Facile synthesis of novel SrO$_{0.5}$:MnO$_{0.5}$ bimetallic oxide nanostructure as a high-performance electrode material for supercapacitors

Vinayak Adimule$^1$, Vinay S Bhat$^2$, Basappa C Yallur$^3$, Adarsha HJ Gowda$^4$, Paola De Padova$^{5,6}$, Gurumurthy Hegde$^{7,10}$ and Arafat Toghan$^{8,9}$

Abstract
Perovskite bimetallic oxides as electrode material blends can be an appropriate method to enhance the supercapacitor properties. In the present research, SrO$_{0.5}$:MnO$_{0.5}$ nanostructures (NS) were synthesized by a facile co-precipitation method and calcinated at 750–800°C. Crystal structure of SrO$_{0.5}$:MnO$_{0.5}$ NS were characterized by X-ray diffraction, surface chemical composition and chemical bond analysis, and dispersion of SrO into MnO was confirmed by X-ray photoelectron spectral studies. Structural morphology was analyzed from scanning electron microscopy. Optical properties of SrO$_{0.5}$:MnO$_{0.5}$ NS were studied using UV-Visible spectrophotometer and SrO$_{0.5}$ and MnO$_{0.5}$ NS showed $\sim$75 nm grain, $\sim$64 nm grain boundary distance, with two maxima at 261 nm and 345 nm as intensity of absorption patterns, respectively. The synthesized SrO$_{0.5}$:MnO$_{0.5}$ NS exhibited high specific capacitance of 392.8 F/g at a current density of 0.1 A/g. Electrochemical impedance spectroscopy results indicated low resistance and very low time constant of 0.2 s $\sim$73% of the capacitance was retained after 1000 galvanostatic charge-discharge (GCD) cycles. These findings indicate that SrO$_{0.5}$:MnO$_{0.5}$ bimetallic oxide material could be a promising electrode material for electrochemical energy storage systems.

Keywords
Nanostructures, SrO$_{0.5}$, MnO$_{0.5}$, co-precipitation, supercapacitor, energy storage, electrochemical, bimetallic

Date received: 19 May 2021; accepted: 15 November 2021

1Angadi Institute of Technology and Management (AITM), Belagavi, India
2Centre for Nano-Materials & Displays, B.M.S. College of Engineering, Bangalore, India
3Ramaiah Institute of Technology, Bangalore, India
4Centre for Research in Medical Devices, National University of Ireland, Galway, Ireland
5Istituto di Struttura della Materia-CNR (ISM-CNR), Rome, Italy
6INFN-LNF, Frascati (Roma), Italy
7Department of Chemistry, Christ (Deemed to be University), Bengaluru, India
8Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt
9Department of Chemistry, College of Science, Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Saudi Arabia
10Centre for Advanced Research and Development (CARD), Christ (Deemed to be University), Bengaluru, India

Corresponding authors:
Vinayak Adimule, Department of Chemistry, Angadi Institute of Technology and Management, Savagaon Road, Belagavi 590009, Karnataka, India.
Email: adimulevinayak@yahoo.in
Gurumurthy Hegde, Department of Chemistry, Christ University, Hosur Road, Bangalore 560029, India.
Email: murthyhegde@gmail.com

Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (https://creativecommons.org/licenses/by/4.0/) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en-us/nam/open-access-at-sage).
Introduction

In recent years, transition metal oxide nanomaterials like TiO₂, MnO₂, V₂O₅ and SrO have attracted research interest as electrode materials due to their stability, tunable material properties and higher energy storage densities than traditional carbon-based electrodes. Different forms of manganese oxides have been vastly researched for its role as electrode material in sensors, batteries and electrolysis, owing to its catalytically active surfaces. The wide spread applications of MnO₂ nanomaterial for energy storage and conversion is due to its theoretical capacity (~300 mA/g), low cost, low toxicity and abundance. MnO₂ possesses polymorphisms and exists in various morphologies due to edge sharing or corner sharing of MnO₆ octahedral units. Consequently, the properties of MnO₂ are also strongly dependent on morphology, crystal structure and particle size. However, electrodes prepared using single metal oxides (MO) have shown poor cyclical stability and low conductivity. Hence, synthesis of binary metal oxides and metal oxide composites has gained attraction for their use in energy storage systems. Recently, Sr-based bimetal oxides (Sr, Mₓ) have been vastly researched for its role as electrode materials due to their stability, tunable material properties and higher energy storage densities than traditional carbon-based electrodes. Different forms of manganese oxides have been vastly researched for its role as electrode material in sensors, batteries and electrolysis, owing to its catalytically active surfaces. The wide spread applications of MnO₂ nanomaterial for energy storage and conversion is due to its theoretical capacity (~300 mA/g), low cost, low toxicity and abundance. MnO₂ possesses polymorphisms and exists in various morphologies due to edge sharing or corner sharing of MnO₆ octahedral units. Consequently, the properties of MnO₂ are also strongly dependent on morphology, crystal structure and particle size. However, electrodes prepared using single metal oxides (MO) have shown poor cyclical stability and low conductivity. Hence, synthesis of binary metal oxides and metal oxide composites has gained attraction for their use in energy storage systems.

