SnO$_2$–TiO$_2$ Binary Nanocomposite and 3DG–SnO$_2$–TiO$_2$ Ternary Nanocomposite at the Range of Scan Rate of 3–50 mV s$^{-1}$ in 6 M KOH

| scan rate (mV s$^{-1}$) | SnO$_2$–TiO$_2$ | 3DG–SnO$_2$–TiO$_2$ |
|------------------------|----------------|---------------------|
| 3                      | 46.16          | 322.45              |
| 5                      | 39.60          | 285.63              |
| 10                     | 30.47          | 235.28              |
| 20                     | 22.63          | 177.68              |
| 30                     | 19.03          | 150.96              |
| 40                     | 16.78          | 127.41              |
| 50                     | 14.69          | 110.43              |

Figure 6. BET analysis of 3DG, SnO$_2$–TiO$_2$, and 3DG–SnO$_2$–TiO$_2$.

Figure 7. (a) Comparison of CV curves of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite and SnO$_2$–TiO$_2$ binary nanocomposite at 3 mV s$^{-1}$. (b) Comparison of GCD curves of both the electrodes at 1 A g$^{-1}$. (c) Variation of capacitance of both the electrodes with different current densities. (d) Nyquist plots of both the electrodes, and the inset is the plot at higher frequencies.
specific capacity of the electrode materials ($Q_s$) using 6 M KOH as an electrolyte is estimated using the following relation (equation 4):

$$Q_s = \frac{I \times \Delta t}{m}$$

(4)

where $I$ is defined as the discharge current (A), $\Delta t$ is the time the electrode needs to be fully discharged, and $m$ is the mass loading of the materials on the coated electrode.

A maximum specific capacity of 232.7 C g$^{-1}$ is obtained for the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite at a current density of 1 A g$^{-1}$. At the same current density, the binary SnO$_2$–TiO$_2$ could achieve only a capacitance of $\sim$23.5 C g$^{-1}$. This demonstrated the importance of addition of 3DG to the binary composite material. In the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite, 3DG acts as a support matrix to develop electroactive species in the nanocomposite, which has a larger surface area and therefore improves the electrochemical performance. Furthermore, the pore size of the ternary composite was more convenient for the solvated ion access of the KOH ions. The solvated ion size of K$^+$ ions (13 nm) was comparable with the pore size (17 nm) of the ternary nanocomposite and hence delivers a higher capacitance. Also, the ionic conductivity of 6 M KOH is larger (626.6 mS cm$^{-1}$) compared to 3 M KOH and 1 M KOH. Hence, the ternary composite electrode delivered a higher capacitance in 6 M KOH.

Similar to the variation of specific capacity with the scan rates, the specific capacity of both the electrodes decreased with the increase in the scan rate (Figure 7c). For the SnO$_2$–TiO$_2$ binary nanocomposite, the increase in current density results in a decrease in the charge and discharge times in the GCD curves of the 3DG–SnO$_2$–TiO$_2$ nanocomposite. The specific capacity of the SnO$_2$–TiO$_2$ nanocomposite decreased to 18.3, 12.95, and 5.6 C g$^{-1}$ at the current density of 2, 5, and 10 A g$^{-1}$, as calculated using eq 2. The binary composite electrode could only retain 24% of its initial capacitance with 10 times increase in current density. Compared with the SnO$_2$–TiO$_2$ binary nanocomposite charge–discharge curves, the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite exhibited superior charge retention. At current densities of 2, 5, and 10 A g$^{-1}$, the specific capacities of the as-prepared 3DG–SnO$_2$–TiO$_2$ electrode are reduced to 208.4, 152.93, and 110.05 C g$^{-1}$, respectively. The 3DG–SnO$_2$–TiO$_2$ electrode could retain a specific capacity of $\sim$48% of its initial capacitance with an increase in current density from 1 to 10 A g$^{-1}$. This showed that the capacitance retention of SnO$_2$–TiO$_2$ almost doubled with the incorporation of 3DG. The decrease in capacitance for both the electrodes with the increase in current density could be attributed to the charge concentration at the electrode–electrolyte interface during the charge storage process.

