

Cite this: *Nanoscale Adv.*, 2023, 5, 1465

Iron-selenide-based titanium dioxide nanocomposites as a novel electrode material for asymmetric supercapacitors operating at 2.3 V†

Muhammad Zia Ullah Shah,^{ab} Hongying Hou,^{*a} Muhammad Sajjad,^{bc} Muhammad Sanaullah Shah,^{ab} Kashif Safeen^d and A. Shah^{*b}

This study portrays a facile wet-chemical synthesis of FeSe₂/TiO₂ nanocomposites for the first time for advanced asymmetric supercapacitor (SC) energy storage applications. Two different composites were prepared with varying ratios of TiO₂ (90 and 60%, symbolized as KT-1 and KT-2) and their electrochemical properties were investigated to obtain an optimized performance. The electrochemical properties showed excellent energy storage performance owing to faradaic redox reactions from Fe²⁺/Fe³⁺ while TiO₂ due to Ti³⁺/Ti⁴⁺ with high reversibility. Three-electrode designs in aqueous solutions showed a superlative capacitive performance, with KT-2 performing better (high capacitance and fastest charge kinetics). The superior capacitive performance drew our attention to further employing the KT-2 as a positive electrode to fabricate an asymmetric faradaic SC (KT-2//AC), exceeding exceptional energy storage performance after applying a wider voltage of 2.3 V in an aqueous solution. The constructed KT-2//AC faradaic SCs significantly improved electrochemical parameters such as capacitance of 95 F g⁻¹, specific energy (69.79 Wh kg⁻¹), and specific power delivery of 11529 W kg⁻¹. Additionally, extremely outstanding durability was maintained after long-term cycling and rate performance. These fascinating findings manifest the promising feature of iron-based selenide nanocomposites, which can be effective electrode materials for next-generation high-performance SCs.

Received 24th November 2022
Accepted 30th December 2022

DOI: 10.1039/d2na00842d

rsc.li/nanoscale-advances

1. Introduction

The increase in global energy consumption, which depends on the combustion of fossil fuels, correlates to the rise in the population worldwide. The surrounding temperature has increased dramatically due to global warming produced by massive carbon dioxide emissions into the atmosphere, reaching an alarming level that causes environmental damage.^{1,2} Another option is finding new electrochemical energy storage systems that are compact, inexpensive, clean, functional, and desired for today's society. One needs to upgrade the existing electrochemical energy storage devices, and batteries and SCs technologies are the solutions to this problem. The superior technology is that of SCs compared to batteries, as the former possess rapid faradaic redox reactions and insertion/desertion

process, which significantly boosts their durability (~10⁵ cycles) and power (~10 kW kg⁻¹) due to pseudocapacitive behavior and stability double-layer capacitance owing to the electrolyte ions at the surface of the charged electrode.³⁻⁹ The truncated energy density (~20 Wh kg⁻¹) of SCs severely obstructs its vast applications compared with that of Li-ion batteries (~300 Wh kg⁻¹).¹⁰⁻¹² Based on the following equation for calculating the energy density for SCs, $E = 0.5C \times V^2$, two factors need to be addressed to enhance the energy density; either the capacitance (C) or the working voltage (V). More specifically, the working voltage is a proficient way to boost the energy density further, as the voltage is proportional to the square of the energy density. Several methods for efficiently increasing energy density have been presented, including the fabrication of symmetric/asymmetric SCs and hybrid or battery-type SCs that vastly increase energy density.¹³⁻¹⁹

In today's electronic market, organic SCs show a promising candidature providing a wide voltage of up to >2.5 V and suffer from flammability, low ionic conductivity, and toxicity. Like organic SCs, ionic liquid supercapacitors display a relatively wide voltage window, up to ~4.0 V.^{20,21} Moreover, the low conductivity of ionic liquid SCs with high equivalent series resistance and viscosity values led to deteriorating power delivery and rate performance. Besides, the severe and high-cost moisture-free manufacturing of the above SCs is due to their

^aFaculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China. E-mail: hongyinghou@kust.edu.cn

^bNational Institute of Lasers and Optronics College, Pakistan Institute of Engineering and Applied Sciences, Nilore, Islamabad 45650, Pakistan. E-mail: attashah168@gmail.com

^cCollege of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua 321004, P. R. China. E-mail: sajjadfisica@gmail.com

^dDepartment of Physics, Abdul Wali Khan University, Mardan 23200, KPK, Pakistan

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2na00842d>



complex purification and moisture-sensitive electrolyte. Aqueous SCs usually show a relatively high capacitance with pseudocapacitive materials due to distinct characteristics of low resistance, smaller ionic size, and high electrical conductivity compared with non-aqueous SCs (ionic liquid and organic SCs).²² However, the low-cost and environmental friendliness merits of aqueous SCs are captivating features for industrial-grade production. Regrettably, the low-voltage of aqueous SCs is confined to a narrow range due to undesirable water decomposition.^{10,23–25}

Transition metal chalcogenides are a novel electrode material that have piqued the scientific community's interest due to their superior electrochemical characteristics. More specifically, sulfides, $\text{Co}_{0.5}\text{Ni}_{0.5}\text{WO}_4$ (CNWO),²⁶ Co_3S_4 (ref. 27) Ni_3S_2 ,^{28,29} MoS_2 ,³⁰ CuS ,^{31,32} FeS ,³³ NiCo_2O_4 ,^{34,35} and NiCo_2S_4 (ref. 10 and 36) have been enormously explored as electrode materials for supercapacitors, and their performance still deteriorates owing to low conductivity and cycling durability. From this perspective, transition metal selenides are a great alternative, as selenium dominates metallicity more than S and O, resulting in higher conductivity. Additionally, transition metal selenides have been reported to display remarkable durability without the formation of polyselenide during redox reactions in the electrochemical process.³⁷ Many literature reports, *e.g.*, $\text{MnSe}/\text{MnSe}_2$,^{14,38} NiSe_2 ,³⁹ and CuSe ,^{40,41} demonstrated attractive electrode materials with remarkable performance. Among these appealing compounds, iron selenide (symbolized as FeSe_2) is a p-type semiconductor with a quiet narrow bandgap energy of (1.0 eV), one of the most appealing candidates for supercapacitors owing to its fascinating features, such as high theoretical capacity, high adsorption coefficient and fast electron transfer applied in batteries, solar cells,^{42–44} and rarely reported for supercapacitors.^{45–47} For example, graphene-wrapped FeS_2 - FeSe_2 core-shell cratered sphere anode was prepared, which delivered remarkable charge storage performance in energy density and 158 Wh kg^{-1} at $2236.16 \text{ W kg}^{-1}$.⁴⁸ Another report involved fabricating flexible asymmetric supercapacitors based on NiCo_2O_4 and FeSe_2 as the cathode and anode, respectively, and operating in a stable operated in a voltage of 1.5 V, which exhibited superior energy storage performance and long-term stability of 1000 successive cycles could be ascribed to the pseudocapacitive charge storage mechanism of both electrodes, which collectively enhanced electrochemical performance substantially.⁴⁶ Shao and co-workers⁴⁹ recently reported the synthesis of cobalt-doped layer double hydroxide// FeSe_2/C to construct an asymmetric supercapacitor that delivered superior stability of 84.8% at a discharge rate of 0.3 mA when scanned for long-term cycling of 10 000 with improved energy and power densities. Pandit *et al.*⁵⁰ prepared iron selenide *via* successive ion layer deposition and reaction methods, which revealed a capacity of 671 F g^{-1} and 431 F g^{-1} , respectively, when tested using cyclic voltammetry and charge-discharge measurements with substantially-improved rate and cycling performance. Based on the above literature reports, it can be seen that the FeSe_2 -based composite electrode material is rarely has been reported so far.