Materials and methods

All the chemicals and reagents purchased from Sigma Aldrich, Alfa Assar and Super capacitor ltd and used without any further purification. Crystallinity and doping of the SrO to MnO have been identified by X-ray diffractometer instrument made by Rigaku MiniFlex 600 with power of 600 W, tube voltage of 40 kV with 600 W X-ray tube, D/teX Ultra silicon strip detector accepting unusual samples having power requirement of 1Ø, 100–240 V 50/60 Hz. Chemical compositional analysis, chemical and electronic states of the bimetallic oxides and exact doping of the bimetallic oxides were measured by using XPS having auger electron spectroscopy instrument with PHI 5000 versus probe II, with Ar ion as well as C60 sputter Guns. Versa Probe chemical state maps are created by scanning the X-ray beam pixel by pixel over the defined area. The dimensions of the mapped area, pixel density and spot size are user adjustable. UV-visible spectroscopy was performed by using instrument by Analytik Jena (An Endress and Hauser Company). Optical properties were recorded using SPECORD 210 PLUS Analytik Jena with variable spectral resolution and cooled double beam detection was incorporated for UV-Visible absorption spectrum. Morphology, grain size distribution and size of the nanoparticles were investigated by using instrument by Nova Nano SEM 230 (5.0 mm AWD with 35° cut off angle) equipped with 5 X to 1,000,000 X HR/UHR mode, high sensitivity, low kV directional backscattered detector and fitted with quadrant semiconductor diode.

Synthesis of SrOₐ: MnOₐ nanostructures

In order to synthesize the nanostructures of SrOₐ: MnOₐ bimetallic oxides, Mn (SO)₄·6H₂O (0.5 M wt. ratio) was dissolved in deionized water and stirred for ~3 h, with addition of TEA (triethanol amine) (1 mL) and CTAB (cetyl trimethyl ammonium bromide) (200 mg). A brown precipitate of MnO was obtained (Reaction (1)) upon adding NH₄OH solution drop wise, which was transferred to another round bottom flask containing SrCl₂·6H₂O (0.5 M wt. ratio) dissolved in 20 mL of deionised water and N₂H₄ (2 mL) which was stirred for 5 h at 80°C. The reaction mixture (RM) was maintained at pH ~11 (alkaline) warmed in a water bath at temperature of 80°C with continuous magnetic stirring for 2 h. The RM was cooled subsequently the precipitated (brown coloured) SrOₐ: MnOₐ NS were filtered, washed with cold water and ethanol was used to remove surface bound impurities, and then the RM was dried at 100–200°C, calcinated at 700–800°C and grounded as fine powder. Schematic illustration of the preparation is shown in Figure 1.
Reactions.

\[
\text{Mn}(\text{SO}_4)_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{MnO}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \quad (1)
\]

\[
\text{SrCl}_2(\text{s}) + \text{N}_2\text{H}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SrO}(\text{s}) + 2\text{HCl}(\text{l}) \\
+ \text{N}_2(\text{g}) + \text{H}_2(\text{g}) \quad (2)
\]

Electrochemical studies

All the electrochemical studies of the synthesized SrO$_{0.5}$:MnO$_{0.5}$ were assessed using AUTOLAB M204 (The Netherlands) in three electrode setups. The working electrode was prepared by mixing 90 wt. % of the active material (SrO$_{0.5}$:MnO$_{0.5}$), 5 wt. % black carbon and 5 wt. % polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) as solvent, followed by drying on a Ni foam current collector (1 × 1 cm$^2$ area) at 100°C overnight. The mass loading of the prepared electrode was ~7 mg. A Pt rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively, using 6.0 M KOH solution as the electrolyte. Cyclic voltammetric (CV) tests were done at potential range of −1 V to 0 at different scan rates (10, 25, 50, 75 and 100 mV/s). Galvanostatic charge-discharge (GCD) tests were done at the same potential window at different current densities (0.15, 0.25, 0.5, 0.75, 1.0 and 2.0 A/g). Specific capacitance ($C_s$) of the electrode from GCD curves were calculated by equation (3) reported in earlier works,\textsuperscript{18,19}

\[
C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (3)
\]