Electrochemical impedance spectroscopy (EIS) measures the characteristic resistances such as electrode resistance ($R_e$) and charge-transfer resistance ($R_{ct}$) during the charge-transfer process. $R_e$ combines the electrolyte resistance, intrinsic resistance of the electroactive material, and contact resistance between the active material and the current collector to determine the high frequency of the EIS spectrum. The $R_e$ value is calculated from the x-intercept of the high-frequency region of the Nyquist plot. The EIS plots of the SnO$_2$–TiO$_2$ binary nanocomposite is compared with the EIS plot of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite in Figure 7d. The high frequencies of the EIS spectra for SnO$_2$–TiO$_2$ and 3DG–SnO$_2$–TiO$_2$ nanocomposites in 6 M KOH are 2.9 and 13 Ω, respectively. The ternary nanocomposite of the 3DG–SnO$_2$–TiO$_2$ electrode has a smaller semicircle in the high-frequency region than the binary nanocomposite of SnO$_2$–TiO$_2$, confirming that the electrode material based on the ternary nanocomposite has the lowest charge-transfer resistance (inset of Figure 7d). The lower electrode resistance of the ternary nanocomposite would have enhanced the electrode–electrolyte ion access and hence delivered a superior specific capacity compared to the binary
composite. Furthermore, the higher surface area of the ternary nanocomposite compared to the binary nanocomposite of SnO$_2$–TiO$_2$ would have increased the electrochemical performance of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite. Intercalation of SnO$_2$–TiO$_2$ with 3DG provides more active sites for rapid redox processes, and the presence of 3DG in the composite can effectively prevent the degradation of the SnO$_2$–TiO$_2$ nanocomposite.

4. CHARACTERIZATION OF ASYMMETRIC SUPERCAPACITORS

An asymmetric supercapacitor (ASC) is made up of two electrodes separated by an electrolyte ion separator, with capacitive materials such as activated carbon serving as the negative electrode and a ternary nanocomposite of 3DG–SnO$_2$–TiO$_2$ serving as the positive electrode. This combines the effects of a capacitor and a battery in a single device to gain the benefits of both systems, resulting in a higher energy density than that of a typical EDLC. The 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite and activated carbon (3DG–SnO$_2$–TiO$_2$//AC) were used as positive and negative electrodes, respectively. The fabricated device was then electrochemically analyzed at room temperature. Figure 8a shows the CV curves at various scan rates (3–100 mV s$^{-1}$). Furthermore, even at higher scan rates, the shape of the CV curves is well preserved, which demonstrates the excellent rate capability of the device. The ASC was built based on the mass loading calculation shown in eq 5

$$m = \frac{Q_{\text{PC}} \times \Delta V}{Q_{\text{EDLC}} \times \Delta V}$$

where $m$, $Q_{\text{PC}}$, and $Q_{\text{EDLC}}$ are the mass loading and specific capacity of the negative electrode; $m$, $Q_{\text{PC}}$, and $Q_{\text{EDLC}}$ are the mass loading and specific capacity of the positive electrode; and $\Delta V$ is the potential window. Figure SS shows the electrochemical characterization of AC in 6 M KOH. The specific capacitance of AC was calculated to be 84 F g$^{-1}$ at 1 A g$^{-1}$. Using eq 5, the AC and 3DG–SnO$_2$–TiO$_2$ mass loadings in ASC were determined to be approximately 1.38 and 2.85 mg, respectively. Cyclic voltammetry (CV), galvanic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were used to investigate the electrochemical performance of AC as a cathode (Supporting Information SS). The AC electrode CV curves show EDLC charge storage with no redox peaks (Figure S5a). The GCD curves (Figure S5b) and Nyquist plot (Figure S5c) illustrate a typical EDLC process, indicating that the electrode is an appropriate negative electrode for the ASC.

Figure 8b shows the GCD curves of the ASC at various current densities (0.5, 1.0, 2.0, 5.0, and 10.0 A g$^{-1}$) at a potential window of 1.5 V. The nonlinear GCD curves demonstrate the presence of faradaic reactions during charge–discharge. The electrochemical behavior of the fabricated ASC was highly reversible. The specific capacity of the ASC was calculated using eq 4, and the variation of specific capacitance of the ASC device at different current densities is indicated in Figure 8c. It can be observed from Figure 8c that the specific capacity of the ASC device is decreased with the increase in scan rate. At the current density of 0.5 A g$^{-1}$, the specific capacity is calculated to be 137.3 C g$^{-1}$.