In this work, we synthesized $\text{FeSe}_2/\text{TiO}_2$ nanocomposites for high-rate performance in faradaic SCs for the first time using a wet-chemical approach to investigate their energy storage properties. According to our findings, the composite KT-2 electrode has significantly enhanced charge storage characteristics than FeSe_2 and TiO_2 electrodes. Finally, a faradaic KT-2//AC SCs was assembled, revealing a remarkable energy storage performance (69.79 Wh kg^{-1} specific energy and 11529 W kg^{-1} specific power) with excellent stability. Our results showed that FeSe_2 -based composite electrodes could be effectively utilized as alternative nanomaterials of high-rate performance for faradaic SCs.

2. Experimental

2.1 Materials and methods

Hydrothermal and sol-gel methods were used for the synthesis of FeSe_2 , TiO_2 , and their nanocomposites. Analytical-grade chemicals were obtained from Sigma Aldrich, including Ti-isopropoxide (97%), acetic acid (98%), and isopropyl alcohol (98%). Iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 99.9%), hydrazine monohydrate ($\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$), ammonia (NH_3), and elemental selenium powder (Se) were used. Deionized water (DI) and ethanol were used to prepare all the standard stock solutions.

2.2 Preparation of FeSe_2 nanoparticles

The FeSe_2 precursor was synthesized using a modified hydrothermal method, and all compounds employed in this study were of analytical grade and were not purified further. First, 2.28 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1.24 g of Se powder were dissolved in 40 mL of deionized water. The mixture was then gently combined with 3 mL hydrazine monohydrate and 6 mL ammonia water (dropwise) (colour changed) and stirred continuously for 30 min. After stirring, the solution was enclosed in a Teflon-lined (stainless-steel) autoclave and then was kept in an oven at $180 \text{ }^\circ\text{C}$ for 20 h to complete the reaction. After cooling, the obtained precipitate was filtered, washed using DI water/ethanol, and dried at $80 \text{ }^\circ\text{C}$, overnight.⁵¹

2.3 Preparation of TiO_2 nanoparticles

As reported in our previous work,⁴⁰ for the synthesis of TiO_2 nanoparticles, first, a solution of isopropyl alcohol (10 mL) and acetic acid (3 mL) was prepared. Then, titanium isopropoxide was added dropwise to the above solution, while stirring it continuously at room temperature for 30 min. Then, 2 mL of deionized water was added drop by drop to the above mixture. The mixture was then heated at $100 \text{ }^\circ\text{C}$ for 3–5 min to obtain a white gel that was washed and dried. The obtained powders were calcined at $550 \text{ }^\circ\text{C}$ for 2 h.

2.4 Preparation of $\text{FeSe}_2/\text{TiO}_2$ nanocomposites

A wet chemical method was employed to prepare $\text{FeSe}_2/\text{TiO}_2$ nanocomposites with varying percentage compositions. TiO_2 percent combination was 90% and 60%, while FeSe_2 was 10% and 40%. Each mixture was blended into 40 mL methanol. Then, the solution was sonicated for 40 min. Afterwards, the residue was thoroughly stirred on a magnetic stirrer for 40 min.



Table 1 Details of the composites prepared

| Samples | Composition | FeSe ₂ (g) | TiO ₂ (g) | Methanol (mL) | Time (h) | Temp (°C) |
|---------|---|-----------------------|----------------------|---------------|----------|-----------|
| KT-1 | 10% FeSe ₂ -90% TiO ₂ | 0.08 | 0.72 | 40 | 18 | 80° |
| KT-2 | 40% FeSe ₂ -60% TiO ₂ | 0.32 | 0.48 | 40 | 18 | 80° |

Afterwards, the mixture was heated for 18 h at 80 °C to remove the unreacted species from the precursor solution. The obtained samples with the ratios of 10% FeSe₂-90% TiO₂ and 40% FeSe₂-60% TiO₂ were marked as KT-1 and KT-2, respectively, as summarized in Table 1 below.

2.5 Fabrication of the asymmetric supercapacitor

The asymmetric faradaic SCs were assembled in a sandwich-type configuration using a FeSe₂/TiO₂ nanocomposite as the cathode, AC as the anode, and 3 M KOH as the electrolyte. The constructed electrodes' specific capacitance, specific power, and specific energy were calculated using eqn (2)–(4) (see ESI in ref. 38).

3. Results and discussion

In this section, we will discuss details related to structural, morphological, and composition analyses of the prepared samples obtained using several characterization tools, such as X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), and energy dispersive X-ray (EDX). As can be seen from Fig. 1a, the XRD pattern of FeSe₂ (black line) is composed of characteristics diffraction reflections at (24.27°), (29.47°), (31.32°), (35.01°), (36.3°), (40.62°), (44.43°), (48.56°), (51.12°), (54.20°), (56.21°), (57.58°), (59.80°), and (64.21°) corresponding to the specified reference miller indices (011), (101), (110), (002), (111), (012), (020), (021), (112), (121), (200), (122), (211), and (031), respectively, which indicated that FeSe₂ had a hexagonal crystal structure that perfectly matched with that from the standard JCPDS card no. (01-074-0247).⁴⁷ Likewise, in the case of pure TiO₂, the diffraction peaks at 2θ values of (25.30°), (38.5°), (48.03°), (53.8°), (55°),

(62.69°), (68.76°), (70.2°), (75.05°), and (82.76°), which are, respectively, assigned to (101), (112), (200), (1050), (211), (204), (116), (220), (215) and (224) planes of the tetragonal anatase structure as they matched well with the peaks from the JCPDS card no. 01-084-1285. According to the XRD results, no intermediate polyselenide by-products were found in FeSe₂, confirming that the product was single-phase combined with high purity and excellent crystallinity. On the contrary, the TiO₂ reflections also showed no impurity peaks, indicating the high purity of the product. Besides, the XRD pattern of the KT-1 and KT-2 composites presented the combination of FeSe₂ and TiO₂ diffraction reflections, proving the successful synthesis of compounds with high purity without any additional traces residing in the peaks, as shown in Fig. 1a. Furthermore, the crystalline size of the product was calculated using the Scherrer formula $D = K\lambda/\beta\cos\theta$, where K is a constant, λ is the wavelength of the incident light, and the corresponding values are listed in Table 2. The FeSe₂ grain size was around 31.2 nm, and TiO₂ was 19.9 nm, showing that the former has a relatively larger grain size than the latter. However, when we move toward the composites, KT-1 has a smaller crystallite size, whereas KT-2 has a slightly higher one. Based on these findings, we concluded that the chosen materials were successfully prepared with high

Table 2 Crystallite size of the samples

| Sample name | Average crystallite sizes (nm) |
|-------------------|--------------------------------|
| FeSe ₂ | 31.2 |
| TiO ₂ | 19.9 |
| KT-1 | 23.62 |
| KT-2 | 27.54 |



Fig. 1 (a) Crystal structure and (b) vibrational modes of the FeSe₂, TiO₂, KT-1, and KT-2 composite.



purity and crystallinity using the wet-chemical method. The Raman analysis was performed to test the characteristic bands of the products, which supported the successful preparation of the samples. The results are shown in Fig. 1b. The Raman shift of the FeSe₂ displayed three vibrational modes at 184.7, 238.5, and 273.3 cm⁻¹ that can be accredited to the vibrational modes, A_g and B_{1g}, which arising due to Se–Se vibrations,⁵² while TiO₂ showed four significant peaks centered at 150 cm⁻¹ (E_g), as well as additional bands at 393.14 cm⁻¹ (B_{1g}), 513.13 cm⁻¹, and (A_{1g}), and 636.01 cm⁻¹ (E_g), as shown in Fig. 1b. Interestingly, a slight increase in the Raman intensity was observed when the content of TiO₂ increased substantially, which may be due to the increased crystallite size, as previously discussed in the XRD analysis. Notably, the composites KT-1 and KT-2 indicated the combined Raman modes of the FeSe₂ and TiO₂ peaks, confirming the successful synthesis of the material.