Where, I is the discharge current, $\Delta t$ is the discharge time, $\Delta V$ is the potential window and m represents mass of the active material. Electrochemical impedance spectroscopy was measured in the frequency region of $10^{-2}$ Hz–$10^5$ Hz in an open potential circuit with AC amplitude voltage of 5 mV. Real ($C'$) and imaginary ($C''$) capacitances were calculated from the complex impedance using the equations (4) and (5)\textsuperscript{20}

\[
C' = \frac{-Z''}{\omega |Z|^2} \quad (4)
\]

\[
C'' = \frac{-Z'}{\omega |Z|^2} \quad (5)
\]

where, $Z''$ and $Z'$ represent imaginary and real part of the complex impedance $Z$ at $\omega (\omega = 1/(2\pi f))$, where f is the applied frequency.

Results and discussion

Optical behaviour

The bimetallic oxides of SrO$_{0.5}$:MnO$_{0.5}$ NPs recorded with UV-Visible spectra (optical absorption) were in powdered form in order to investigate NPs optical behaviour (absorptivity, band gap and NPs interaction with photons).
SrO$_{0.5}$:MnO$_{0.5}$ NPs exhibited absorptivity from near to far UV when exposed to the radiation source of 100 nm–1000 nm. UV-Visible spectrum of SrO$_{0.5}$:MnO$_{0.5}$ NPs showed absorptivity at two different regions in the UV-Visible spectrum having sharp absorption wavelength of 261 nm and 345 nm, respectively, (maxima 1 and maxima 2, respectively) as shown in the Figure 2 and this was attributed to the presence of SrO and MnO NPs. Maximum and minimum absorptivity region of the bare SrO NPs and MnO NPs are summarized in Table 1. Recent studies on the SrBi$_2$B$_2$O$_7$ nanocrystals coated over glass substrate revealed sharp optical absorptivity ranging from 400–500 nm (UV–Visible region). Nanomaterials of Sr-doped SnO$_2$ exhibited absorption edge of 350 nm and 370 nm, respectively, and Sr$^{2+}$ ions incorporated into SnO$_2$ NS provided additional energy levels between the conduction and valence band. Increase in the Sr$^{2+}$ impurity decreases the band gap of SrO/SnO$_2$ NS. The red shift in the absorptivity at two different regions in the UV-Visible spectrum is due to the presence of bimetallic oxide of Sr and Mn densely agglomerated into the crystal structure. The NPs of SrO$_{0.5}$:MnO$_{0.5}$ possesses interaction with near UV and far UV energized photons indicating the increased optical activity and absorption of photons of lower wavelength (higher energy). No intense peaks were observed in the visible region of the spectrum. However, optical absorptivity of the SrO quantum dots shows sharp edge at 203 nm confirming the presence of indirect band gap (6.1 eV) and also reported that SrO quantum dots are defect-free in nature. Absorptive wavelengths and band gap of SrO$_{0.5}$:MnO$_{0.5}$ NPs were calculated using the formula $h\gamma = A (h\gamma - E_g)^2$, where, $A$ is the absorptivity constant, $\gamma$ the frequency of the source radiation and $E_g$ is the optical gap of nanomaterials.

**Elemental compositional analysis of SrO$_{0.5}$:MnO$_{0.5}$ NPs**

Purity of NPs and chemical composition are the two main important parameters to be investigated before NPs are deployed for application. NPs of SrO$_{0.5}$:MnO$_{0.5}$ were obtained by co-precipitation method and subsequent reduction during the conversion from bulk to nanoparticles, where the solvent and solution react to form metal oxide semiconductor nanoparticles (MOS NPs). The SrO$_{0.5}$:MnO$_{0.5}$ NPs populated in the crystal structure and their composition can be understood with the elemental compositional analysis by XPS. Table 2 shows the percentage composition of various elements present in SrO$_{0.5}$:MnO$_{0.5}$ nanostructures.