To estimate the efficiency of the assembled device, the key parametric quantities are specific energy ($E$) and specific power ($P$), which have been calculated using eqs 6 and 7:

$$E(\text{Wh/kg}) = \frac{\Delta V \times Q_s}{2 \times 3.6}$$

(6)

$$P(\text{W/kg}) = \frac{E \times 3600}{\Delta t}$$

(7)

where $\Delta V$ (V) represents the potential range, $Q_s$ (C g$^{-1}$) is the specific capacity, and $\Delta t$ is the time required to fully discharge (s). A maximum energy density ($E_0$) of 28.6 Wh kg$^{-1}$ is obtained at a power density ($P_0$) of 367.7 W kg$^{-1}$ at 0.5 A g$^{-1}$, which is comparable with the reported carbon-based nanocomposites such as PANI–SnO$_2$–TiO$_2$//AC with energy density of 27 Wh kg$^{-1}$, MnO$_2$/CNT//AC with energy density of 23.2 Wh kg$^{-1}$, CoS/graphene//AC with energy density of 29 Wh kg$^{-1}$, and Al$_2$O$_3$-doped Co$_3$O$_4$/graphene//AC with energy density of 40.1 Wh kg$^{-1}$. Figure 8d shows the Nyquist plot of ASC based on the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite in the frequency range from 0.01 to 100 kHz at an AC voltage of 10 mV. The EIS plot of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite shows a semicircle in the high-frequency region and a straight line in the low-frequency region, as expected for an assembled ASC. The $R_s$ value calculated from the high frequency EIS for the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite is 0.99. The semicircle diameter measurement indicates a low resistance of the cell, which implies a short charge-transfer path. The high slope of the line in the Nyquist plot in the low-frequency region shows a low interfacial diffusion resistance, implying fast ion diffusion and mass transport at the electrode/electrolyte interface.

The cyclic stability of an ASC based on the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite at a current density of 5 A g$^{-1}$ is shown in Figure 9. The ASC based on the prepared ternary nanocomposite could retain ~97% of its initial capacitance after 5000 cycles, which is a good indication of its high cyclic stability. Based on the results, the cyclic stability and surface area of the SnO$_2$–TiO$_2$ nanocomposite eventually improved by the incorporation of 3DG with the SnO$_2$–TiO$_2$ nanocomposite, which helps to make it a suitable material for energy storage devices.

Furthermore, the superiority of the present work over the other SnO$_2$–TiO$_2$ composites for supercapacitors could be observed from Table 2. Table 2 compares the specific
Table 2. Comparison of Specific Capacity and Cyclic Stability of SnO$_2$–TiO$_2$-Based Supercapacitors

| materials      | specific capacitance (F/g) | $Q_{\text{retention}}$/cycle number | electrolyte          | current density | ref       |
|----------------|-----------------------------|--------------------------------------|----------------------|----------------|-----------|
| three-electrode configuration |                           |                                      |                      |                |           |
| 3DG–PANI       | 346                         | 70%/600                              | 1 M H$_2$SO$_4$      | 4 A/g          | 47        |
| 3D–RGNi        | 1328                        | 87%/2000                             | 2 M KOH              | 1 A/g          | 15        |
| SnO$_2$–TiO$_2$ nanoflowers | 500                           |                                       | 6 M KOH              | 1 A/g          | 10        |
| SnO$_2$–TiO$_2$ nanofibers | 350                           |                                       | 6 M KOH              | 1 A/g          |           |
| 3DG–SnO$_2$–TiO$_2$ | 284.5                     |                                       | 1 M KOH              | 1 A/g          | this work |
|                 | 350.95                      |                                       | 3 M KOH              | this work      |           |
|                 | 665.70                      |                                       | 6 M KOH              | this work      |           |
| two-electrode configuration |                           |                                      |                      |                |           |
| hydrogenation of TiO$_2$@GO | 51.10                      | 80%/10000                            | 1 M Na$_2$SO$_4$     | 1 A/g          | 48        |
| PANI–SnO$_2$–TiO$_2$    | 540                         | 85%/6000                             | 1 M H$_2$SO$_4$      | 0.35 A/g       | 8         |
| 3DG–TiO$_2$      | 64.90                       | 90%/5000                             | 1 M KOH              | 0.2 A/g        | 16        |
| 3DG–SnO$_2$–TiO$_2$ | 91.53                       | 97%/5000                             | 6 M KOH              | 0.5 A/g        | this work |

The specific capacitance of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite is because of the presence of 3DG that provides more active sites for the rapid electron transfer rate.