The morphology of the samples was examined using FESEM analysis of the prepared materials, as shown in Fig. 2. As shown in 2a, the FeSe₂ is composed of nanoparticle morphology, with aggregation observed on its surface. The nanoparticles are smaller with different sizes and shapes, with open network channels on their surface, facilitating rapid charge transport and shortening the diffusion path for the electrolyte ions. Similarly, the TiO₂ showed amorphous morphology (see Fig. 2b) without any distinct shape, providing enough space for mass diffusion and alleviating the volume change without sacrificing morphological failure during the long-term pseudocapacitive insertion/desertion process. Fig. 2c and c1 shows the combined morphology of FeSe₂ and TiO₂, meaning that the nanoparticles were present on the surface of the TiO₂ network, indicating good integration of the two compounds in a composite structure coupled with gaps/voids on their surface. It is noteworthy to

observe that the KT-2 (see Fig. 2d and d1) revealed a loose structure when compared with KT-1 and forms significant voids/gaps on their surface, which seems to be more promising for mass diffusion during the electrochemical process, which appeared to reduce the volume changes, and boosts the electrochemical performance of the sample. Based on the FESEM results, we expected that the KT-2 sample remarkably performed well for faradaic SCs.

The elemental analysis of the samples was also performed to verify the successful formation and purity, as clearly discussed in the XRD and FESEM sections. The EDX analysis of the samples is provided in Fig. 3. More specifically, all samples showed high purity and successful synthesis due to the presence of only Fe and Se atoms in FeSe₂ and Ti and O in TiO₂. Moreover, the presence of Fe, Se, Ti, and O in KT-1 and KT-2 composites confirmed the successful formation of our materials, as presented in Fig. 3a–d. The high purity may be helpful for the good electrochemical performance of the samples during electrochemical activities. Furthermore, the distribution of elements on the surface of the composites of the samples was further studied using EDX mapping analysis, as shown in Fig. 4. Subsequently, Fig. 4a and b show the mapping results of FeSe₂ and FeSe₂/TiO₂ nanocomposite, demonstrating the homogeneous distributions of the elements on the surface of pure and composite materials, supporting our previous findings.

4. Charge storage mechanism in FeSe₂ systems

It has been reported that “materials of the twenty-first century,” known as “nanocomposites,” with sizes ranging from 10⁻⁹ nm,



Fig. 2 FESEM images of (a) FeSe₂ and (b) TiO₂ (c, c1) KT-1 (d, d1) KT-2.





Fig. 3 EDX of (a) FeSe₂ and (b) TiO₂, and (c) KT-1 (d) KT-2 composites.

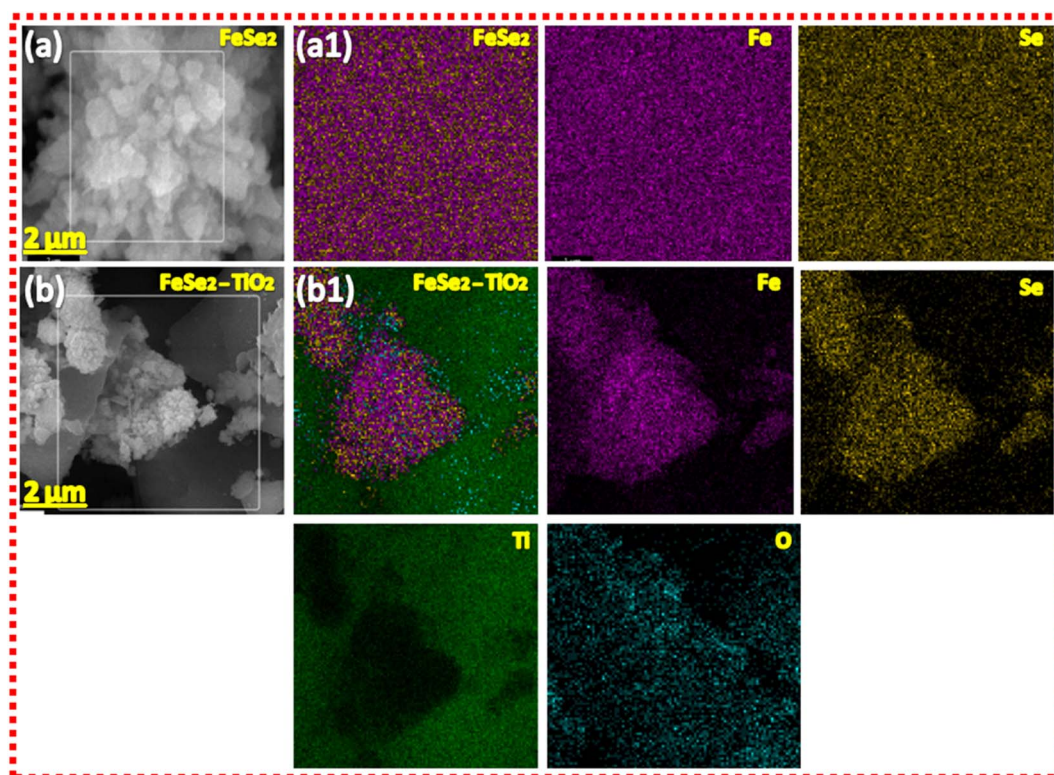


Fig. 4 EDS mapping images of (a and a1) FeSe₂ and (b and b1) FeSe₂/TiO₂ composites.





Scheme 1 The energy storage mechanism in the layered structure of FeSe₂.



Fig. 5 Energy storage characteristics of the samples in a three-electrode setup for the electrode materials, CV curves of (a) FeSe₂, (b) TiO₂, (c) KT-1, (d) KT-2, and (e) comparative CV curves for all electrodes.



have unique architecture and properties.⁵³ Nowadays, researchers and scientists are trying to develop numerous nanocomposite materials utilizing several techniques and approach diverse morphologies and distinct structures.^{54–58} More interestingly, these nanocomposites are deemed in various fields, *e.g.*, biomedical, engineering, energy domain, electronics, and industrial-grade applications,^{59–61} but not limited to this end. Meanwhile, the diverse chemical and physical properties combined with other capabilities/characteristics turn nanocomposite materials well distinguished from their bulk counterparts.^{10,62,63} Therefore, considering these supreme properties and features, we concluded that making composite materials substantially impacted the electrochemical charge storage performance of the active electrode materials. As discussed, the layered structure of the FeSe₂ initiates various oxidation states, *e.g.*, Fe²⁺/Fe³⁺ and Fe⁰ participated during the charge storage processes, as illustrated in

Scheme 1. Subsequently, FeSe₂ offers several redox reactions owing to Fe²⁺/Fe³⁺, Fe⁰/Fe³⁺, and Fe⁰/Fe²⁺, leading to increased charge storage capacity, thus expanding the energy storage performance to a great extent.⁶⁴ During charging, the electrolyte ion K⁺ and the diffusion of OH⁻ occupy all available area/volume at a slow scan and current rate, leading to high capacity. The weaker selenium (Se) bonding, either chemical or electronic, in the Fe–Se system may alter owing to the existing oxidation states, leading to more activity during the electrochemical reactions.^{65,66} It is known that the excessive contact between active electrodes and electrolyte promotes active material utilization, resulting in an incremental increase in the performance of supercapacitor properties.⁶⁵ Instead, during the discharge process, the host ions reverse back to the electrolyte, and the external electrons keep balance the charge neutrality.