**Crystallinity**

Crystallinity of the SrO$_{0.5}$:MnO$_{0.5}$ NPs was examined by XRD analysis with radiation from Cu-K alpha at $\lambda = 1.5406$ Å. X-Ray diffraction patterns were recorded over a range of 20 from 20 to 90° (Figure 3). Peaks observed around 29.97°, 31.8°, 32.8°, 33.6°, 38.38° and 40.0° can be attributed to MnO diffraction peaks of (222), (201), (111), (211) planes which have grater similarity to JCPDS file number 04-0326 corresponding to Mn$_3$O$_4$ with lattice constants a = 0.576 and b = 0.976. Diffraction peaks centred at 43.52°, 45.7°, 47.78°, 48.76°, 49.75°, 50.5° and 58.28° corresponds to planes (011), (112), (201), (011), (221) of SrO. The obtained 2θ values match well with the JCPDS file number 00-006-0520 for SrO.xH$_2$O as well as JCPDS file number of 00-019-1276 of SrCO$_3$. However, NPs of Mn$_3$O$_4$ with tetragonal crystal structure reported dramatic change in the decomposition behaviour under the reaction conditions. Change in the reaction temperature results in the variation of MnO NPs size. The conversion of hexagonal square and cross-shaped MnO NPs mixed with Mn$_3$O$_4$ and XRD lattice patterns confirms (Figure 3) the

![Image](62x208 to 277x371)

**Figure 2.** UV-Visible spectra of SrO$_{0.5}$:MnO$_{0.5}$ NPs recorded as powder sample.

| Nano structures | $\lambda_{\text{max}}^1$ (nm) | $\lambda_{\text{max}}^2$ (nm) | $\lambda_{\text{min}}$ (nm) | Absorptivity region |
|-----------------|-----------------|-----------------|-----------------|------------------|
| MnO             | 370             | —               | 300              | Ultraviolet      |
| SrO             | 330             | —               | 280              | Ultraviolet      |
| SrO$_{0.5}$:MnO$_{0.5}$ | 261             | 345             | —               | Ultraviolet      |

**Table 1.** Comparative UV-Visible spectrophotometer data of the bare SrO, MnO and SrO$_{0.5}$:MnO$_{0.5}$ NS
retention of size and shape of the NPs under applied conditions.\textsuperscript{25,26} By using the Scherrer equation (6)

\[ D = \frac{0.9λ}{β \cos θ} \]

where \( λ \) is the wavelength of the X-ray radiation (1.5418 Å) and \( β \) is the full width at half maximum (FWHM) of the peak at diffraction angle \( θ \), a total of 14 diffraction peaks of the NPs were obtained, and the crystal nature that has been estimated from the intense peak of SrO\(_0.5\):MnO\(_0.5\) with (011), (111), (201), (112) diffraction planes and average crystallinity were found to be 55 nm. The XRD reflection peaks of SrO (011), (112), (112), (201), (011), (221) and MnO (222), (201) (201), (111), (211) confirms core shell configuration of synthesized NPs which indicates the orthorhombic crystal structure (agglomerated). These observations confirm that flake kind of NPs of SrO:MnO NPs as shown in Figure 4. Comparison of the XRD patterns, crystal structure of the SrO:MnO NPs are summarized in the Table 2. SrO NPs reported in earlier works suggest trigonal crystal structure and the tetragonal crystal shape for MnO NPs.\textsuperscript{27,28} Furthermore, MnO NPs when dispersed onto graphene nanosheets (GNs), MnO NPs were found to act as nanoscale spacers increasing the spacing between adjacent C-atoms in the hybrid NS\textsuperscript{29} which was confirmed by the shift in the diffraction peaks and formation of crystalline MnO NPs over outer surface of GNs.

![XRD Spectrum of SrO\(_0.5\):MnO\(_0.5\) NPs](image.png)

**Figure 3.** X-ray powder diffraction patterns of SrO\(_0.5\):MnO\(_0.5\) nanostructures.

| Sample            | SrO (%) | MnO (%) | Na (%) | O (%) | K (%) | Purity (%) |
|-------------------|---------|---------|--------|-------|-------|------------|
| MnO NPs           | 0.05    | 95.8    | 1.02   | 1.8   | 0.2   | 95.85      |
| SrO NPs           | 94.7    | 0.08    | 1.12   | 1.67  | 0.11  | 94.7       |
| SrO\(_0.5\):MnO\(_0.5\) NPs | 46.94  | 50.12   | 0.68   | 1.64  | 0.21  | 97.06      |