**CONCLUSIONS**

The 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite prepared by the hydrothermal method indicated the highest specific capacity (232.7 F g$^{-1}$) in 6 M KOH compared to the SnO$_2$–TiO$_2$ binary nanocomposite (23.45 F g$^{-1}$) because of the successful incorporation of 3DG into the SnO$_2$–TiO$_2$ nanocomposite. The addition of the SnO$_2$–TiO$_2$ nanocomposite to the 3DG matrix enhanced the surface area and increased the specific capacity almost 10 times in comparison with the binary nanocomposite of SnO$_2$–TiO$_2$. Moreover, the presence of 3DG can effectively prevent the degradation of the SnO$_2$–TiO$_2$ nanocomposite and provide more active sites for a rapid redox process. An ASC was also made for the first time with the 3DG–SnO$_2$–TiO$_2$ composite, and the assembled device had a specific energy of 28.6 Wh kg$^{-1}$ and a specific power of 367.7 W kg$^{-1}$ at a current density of 0.5 A g$^{-1}$. As a result, the ASC could retain 97% of its initial capacitance after 5000 cycles, demonstrating superior cycling stability. The electrochemical performance of the 3DG–SnO$_2$–TiO$_2$ ternary nanocomposite proves to be an appropriate candidate for electrodes in energy storage systems.

---

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c05343.

---

**AUTHOR INFORMATION**

**Corresponding Authors**

Golnoush Zamiri — Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; Centre of Advanced Materials, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; orcid.org/0000-0003-4223-5062; Email: golnoush.Zamiri@um.edu.my

A.S. Md. Abdul Haseeb — Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; Centre of Advanced Materials, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; Email: haseeb@um.edu.my

Syam G. Krishnan — Sustainable Energy Materials Lab, School of Chemistry and Physics, Faculty of Science, Queensland University of Technology, 4000 Brisbane, Queensland, Australia; orcid.org/0000-0002-8549-4323; Email: syam.gopalakrishnan@qut.edu.au

**Authors**

Priyanka Jagadish — Graphene & Advanced 2D Materials Research Group (GAMRG), School of Science and Technology, Sunway University, 47500 Subang Jaya, Selangor, Malaysia

Mohammad Khalid — Graphene & Advanced 2D Materials Research Group (GAMRG), School of Science and Technology, Sunway University, 47500 Subang Jaya, Selangor, Malaysia

Ing Kong — School of Engineering and Mathematical Sciences, La Trobe University, 3552 Bendigo, Victoria, Australia
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05343

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the University of Malaya grant through the Postdoctoral Research Fellowship (G.Z.) and Impact-Oriented Interdisciplinary Research Programme (IIRG) (no.: IIRG018C-2019).