The charge storage performance of the prepared electrode materials was further measured with several electrochemical

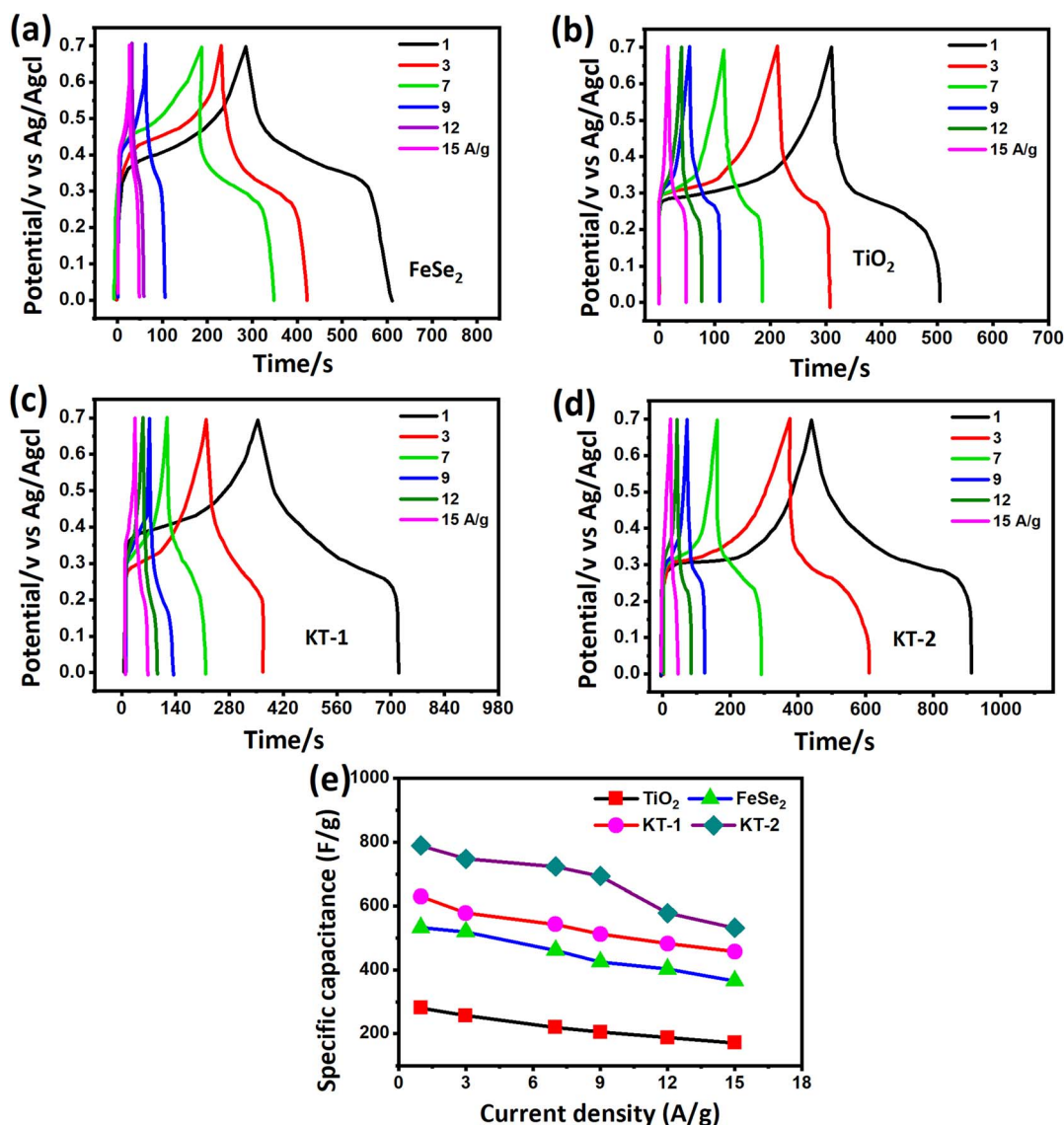


Fig. 6 GCD curves of (a) FeSe₂, (b) TiO₂, (c) KT-1, (d) KT-2, and (e) comparative capacitance performance of all electrodes at different discharge currents.



energy storage techniques, CV, GCD, and impedance, to study their energy storage capacities, reversibility, and capacitive charge storage nature. The CV measurements of the electrode materials were evaluated, and their corresponding results are provided in Fig. 5. Based on their charge storage mechanism, our prepared electrode materials typically follow the pseudo-capacitive charge storage mechanism originating due to faradaic redox reactions with well-defined redox peaks, as shown in Fig. 5a–d. The redox peaks in the FeSe₂ electrode could be attributed to Fe²⁺/Fe³⁺ due to FeSe₂ + OH⁻ → FeSe₂OH + e⁻, while those in the TiO₂ were due to Ti³⁺/Ti⁴⁺ during the electrochemical process.^{45,67} The enclosed CV loop current of the FeSe₂ electrode is more significant than that of the TiO₂ electrode (see Fig. 5a and b), specifying a high capacitance as that of the latter counterpart. Subsequently, the KT-2 electrode showed a larger area and current response than the KT-1 electrode, demonstrating that the former electrode has the highest energy storage performance, as shown in Fig. 5c and d. More importantly, the set voltage gap (0.0 V to 0.7 V) is the highest potential window for both pure and composite so far. The increasing trend is observed with the upsurge in scanning speeds, documenting the electrodes' good reversibility and rate performance. Comparative CV curves were plotted at a fixed scanning speed better to understand the improved performance between different electrode materials, as shown in Fig. 5e. Evidently, the KT-2 electrode showed the best performance among other electrodes, which can be further verified *via* GCD and impedance analysis.

Table 3 The capacitance of the electrodes was calculated from the GCD profile

| Current density (A g ⁻¹) | FeSe ₂ | TiO ₂ | KT-1 | KT-2 |
|--------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 1 | 533 F g ⁻¹ | 281.4 F g ⁻¹ | 630 F g ⁻¹ | 789.2 F g ⁻¹ |
| 3 | 519.6 F g ⁻¹ | 257.5 F g ⁻¹ | 578 F g ⁻¹ | 747.2 F g ⁻¹ |
| 7 | 461.1 F g ⁻¹ | 220.3 F g ⁻¹ | 543.1 F g ⁻¹ | 723.1 F g ⁻¹ |
| 9 | 425 F g ⁻¹ | 205 F g ⁻¹ | 512.2 F g ⁻¹ | 693.4 F g ⁻¹ |
| 12 | 402.8 F g ⁻¹ | 188.7 F g ⁻¹ | 482.4 F g ⁻¹ | 578.2 F g ⁻¹ |
| 15 | 365.6 F g ⁻¹ | 171.4 F g ⁻¹ | 457.1 F g ⁻¹ | 532.3 F g ⁻¹ |

To further prove the excellent energy storage performance of the electrodes (as discussed in the CV analysis), we measured the GCD profile more effectively and clearly for better understanding. Fig. 6 shows the GCD curves of different electrode materials at similar discharge current rates between the time frame (s) and potential (V). The curves were obtained at a fixed potential window (0.0 to 0.7 V) at different discharge currents from 1, 3, 7, 9, 12, and 15 A g⁻¹ for all electrodes. FeSe₂ and TiO₂ electrodes showed a clear voltage plateau in their GCD profiles (see Fig. 6a and b), consistent with the CV outcomes. Compared with TiO₂, the FeSe₂ reveals a longer discharge time, proving the highest energy storage performance in capacitance.