**Table 2.** Elemental compositional analysis of bare SrO, MnO and SrO: MnO NS.

TiO\(_2\) when, loaded with SrO NPs exhibited same crystal size and shape during the anodization process.\textsuperscript{30} Crystallographic structure of the SrO-decorated graphene oxide (GO) NS showed monoclinic structure with the absence of impurities like Sr\(_2\)O or SrO(OH)\(_2\).\textsuperscript{31} Whereas, binary composites of SrO/PANI crystallographic morphology indicates well incorporation of SrO nanorods\textsuperscript{32} with JCPDS for SrO file No 01-075-0263. The authors demonstrated in the present work, flake-like structure of NPs with particle agglomeration and orthorhombic structure of the synthesized SrO:MnO NPs. Table 3 summarizes the corresponding planes, peak values, ratio and the reflection peaks. Data obtained from XRD patterns suggest that complete dispersion of SrO and MnO into the orthorhombic crystal phase and the orthorhombic crystal sample produce sharp diffraction peaks with the plane orientation of intense peaks of (111), (201) corresponds to MnO and (011), (112) peaks for SrO, respectively.

The XRD patterns also indicate the dispersion of SrO into MnO-layered solid successfully with no additional peaks. Unit cell volume, Sr-Mn bond distance, length, bond energy, \( α \) parameters, SrO:MnO crystal size (\( D \)) were calculated by Debye–Scherer’s formula. \( D = \frac{Kλ}{β \cos θ} \), where \( K \) is dimensionless shape factor, \( λ \) X-ray wavelength, \( β \) full width half maximum intensity (FWHM) and \( θ \) is Bragg angle. The decrease in the interplanar distance was observed which is due to decrease in the unit cell volume as a result of the introduction of SrO into the MnO nanostructures.\textsuperscript{31,32}

**Morphological characterization**

**Scanning electron microscopy.** Surface morphology of the synthesized SrO\(_{0.5}\):MnO\(_{0.5}\) NPs has been investigated by SEM techniques. SEM images of SrO\(_{0.5}\):MnO\(_{0.5}\) NS with different magnifications as shown in the Figure 4(a)–(d). The corresponding energy dispersive xrays (EDX) image with selected area and compositional spectrum presented in Figure 5. A vertically grown flake-like morphology of SrO and MnO NPs can be seen with proper orientation and distribution. The high density of NPs of SrO\(_{0.5}\):MnO\(_{0.5}\) having size of \( \sim 75 \) nm, grain diameter of \( \sim 80 \) nm, distance of \( \sim 95 \) nm and \( \sim 30 \) µm in length were observed. Morphology and distribution of the SrMnO\(_3\) NPs depend on different preparation approaches such as co-precipitation, hydrothermal and microwave irradiation. In most of the cases, NS does not form recognisable structure with agglomeration. Further, crystal structure of Sr
and Mn containing La composites (La$_{0.7}$Sr$_{0.3}$Mn$_{0.65}$Fe$_{0.35}$O$_3$) exhibited rhombohedral structure.\textsuperscript{33,34} Nanocrystals of La$_{0.7}$Sr$_{0.3}$MnO$_3$ showed homogeneous dispersion of Sr and MnO$_3$ NPs.\textsuperscript{35} SEM micrographs and cross-sectional micrographs of Ba$_{0.5}$Sr$_{0.5}$Zn$_2$Si$_2$O$_7$ studied under different conditions of heat treatment which are observed with several backscattered cracks in the crystal structure.\textsuperscript{36} SEM images of ultrathin MnO$_2$ coated graphene oxide NS improves

**Figure 4.** Scanning electron microscopy images of the SrO$_{0.5}$:MnO$_{0.5}$ (top view) of NPs recorded at different distances (a) at 2 µm (b) 10 µm (c) 4 µm (d) 20 µm.

**Table 3.** XRD spectral diffraction patterns of SrO$_{0.5}$:MnO$_{0.5}$ NS

| Nanostructures of the crystal (Scherer method) | Morphology index (MI) (unitless) | Relative texture coefficient (Tc) | FWHM (°) | Lattice parameter (nm) | Crystallite size (D) (nm) |
|------------------------------------------------|---------------------------------|---------------------------------|----------|-----------------------|--------------------------|
| SrO$_{0.5}$:MnO$_{0.5}$                        | 1.124                           | 0.985                           | 0.186    | 0.576                 | 55                       |