■ REFERENCES

(1) Iqbal, M. Z.; Faisal, M. M.; Ali, S. R.; Afzal, A. M. Hydrothermally synthesized zinc phosphate-gOG composites for supercapacitve devices. J. Electrochem. Chem. 2020, 871, 114299.
(2) (a) Wang, G.; Zhang, L.; Zhang, J.; Yao, S. A review of electrode materials for electrochemical supercapacitors. Chem. Soc. Rev. 2012, 41, 797–828. (b) Zhu, Y. Nanomaterial-enabled stretchable conductors: strategies, materials and devices. Adv. Mater. 2015, 27, 1480–1511.
(3) Krishnan, S. G.; Archana, P. S.; Vidyadharan, B.; Misnon, I. L.; Vijayan, B. L.; Nair, V. M.; Gupta, A.; Jose, R. Modification of capacitive charge storage of TiO2 with nickel doping. J. Alloys Compd. 2016, 684, 328–334.
(4) Dubal, D. P.; Ayyad, O.; Ruiz, V.; Gómez-Romero, P. Hybrid energy storage: the merging of battery and supercapacitor chemistries. Chem. Soc. Rev. 2015, 44, 1777–1790.
(5) (a) Stevenson, A. J.; Gromadski, D. G.; Hu, D.; Chae, J.; Guan, L.; Yu, L.; Chen, G. Z. Supercapacitors with hybrids of redox active polymers and nanostructured carbons. Nanocarbons for Advanced Energy Storage 2015, 1, 179–210. (b) Shao, H.; Padmanathan, N.; McNulty, D.; O’Dwyer, C.; Raseeb, K. M. Supercapacitor based on binder-free Co3 (PO4) 2: 8H2O multilayer nano/microflakes on nickel foam. ACS applied materials & interfaces 2016, 8, 28592–28598.
(6) Krishnan, S. G.; Harilal, M.; Arshid, N.; Jagadish, P.; Khalid, M.; Li, L. P. Rapid microwave-assisted synthesis of MnCo2O4 nanolakes as a cathode for battery-supercapacitor hybrid. J. Energy Storage 2021, 44, 103566.
(7) Krishnan, S. G.; Arulraj, A.; Khalid, M.; Reddy, M. V.; Jose, R. Energy storage in metal cobaltite electrodes: Opportunities & challenges in magnostum cobalt oxides. Renewable and Sustainable Energy Reviews 2021, 141, 110798.
(8) Bolagam, R.; Modula, R.; Srinivasan, P. Hybrid material of PANi with TiO2-SnO2: pseudocapacitor electrode for higher performance supercapacitors. ChemistrySelect 2017, 2, 65–73.
(9) Fan, S.; Zhang, J.; Teng, X.; Wang, X.; Li, H.; Li, Q.; Xu, J.; Cao, D.; Li, S.; Hu, H. Self-supported amorphous SnO2-TiO2 nanocomposite films with improved electrochemical performance for lithium-ion batteries. J. Electrochem. Soc. 2019, 166, A3072.
(10) Pal, B.; Bakr, Z. H.; Krishnan, S. G.; Yusoff, M. M.; Jose, R. J. Large scale synthesis of 3D nanoflowers of SnO2/TiO2 composite via electrospinning with synergistic properties. Mater. Lett. 2018, 225, 117–121.
(11) Iqbal, J.; Numan, A.; Ansari, M. O.; Jagadish, P. R.; Jafar, R.; Bashir, S.; Mohammad, S.; Ramesh, K.; Ramesh, S. Facile synthesis of ternary nanocomposite of polyypyrrole incorporated with cobalt oxide and silver nanoparticles for high performance supercapacitry. Electrochim. Acta 2020, 348, 136313.
(12) Bose, S.; Kuila, T.; Mishra, A. K.; Rajasekar, R.; Kim, N. H.; Lee, J. H. Carbon-based nanostructured materials and their composites as supercapacitor electrodes. RSC Adv., 2012, 22, 767–784.
(13) (a) Wang, Y.; Guo, C. X.; Liu, J.; Chen, T.; Yang, H.; Li, C. M. CeO2 nanoparticles/graphene nanocomposite based high performance supercapacitor. Dalton Trans. 2011, 40, 6388–91. (b) Ramadoss, A.; Yoon, K.-Y.; Kwak, M.-J.; Kim, S.-I.; Ryu, S.-T.; Jang, J.-H. Fully flexible, lightweight, high performance all-solid-state supercapacitor based on 3-Dimensional-graphene/graphite-paper. J. Power Sources 2017, 337, 159–165.
(14) Iqbal, J.; Numan, A.; Jafar, R.; Bashir, S.; Jalani, A.; Mohammad, S.; Khalid, M.; Ramesh, K.; Ramesh, S. Compounds. Ternary nanocomposite of cobalt oxide nanograins and silver nanoparticles grown on reduced graphene oxide conducting platform for high-performance supercapacity electrode material. J. Alloys and Compounds 2020, 821, 153452.