Meanwhile, the KT-2 electrode showed a relatively longer discharge time than the pure and KT-1 composite electrodes, indicating its best performance among all other electrode materials (see Fig. 6a–d). Noteworthily, at notably higher current rates, the shape of the GCD curves was still sustained, proving the superior rate performance of the active electrodes. The energy storage performance was judged by different parameters, such as capacitance, rate performance, cycling durability, and more negligible impedance. Based on the GCD curves, the capacitance was calculated at each current rate for all the electrodes and plotted simultaneously to compare their capacitive performances more constructively, as depicted in Fig. 6e. As discussed earlier and shown in Fig. 6e, KT-2 achieved the highest capacitance compared with the KT-1 composite electrode and their pristine counterparts. Their calculated values are tabulated in Table 3. The excellent performance can be attributed to the gap/open channels offered by KT-2, which could accommodate enough electrolyte ions to reduce the dead volume on the substrate. The excellent conductivity led to fast charge transport kinetics, resulting in a reasonable rate and energy storage performance. To support the above claims, we tested the charge transportation behavior of the electrodes during the charge–discharge process as an impedance plot (see Fig. 7). It is evident that all plots show a visible semicircle, presenting the charge transfer resistance (R_{ct}), and intercept at the real axis, specifying the solution resistance (R_s), as seen in Fig. 7a and b. The R_{ct} and R_s values were calculated using the Z-view software by fitting, and the corresponding values are listed



Fig. 7 (a) Impedance plots, inset is the equivalent circuit model, and the (b) zoomed view.



in Table 4. From these values, it is observed that KT-2 reflected the lowest R_{ct} and R_s values of 5.9 and 1.98 Ω , respectively, as compared with other electrodes KT-1 (7.23, 1.62 Ω), TiO_2 (9.21, 2.10 Ω), and $FeSe_2$ (8.12, 1.99 Ω), suggesting the fast charge kinetics of KT-2 and $FeSe_2$ when compared with their counterparts. These results again prove the best performance of the KT-2 electrode material, supporting our previous results. The

Table 4 Impedance plot parameters determined from the Z-view software

| Sample | $FeSe_2$ | TiO_2 | KT-1 | KT-2 |
|----------|---------------|---------------|---------------|---------------|
| R_s | 2.15 Ω | 2.10 Ω | 1.57 Ω | 1.98 Ω |
| R_{ct} | 7.36 Ω | 9.03 Ω | 7.05 Ω | 5.94 Ω |

equivalent circuit model is presented in the inset in Fig. 7a, revealing the resistance, capacitor, and Warburg impedance according to the impedance analysis.

We investigated more realistic practical aspects (two-electrode system) based on the outstanding energy storage properties of the electrodes developed in this work. We built an asymmetric faradaic SC in a sandwich-type configuration (KT-2//AC) in the KOH electrolyte and scanned it at relative potential windows separately. Fig. 8a shows the CV curves of the AC and KT-2 electrodes in a possible window of -1.2 V to 0.0 V and 0.0 to 0.9 V at a fixed scanning speed (Fig. 8a) that successfully achieved the highest voltage of 2.3 V so far. The suitability of the obtained potential was tested at different scanning rates, which sustained the set voltage without any noticeable distortion

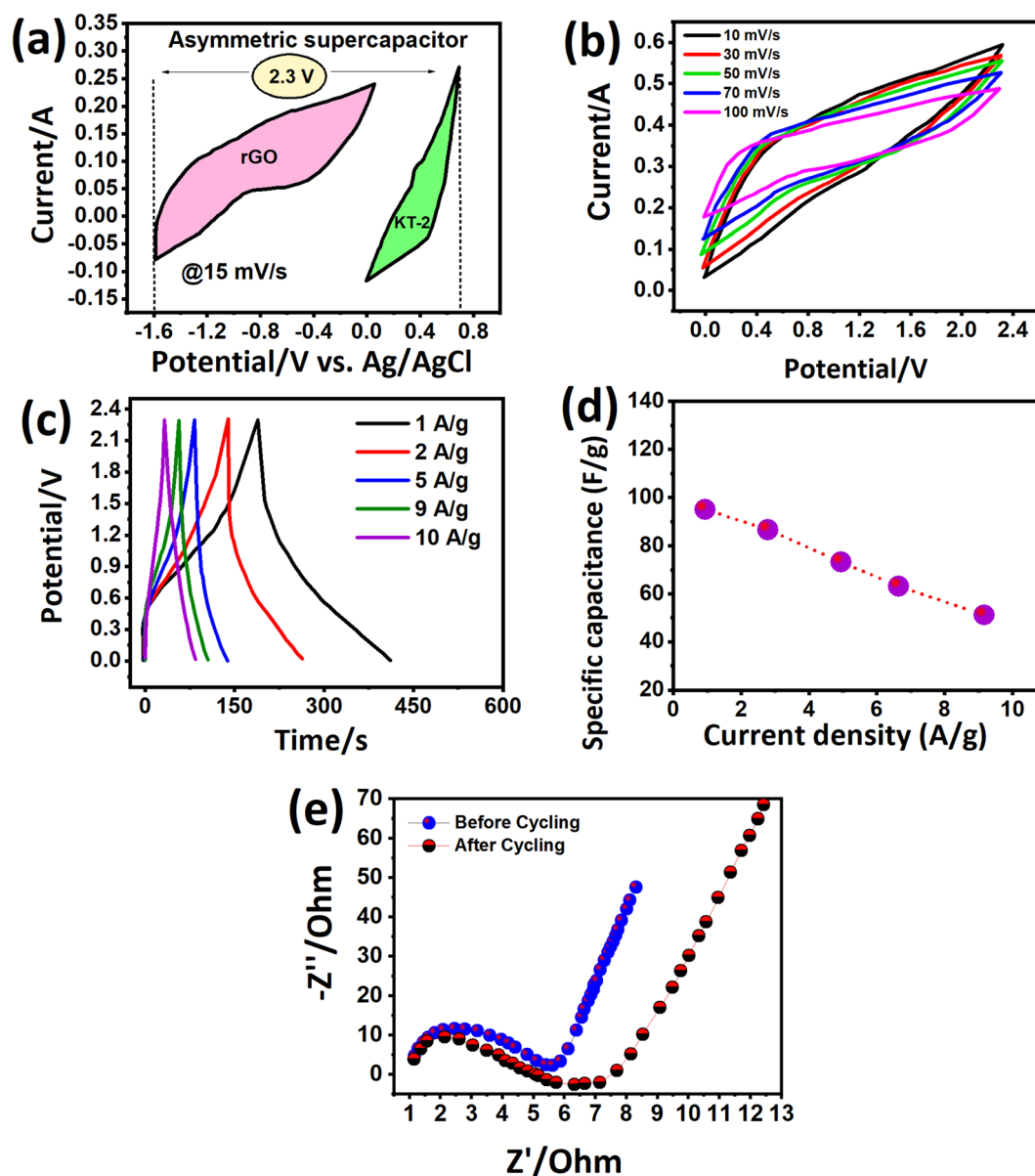


Fig. 8 Energy storage characteristics of KT-2//AC asymmetric faradaic SC, (a) CV curves at different potential frames, (b) CV curves at 2.3 V, (c) charge profiles at different rates, (d) decay in capacitance w.r.t current, (e) impedance plots.



observed in the CV loops, as depicted in Fig. 8b, suggesting the remarkable energy storage performance with good reversibility and rate capability. Fig. 8c presents the successive GCD profiles at different discharge rates and well-defined GCD curves, indicating the fast redox reactions on the surface of KT-2//AC asymmetric faradaic SCs. The superb performance was proved at sustainably-prolonged current rates, *e.g.*, 10 A g⁻¹, and no disruption was seen in the GCD shape. Building a robust faradaic SC at a relatively higher current response from a practical perspective is challenging. We hope that iron-based selenides may work smoothly in real-life applications. The charge storage capacitance was calculated and plotted against discharge rates, as shown in Fig. 8d. A high capacitance of 95 F g⁻¹ was reported at 1 and it dropped to 51 F g⁻¹ when the current discharge rates increased 10 times, implying the excellent rate performance of the KT-2//AC asymmetric faradaic SC, as listed in Table 5. A smooth and continuous drop in the capacitance was observed at current upsurge rates, suggesting that fewer ions reached the electrode surface due to the speedy charge-discharge process. Fig. 8e shows the impedance spectra before cycling, which displayed a semi-circle with ($R_{ct} = 5.8 \Omega$ and $R_s = 1.4 \Omega$), specifying the rapid charge movement and lower electrolyte resistance of the active material/electrolyte ions, and the current collector during the electrochemical process. After the cycling test, the semi-circle enlarged with the R_{ct} value of 6.3 Ω with an almost similar R_s value. The straight line at a high-frequency region indicates the low diffusion impedance and good capacitive feature of the assembled KT-2//AC asymmetric faradaic SC before cycling compared with the after cycling test.

Table 5 Ragone plot parameters and capacitance concerning current rates

| Current density (A g ⁻¹) | 1 | 2 | 5 | 9 | 10 |
|---|-------|-------|-------|-------|-------|
| Specific capacitance (F g ⁻¹) | 95 | 86 | 73 | 63 | 51 |
| Energy density (Wh kg ⁻¹) | 69.79 | 63.18 | 53.63 | 46.28 | 37.47 |
| Power density (W kg ⁻¹) | 1147 | 2297 | 5678 | 10413 | 11529 |

The KT-2//AC asymmetric faradaic SC was explored further, and its energy and power density were determined to report their importance. To achieve optimized performance for KT-2//AC asymmetric faradaic SC, one needs to balance the masses of the cathode and anode materials by using the formula $Q_+ = Q_-$, where ($Q = C \times m \times \Delta u$). The mass ratio was determined and optimized based on the capacitance and potential window of the cathode and anode.^{57,68} We calculated the specific energy and power based on the following equations, and the results are plotted as the Ragone plot (Fig. 9a). Impressively, a reasonably high specific energy of 69.79 Wh kg⁻¹ was obtained at 1 A g⁻¹ with a specific power of 1147 W kg⁻¹ and a drop in specific energy of 37.47 Wh kg⁻¹. A rise in the specific power was attained until 11529 Wh kg⁻¹ when the discharge increased to 10 A g⁻¹, and the corresponding values are tabulated in Table 5. The performance comparison of this work with that already reported in the literature is shown in Table 6, indicating the promising prospect of the FeSe₂- and TiO₂-based composite for future energy storage applications. This outstanding energy storage performance demonstrated the importance of iron-based selenides as an effective alternative for achieving a robust, energy-efficient energy storage performance.

Modern electronics need ample energy storage, and long-term running functional materials are in high demand. Various materials are being tested and their performance is scalable at industrial grade and are commercialized to fulfill this gap. Cycling durability is also essential in judging the best version of the active electrode material, as previously mentioned in the GCD analysis. The cycling test of the KT-2//AC asymmetric faradaic SC was performed at 10 A g⁻¹ for 15 000 cycles and its performance was checked, as shown from the data in Fig. 9b. We observed that the KT-2//AC asymmetric faradaic SC offered superb cycling durability of 93.5% after the long-term cycling test. It is worth noticing that only a 6.5% capacitance fade was seen, proving its supreme stability. Not only that, a steady and stable cycling performance was revealed, suggesting the excellent integration of FeSe₂ and TiO₂ in a composite coupled with good structural integrity. Thus, these outstanding results evidence iron selenide's importance based on other nanomaterials for energy conversion and storage applications.



Fig. 9 (a) The Ragone plot (b) stability test data.



Table 6 Comparison of the electrochemical performance with other reported electrodes

| Electrode materials | Electrolytes | Voltage window (V) | Specific capacitance (F g ⁻¹) | Specific energy (Wh kg ⁻¹) | Specific power (W kg ⁻¹) | Cycling stability (%) |
|--|-------------------------------------|--------------------|---|--|--------------------------------------|-----------------------|
| GW-FeSe ₂ -FeSe ₂ -CSS ⁴² | 6 M KOH | 0–1.8 | 634.6 | 158.53 | 2236.16 | 91.7@5k |
| FeSe ₂ (ref. 50) | 0.5 M NaOH | 0–1.7 | 671.7 CV/434.6 GCD | 13.4 | 5.1k | 91.9@4k |
| FeS/RGO/FeS ⁶⁹ | 2 M KOH | 0–1.8 | 206.2 | 34.07 | 20k | 90@3k |
| Fe/N-BCNTs ⁷⁰ | PVA/H ₂ SO ₄ | — | 236 | 6.4 | 1990 | 97@10k |
| TiO ₂ /rGO ⁷¹ | 1 M Na ₂ SO ₄ | 0–1.8 | 51 | 6.2 | 6200 | 80@10k |
| Pani/Mn–TiO ₂ (ref. 72) | 2 M KOH | — | 635.87 | 18.6 | — | 91@5k |
| MnSe ₂ /rGO ⁷³ | 3 M KOH | 0–1.6 | 326.2 | 10 | 7200 | 99.4@10k |
| MnSe ₂ /CoSe ₂ (ref. 74) | 1 M KOH | 0–1.5 | 373 | 73 | 750 | 95.86@5k |
| CoSe ₂ (ref. 75) | 3 M KOH | 0–1.42 | 759.5 | 24 | 7354 | 78.8@5k |
| CuSe@TiO ₂ (ref. 76) | 3 M KOH | 0–1.8 | 370 | 31.5 | 4500 | 99@10k |
| MnSe ₂ /CoSe ₂ /rGO ⁷⁷ | 2 M KOH | 0–1.8 | 1138C g ⁻¹ | 45.8 | 853.1 | 98.5@5k |
| α-MnSe ⁷⁸ | 1 M Li ₂ SO ₄ | 0–0.8 | 96 | 8.60 | — | 103@2k |
| CuSe–TiO ₂ (ref. 41) | 3 M KOH | 2.2 | 40 | 11.4 | 7125.5 | 90@20k |
| KT-2 (FeSe ₂ –TiO ₂) (this work) | 3 M KOH | 2.3 | 789.2F g ⁻¹ | 69.79 | 11529 | 93.5@15k |

5. Conclusion

In summary, facile wet-chemical synthesis of FeSe₂/TiO₂ nanocomposite for advanced asymmetric faradaic SCs is reported for the first time. Two different composites were prepared with varying ratios of TiO₂ (10 and 40%) and investigated their electrochemical properties in two/three electrode cell. The FESEM, XRD, EDX, and mapping studies revealed that the structural and morphological properties exhibited high purity and crystallinity with hexagonal and tetragonal anatase crystal structure, and nanoparticle-like morphology of FeSe₂ with distinctive TiO₂ morphological features. The electrochemical properties showed fast redox reactions owing to Fe²⁺/Fe³⁺, while in TiO₂ due to Ti³⁺/Ti⁴⁺ with high reversibility and good redox activities. The KT-2 electrode realized supreme capacitive properties in three-electrode configurations in aqueous solutions with superior charge storage performance (high capacitance, fastest charge kinetics). The superlative capacitive performance turned our attention to utilizing the KT-2 electrode as the positive electrode to develop an asymmetric faradaic SC (KT-2//AC), additionally reflecting remarkable energy storage performance when adding a widened voltage of 2.3 V, enhancing the capacitance, specific energy, and power to 95 F g⁻¹, 69.79 Wh kg⁻¹, 11529 W kg⁻¹, respectively. Not only that, extremely outstanding durability was observed after long-term cycling, proving the promising prospect for high voltage faradaic SCs.