(15) Trung, N. B.; Tam, T.; Dang, D. K.; Babu, K. F.; Kim, E. J.; Kim, J.; Choi, W. M. Facile synthesis of three-dimensional graphene/nickel oxide nanoparticles composites for high performance supercapacitor electrodes. Chem. Eng. J. 2015, 264, 603–609.
(16) Li, S.; Jiang, H.; Yang, K.; Zhang, Z.; Li, S.; Luo, N.; Liu, Q.; Wei, R. Compounds. Three-dimensional hierarchical graphene/TiO2 composite as high-performance electrode for supercapacitor. J. Alloys Compd. 2018, 746, 670–676.
(17) Kim, Y.-R.; Bong, S.; Kang, Y.-J.; Yang, Y.; Mahajan, R. K.; Kim, J. S.; Kim, H. Electrochemical detection of dopamine in the presence of ascorbic acid using graphene modified electrodes. Biosens. Bioelectron. 2010, 25, 2366–2369.
(18) Babadi, A. A.; Wan-Mohtar, W. A. A. Q. I.; Chang, J.-S.; Ilham, Z.; Jamaludin, A. A.; Zamiri, G.; Akbarzadeh, O.; Basirun, W. J. High-performance enzymatic biofuel cell based on three-dimensional graphene. Int. J. Hydrogen Energy 2019, 44, 30367–30374.
(19) Zamiri, G.; Haseeb, A.; Krishnan, S. G.; Numan, A.; Jagadish, P.; Khalid, M. Ternary nanocomposite cathodes based on 3D graphene-Ag nanoparticle-polyaniline for hybrid electrochemical energy device. Synthetic Metals 2021, 282, 116932.
(20) Messaadi, C.; Ghrib, T.; Jalali, J.; Ghrib, M.; Alyami, A. A.; Gaidi, M.; Silvan, M. M.; Ezzouaia, H. J. C. N. Synthesis and Characterization of SnO2-TiO2 Nanocomposites. Photocatalysts 2019, 15, 398–406.
(21) Bondavalli, P. Graphene and related nanomaterials: properties and applications; Elsevier, 2017.
(22) Syama, S.; Mohanan, P. V. Comprehensive application of graphene: emphasis on biomedical concerns. Nano-Micro Lett. 2019, 11, 1–31.
(23) K Anchade, P.; Phaphan, M. I. Selective optical sensor based on plasticized membrane incorporating ethyl protocatechuate compared with naked-eye screening method, 2020.
(24) Meng, Y.; Wang, K.; Zhang, Y.; Wei, Z. Hierarchical porous graphene/polyaniline composite film with superior rate performance for flexible supercapacitors. Adv. Mater., 2013, 25, 6985–6990.
(25) Mohammad, A.; Khan, M. E.; Cho, M. H.; Yoon, T. Fabrication of binary SnO2/TiO2 nanocomposites under a sonication-assisted approach: Tuning of band-gap and water depollution applications under visible light irradiation. Ceram. Int. 2021, 47, 15073–15081.
(26) Jia, Y.; Hu, D.; Wang, X.; Zhang, H.; Du, P. Carbon layer coated nickel phosphide nanoparticles embedded in three-dimensional graphene network for high-performance supercapacitor. J. Energy Storage 2022, 50, 104713.
(27) Fang, S.; Huang, D.; Lv, R.; Bai, Y.; Huang, Z.-H.; Gu, J.; Kang, F. Three-dimensional reduced graphene oxide powder for efficient microwave absorption in the S-band (2–4 GHz). RSC Advances. 2017, 7, 25773–25779.
(28) Challagulla, S.; Tarafder, K.; Ganesan, R.; Roy, S. Structure sensitive photocatalytic reduction of nitroarenes over TiO2. Sci. Rep. 2017, 7, 1–11.
(29) Zhao, Q.; Ju, D.; Deng, X.; Huang, J.; Cao, B.; Xu, X. J. S. r. Morphology-modulation of SnO2 hierarchical architectures by Zn doping for glycol gas sensing and photocatalytic applications. Sci. Rep. 2015, 5, 1–9.
(30) (a) Zazouli, M. A.; Yousefi, M.; Ghanbari, F.; Babanezhad, E. Engineering. Performance of photocatalytic ozonation process for pentachlorophenol (PCP) removal in aqueous solution using graphene-TiO2 nanocomposite (UV/G-TiO2/O3). J Environ Health Sci Eng 2020, 18, 108–109. (b) Stepić, K.; Jupković, R.; Icković; J.;
(31) Kunwar, R.; Krishnan, S. G.; Misnon, I. I.; Zabibi, F.; Yang, S.; Yang, C.-C.; Jose, R. Transformation of Supercapacitive Charge Storage Behaviour in a Multi elemental Spinel CuMnO3 Nanofibers with Alkaline and Neutral Electrolytes. Adv. Fiber Materials 2021, 3, 265–274.