Conflicts of interest

The authors declare no conflict of interest.

References

- M. Z. U. Shah, M. Sajjad, H. Hou, S. ur Rahman, A. Mahmood, U. Aziz and A. Shah, *J. Energy Storage*, 2022, **5**, 105492.
- X. Zhao, Q. Ma, K. Tao and L. Han, *ACS Appl. Energy Mater.*, 2021, **4**, 4199–4207.
- P. Simon, Y. Gogotsi and B. Dunn, *Science*, 2014, **343**, 1210–1211.
- P. Simon and Y. Gogotsi, *Acc. Chem. Res.*, 2013, **46**, 1094–1103.
- J. Hu, J. Luo, Z. Xu, K. Xie, H. Yu, H. Wang, C. Shen, L.-h. Qi and B. Wei, *Appl. Phys. Rev.*, 2021, **8**, 011401.
- X. Li, C. Guan, Y. Hu and J. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 26008–26015.
- Q. Cao, H. Gao, Y. Gao, J. Yang, C. Li, J. Pu, J. Du, J. Yang, D. Cai and Z. Pan, *Adv. Funct. Mater.*, 2021, **31**, 2103922.
- X. Xu, C. Guan, L. Xu, Y. H. Tan, D. Zhang, Y. Wang, H. Zhang, D. J. Blackwood, J. Wang and M. Li, *ACS Nano*, 2019, **14**, 937–947.
- Z. Xue, C. Yang, K. Tao and L. Han, *Appl. Surf. Sci.*, 2022, **592**, 153231.
- M. Sajjad and W. Lu, *J. Energy Storage*, 2021, **44**, 103343.
- P. Simon and Y. Gogotsi, *Nat. Mater*, 2020, **19**, 1151–1163.
- F. Zhan, H. Wang, Q. He, W. Xu, J. Chen, X. Ren, H. Wang, S. Liu, M. Han and Y. Yamauchi, *Chem. Sci.*, 2022, 11981–12015.
- P. Simon and Y. Gogotsi, *Joule*, 2022, **6**, 28–30.
- J. Ismail, M. Sajjad, M. Z. U. Shah, R. Hussain, B. A. Khan, R. Maryam, A. Shah, A. Mahmood and S. ur Rahman, *Mater. Chem. Phys.*, 2022, 126059.
- L. Li, J. Gong, C. Liu, Y. Tian, M. Han, Q. Wang, X. Hong, Q. Ding, W. Zhu and J. Bao, *ACS Omega*, 2017, **2**, 1089–1096.
- I. Hussain, S. Sahoo, M. S. Sayed, M. Ahmad, M. S. Javed, C. Lamiel, Y. Li, J.-J. Shim, X. Ma and K. Zhang, *Coord. Chem. Rev.*, 2022, **458**, 214429.
- M. S. Javed, T. Najam, I. Hussain, S. S. A. Shah, S. Ibraheem, A. Mahmood, M. Imran, M. A. Assiri and S. H. Siyal, *Mater. Lett.*, 2021, **303**, 130478.
- M. S. Javed, T. Najim, I. Hussain, S. Batool, M. Idrees, A. Mehmood, M. Imran, M. A. Assiri, A. Ahmad and S. S. A. Shah, *Ceram. Int.*, 2021, **47**, 25152–25157.
- Y. Li, B. Huang, X. Zhao, Z. Luo, S. Liang, H. Qin and L. Chen, *J. Power Sources*, 2022, **527**, 231149.
- V. Vijayakumar, B. Anothumakkool and A. Torris, *J. Mater. Chem. A*, 2017, **5**, 8461–8476.



- 21 Z. Song, H. Duan, D. Zhu, Y. Lv, W. Xiong, T. Cao, L. Li, M. Liu and L. Gan, *J. Mater. Chem. A*, 2019, **7**, 15801–15811.
- 22 L. Mao, X. Zhao, Y. Li and L. Chen, *J. Colloid Interface Sci.*, 2022, **624**, 482–493.
- 23 J. Zhang, J. Sun, Y. Hu, D. Wang and Y. Cui, *J. Alloys Compd.*, 2019, **780**, 276–283.
- 24 S. Maiti, A. Pramanik, S. Chattopadhyay, G. De and S. Mahanty, *J. Colloid Interface Sci.*, 2016, **464**, 73–82.
- 25 M. Sajjad, Y. Khan and W. Lu, *J. Energy Storage.*, 2021, **35**, 102336.
- 26 B. Huang, H. Wang, S. Liang, H. Qin, Y. Li, Z. Luo, C. Zhao, L. Xie and L. Chen, *Energy Storage Mater.*, 2020, **32**, 105–114.
- 27 S. Tan, Z. Xue, K. Tao and L. Han, *ChemComm.*, 2022, **58**, 6243–6246.
- 28 M. Sajjad and Y. Khan, *CrystEngComm*, 2021, **23**, 2869–2879.
- 29 K. Krishnamoorthy, G. K. Veerasubramani, S. Radhakrishnan and S. J. Kim, *Chem. Eng. J.*, 2014, **251**, 116–122.
- 30 D. Sarkar, D. Das, S. Das, A. Kumar, S. Patil, K. K. Nanda, D. Sarma and A. Shukla, *ACS Energy Lett.*, 2019, **4**, 1602–1609.
- 31 R. BoopathiRaja, M. Parthibavarman, S. Prabhu and R. Ramesh, *Mater. Today: Proc.*, 2020, **26**, 3507–3513.
- 32 M. Z. U. Shah, M. Sajjad, H. Hou, S. ur Rahman and A. Shah, *J. Energy Storage.*, 2022, **55**, 105651.
- 33 S. S. Karade, P. Dwivedi, S. Majumder, B. Pandit and B. R. Sankapal, *Sustain. Energy Fuels*, 2017, **1**, 1366–1375.
- 34 N. Zhao, H. Fan, M. Zhang, J. Ma, W. Zhang, C. Wang, H. Li, X. Jiang and X. Cao, *Electrochim. Acta*, 2019, **321**, 134681.
- 35 G. Zhang, T. Wang, X. Yu, H. Zhang, H. Duan and B. Lu, *Nano Energy*, 2013, **2**, 586–594.
- 36 M. Sajjad, Y. Jiang, L. Guan, X. Chen, A. Iqbal, S. Zhang, Y. Ren, X. Zhou and Z. Liu, *Nanotechnology*, 2019, **31**, 045403.
- 37 M. Sajjad, M. Amin, M. S. Javed, M. Imran, W. Hu, Z. Mao and W. Lu, *J. Energy Storage.*, 2021, **43**, 103176.
- 38 M. Sajjad, J. Ismail, A. Shah, A. Mahmood, M. Z. U. Shah, S. ur Rahman and W. Lu, *J. Energy Storage.*, 2021, **44**, 103318.
- 39 M. Sajjad, Y. Khan and W. Lu, *J. Energy Storage*, 2021, **35**, 102336.
- 40 M. Z. U. Shah, M. S. Javed, M. Sajjad, A. Shah, M. S. Shah, S. ur Rahman, A. Mahmood, M. Ahmad, M. A. Assiri and H. Hou, *J. Sci.: Adv. Mater. Devices*, 2022, 100418.
- 41 M. Z. U. Shah, M. S. Javed, M. Sajjad, A. Shah, M. S. Shah, S. ur Rahman, A. Mahmood, M. Ahmad, M. A. Assiri and H. Hou, *J. Sci.: Adv. Mater. Devices*, 2022, **7**, 100418.
- 42 Y. Guan, Y. Feng, Y. Mu, H. Zhang and Y. Wang, *Electrochim. Acta*, 2017, **247**, 435–442.
- 43 J. H. Choi, S. K. Park and Y. C. Kang, *Small*, 2019, **15**, 1803043.
- 44 J. Yang, Y. Niu, J. Huang, L. Liu and X. Qian, *Electrochim. Acta*, 2020, **330**, 135333.
- 45 Z. Tian, Z. Zhao, X. Wang, Y. Chen, D. Li, Y. Linghu, Y. Wang and C. Wang, *Nanoscale*, 2021, **13**, 6489–6498.
- 46 C. Ji, F. Liu, L. Xu and S. Yang, *J. Mater. Chem. A*, 2017, **5**, 5568–5576.
- 47 S. A. Ahmad, M. Z. U. Shah, S. ur Rahman, M. Arif, J. Lu, T. Huang, A. Ahmad, A. A. Al-Kahtani, A. M. Tighezza and M. Sajjad, *J. Sci.: Adv. Mater. Devices*, 2022, **7**, 100489.
- 48 A. M. Zardkhoshoui, S. S. H. Davarani, M. M. Ashtiani and M. Sarparast, *J. Mater. Chem. A*, 2019, **7**, 10282–10292.
- 49 W. Shao, Q. Wang, C. Huang and D. Zhang, *Adv. Mater.*, 2022, **3**, 1816–1824.
- 50 B. Pandit, S. R. Rondiya, S. Shegokar, L. K. Bommineedi, R. W. Cross, N. Y. Dzade and B. R. Sankapal, *Sustain. Energy Fuels*, 2021, **5**, 5001–5012.
- 51 Z. Yang, J.-Y. Zhang, Z. Liu, Z. Li, L. Lv, X. Ao, Y. Tian, Y. Zhang, J. Jiang and C. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 40351–40359.
- 52 H. Lutz and B. Müller, *Phys Chem Miner.*, 1991, **18**, 265–268.
- 53 P. H. C. Camargo, K. G. Satyanarayana and F. Wypych, *Mater. Res.*, 2009, **12**, 1–39.
- 54 I. Hussain, S. Iqbal, T. Hussain, W. L. Cheung, S. A. Khan, J. Zhou, M. Ahmad, S. A. Khan, C. Lamiel and M. Imran, *Mater. Today Phys.*, 2022, **23**, 100655.
- 55 P. Bandyopadhyay, G. Saeed, N. H. Kim and J. H. Lee, *Chem. Eng. J.*, 2020, **384**, 123357.
- 56 Q. Abbas, A. Mateen, A. J. Khan, G. E. Eldesoky, A. Idrees, A. Ahmad, E. T. Eldin, H. T. Das, M. Sajjad and M. S. Javed, *Nanomaterials*, 2022, **12**, 3154.
- 57 S. BiBi, M. Z. U. Shah, M. Sajjad, H. Z. Shafi, B. Amin, M. A. Bajaber and A. Shah, *Electrochim. Acta*, 2022, **430**, 141031.
- 58 M. S. Javed, X. Zhang, S. Ali, A. Mateen, M. Idrees, M. Sajjad, S. Batool, A. Ahmad, M. Imran and T. Najam, *Nano Energy*, 2022, **101**, 107624.
- 59 M. Hamzeh and G. I. Sunahara, *Toxicol. in Vitro*, 2013, **27**, 864–873.
- 60 Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu and S. Yang, *Prog. Mater. Sci.*, 2014, **60**, 208–337.
- 61 I. Hussain, S. Sahoo, D. Mohapatra, M. Ahmad, S. Iqbal, M. S. Javed, S. Gu, N. Qin, C. Lamiel and K. Zhang, *Appl. Mater. Today*, 2022, **26**, 101297.
- 62 U. Amara, M. T. Mehran, B. Sarfaraz, K. Mahmood, A. Hayat, M. Nasir, S. Riaz and M. H. Nawaz, *Microchim. Acta*, 2021, **188**, 1–13.
- 63 U. Amara, K. Mahmood, M. Awais, M. Khalid, M. Nasir, S. Riaz, A. Hayat and M. H. Nawaz, *Dalton Trans.*, 2022, **51**, 5098–5107.
- 64 B.-C. Kim, K. Takada, N. Ohta, Y. Seino, L. Zhang, H. Wada and T. Sasaki, *Solid State Ionics*, 2005, **176**, 2383–2387.
- 65 C.-H. Wang, H.-C. Hsu and J.-H. Hu, *J. Power Sources*, 2014, **249**, 1–8.
- 66 K. Akbar, J. H. Jeon, M. Kim, J. Jeong, Y. Yi and S.-H. Chun, *ACS Sustainable Chem. Eng.*, 2018, **6**, 7735–7742.
- 67 D. J. Ahirrao, H. M. Wilson and N. Jha, *Appl. Surf. Sci.*, 2019, **491**, 765–778.
- 68 P. Pazhamalai, K. Krishnamoorthy, S. Sahoo and S.-J. Kim, *J. Alloys Compd.*, 2018, **765**, 1041–1048.
- 69 X. Shao, Z. Zhu, C. Zhao, C. Zhao and X. Qian, *Inorg. Chem. Front.*, 2018, **5**, 1912–1922.
- 70 R. C. Shende, M. Muruganathan, H. Mizuta, M. Akabori and R. Sundara, *ACS Omega*, 2018, **3**, 17276.
- 71 V. H. Pham, T.-D. Nguyen-Phan, X. Tong, B. Rajagopalan, J. S. Chung and J. H. Dickerson, *Carbon*, 2018, **126**, 135–144.
- 72 M. B. Poudel, C. Yu and H. J. Kim, *Catalysts*, 2020, **10**, 546.



- 73 M. Sajjad, J. Ismail, A. Shah, A. Mahmood, M. Z. U. Shah, S. ur Rahman and W. Lu, *J. Energy Storage*, 2021, **44**, 103318.
- 74 M. S. Vidhya, R. Yuvakkumar, G. Ravi, E. S. Babu, B. Saravanakumar, O. Nasif, S. A. Alharbi and D. Velauthapillai, *Ceram. Int.*, 2021, **47**, 11786–11792.
- 75 T. Chen, S. Li, J. Wen, P. Gui, Y. Guo, C. Guan, J. Liu and G. Fang, *Small*, 2018, **14**, 1700979.
- 76 M. Sajjad, M. Z. U. Shah, M. S. Javed, M. S. Shah, A. Shah, W. Lu and Z. Mao, *J. Energy Storage.*, 2022, **55**, 105304.
- 77 H. Xuan, G. Zhang, X. Han, R. Wang, X. Liang, Y. Li and P. Han, *J. Alloys Compd.*, 2021, **863**, 158751.
- 78 S. Sahoo, P. Pazhamalai, K. Krishnamoorthy and S.-J. Kim, *J. Alloys Compd.*, 2018, **268**, 403–410.