(32) Zhao, Y.; Hao, M.; Wang, Y.; Sha, Y.; Su, L. Effect of electrolyte concentration on the capacitive properties of NiO electrode for supercapacitors. J. Solid State Electrochem. 2016, 20, 81–85.

(33) Nithya, V.; Kalai Selvan, R. K.; Kalpana, D.; Vasylichekho, L.; Sanjeeviraja, C. Synthesis of Bi2WO6 nanoparticles and its electro-chemical properties in different electrolytes for pseudocapacitor electrodes. Electrochimica Acta. 2013, 109, 720–731.

(34) Chodankar, N. R.; Pham, H. D.; Nanjundan, A. K.; Fernando, J. F. S.; Jayaramulu, K.; Golberg, D.; Han, Y.-K.; Dubal, D. P. True Meaning of Pseudocapacitors and Their Performance Metrics: Asymmetric versus Hybrid Supercapacitors. Small 2020, 16, 2002806.

(35) Ramadoss, A.; Kim, S. J. Improved activity of a graphene–TiO2 hybrid electrode in an electrochemical supercapacitor. Carbon. 2013, 63, 434–445.

(36) Wei, Z.; Liu, M.; Li, H.; Sun, S.; Yang, L. J. SnO2 quantum dots decorated reduced graphene oxide nanosheets composites for electrochemical supercapacitor applications. Int. J. Electrochem. Sci. 2020, 15, 6257–6268.

(37) Racchini, R.; Varzi, A.; Passerini, S.; Scrosati, B. The role of graphene for electrochemical energy storage. Nat. Mat. 2015, 14, 271–279.

(38) Krishnan, S. G.; Reddy, M. V.; Harilal, M.; Vidyadharan, B.; Misnon, I. I.; Rahim, M. H. A.; Ismail, J.; Jose, R. Characterization of MgCo2O4 as an electrode for high performance supercapacitors. Electrochim. Acta. 2015, 161, 312–321.

(39) Nandi, D.; Mohan, V. B.; Bhownick, A. K.; Bhattacharyya, D. Metal/metal oxide decorated graphene synthesis and application as supercapacitor: a review. J. Mater. Sci. 2020, 55, 6375–6400.

(40) Misnon, I. I.; Aziz, R. A.; Zain, N. K. M.; Vidyadharan, B.; Krishnan, S. G.; Jose, R. High performance MnO2 nanoflower electrode and the relationship between solvated ion size and specific capacitance in highly conductive electrolytes. Mater. Res. Bull. 2014, 57, 221–230.

(41) Vidyadharan, B.; Misnon, I. I.; Aziz, R. A.; Padmasree, K. P.; Yusoff, M. M.; Jose, R. Superior supercapacitive performance in electrosyn copper oxide nanowire electrodes. J. Mater. Chem. A 2014, 2, 6578–6588.

(42) Vivek, E.; Arulraj, A.; Krishnan, S. G.; Khalid, M.; I. V. P. Novel Nanostructured Nd(OH)3/g-C3N4 Nanocomposites (Nanorolls Anchored on Nanosheets) as Reliable Electrode Material for Supercapacitors. Energy Fuels. 2021, 35, 15205–15212.

(43) Xia, H.; Huo, C. Materials Electrochemical properties of MnO2/CNT nanocomposite in neutral aqueous electrolyte as cathode material for asymmetric supercapacitors. Emergent Materials 2011, 2, 283–291.

(44) Shi, J.; Li, X.; He, G.; Zhang, L.; Li, M. J. Electrodeposition of high-capacitance 3D CoS/graphene nanosheets on nickel foam for high-performance aqueous asymmetric supercapacitors. J. Mater. Chem. A 2015, 3, 20619–20626.

(45) Zhang, G.-F.; Qin, P.; Song, J.-M. Facile fabrication of Al2O3-doped Co3O4/graphene nanocomposites for high performance asymmetric supercapacitors. Appl. Surf. Sci. 2019, 493, 55–62.

(46) Mei, B.-A.; Munteshri, O.; Lau, J.; Dunn, B.; Pilon, L. J. Physical interpretations of Nyquist plots for EDLC electrodes and devices. J. Phys. Chem. C 2018, 122, 194–206.

(47) Dong, X.; Wang, J.; Wang, J.; Chan-Park, M. B.; Li, X.; Wang, L.; Huang, W.; Chen, P. Physics. Supercapacitor electrode based on three-dimensional graphene–polyaniline hybrid. Mater. Chem. Phys. 2012, 134, 576–580.

(48) Pham, V. H.; Nguyen-Phan, T.-D.; Tong, X.; Rajagopalan, B.; Chung, J. S.; Dickerson, J. H. J. C. Hydrogenated TiO2@ reduced