**Figure 5.** (a) Scanning electron microscopy selected area to analyse the composition of SrO$_{0.5}$:MnO$_{0.5}$ NPs (b) SEM EDX compositional analysis with Sr$_{0.5}$ and Mn$_{0.5}$ nanoparticles.
electrochemical performance by occupying the porous network and homogeneous dispersion over the graphene oxide (GO) nanosheets. Pure SrO reported in the literature with average grain size of \(~\text{65 nm}\), grain boundary distance varies from \(~\text{40 nm}\) to \(~\text{80 nm}\) and grain distance of \(~\text{55 nm}\)–\(~\text{75 nm}\) whereas, MnO NPs has grain diameter of \(~\text{60 nm}\), particle size varies in between \(~\text{45 nm}\) to \(~\text{70 nm}\). Overall, from top view of the SEM images it can be concluded that orthorhombic SrO:MnO structure forms with more agglomeration of the NPs in the nanomatrix. EDX composition (atomic weight ratio and net ratio) of different metal oxides present in the NS is summarized in Table 4.

**Cross section morphologies of SrO\(_{0.5}\):MnO\(_{0.5}\) NPs.** Typical SEM backscatter images of samples are shown in Figure 6. Images in Figure 6(a) (20 \(\mu\text{m}\)), Figure 6(b) (4 \(\mu\text{m}\)), Figure 6(c) (10 \(\mu\text{m}\)) and Figure 6(d) (20 \(\mu\text{m}\)) clearly show nanoflake-like structures with thickness varying from \(~\text{30 nm}\) to \(~\text{80 nm}\). Cross-sectional images also depicted the width and thickness of NPs. The magnified SEM cross-sectional images of SrO\(_{0.5}\):MnO\(_{0.5}\) showed particle distribution between \(~\text{30 nm}\) to \(~\text{75 nm}\) as observed in Supplemental Figure S2 and S3, respectively and EDX composition of SrO: MnO NPs is summarized in Supplemental Table S1, S2 and S3 and their spectrum shown in Supplemental Figure S5, S6 and S7, respectively. The magnified images showed highly entangled SrO\(_{0.5}\):MnO\(_{0.5}\) NPs as shown in Figure 6. The NPs of SrO\(_{0.5}\):MnO\(_{0.5}\) SEM images show nanoflake-like compact deposited on the surface as shown in Figure 6. Each nanoflake connected with each other neighbouring flakes having \(~\text{110 nm}\) in diameter with \(~\text{30–40 nm}\) thickness. High agglomeration of the dispersed NPs observed for hydroxypatite on surface of SiO\(_2\)-P\(_2\text{O}_5\)-CaO-SrO-ZnO as compared with other apatite and dispersed phase was spherical in nature. The cross-sectional SEM images also exhibited nanoflakes dominantly coated over the particle surface, the compositional table comprising K ratio, Z, A, F values of SrO and MnO NS as depicted in Table 4 also comprises the EDAX compositional analysis of the SrO\(_{0.5}\):MnO\(_{0.5}\) nanostructures. The EDAX composition of top view of the SrO\(_{0.5}\):MnO\(_{0.5}\) nanostructures analysed with different areas as shown in Figure 5(a) and (b) and Supplemental Figure S3 respectively (supplementary). Studies related to the insertion of MnO NPs inside porous C-nanotubes (CNT) observed under low amplification in which MnO NPs occupied in the void space of CNT networks, separated NPs of MnO having diameter of \(~\text{15–25 nm}\) and they get expanded during charge and discharge cycles. The assimilation of NPs of SrO \(_{0.5}\):

### Table 4. EDX compositions of SrO\(_{0.5}\):MnO\(_{0.5}\) NS

| Element | Atomic (%) |
|---------|------------|
| Mg      | 1.40       |
| Sr      | 26.38      |
| K       | 3.34       |
| Mn      | 65.14      |
| Fe      | 1.18       |
| Co      | 2.56       |

**Figure 6.** Cross sectional scanning electron microscopy images of low- and high-resolution flake like SrO\(_{0.5}\):MnO\(_{0.5}\) nanostructures recorded at different distances (a) 20 \(\mu\text{m}\) (b) 4 \(\mu\text{m}\) (c) 10 \(\mu\text{m}\) and (d) 20 \(\mu\text{m}\) respectively.
MnO$_{0.5}$ on a coated surface is due to reaction inside the particles and is limited to the small cavity among NS with interplanar distance of 0.251 nm.

### Surface chemistry

The chemical states and elemental composition of synthesized SrO$_{0.5}$:MnO$_{0.5}$ NCs has been studied using XPS (X-ray photoelectron spectroscopy) analysis. The selected XPS results obtained are depicted in the Figure 7 (see Figure S1 for the overview XPS spectrum). XPS spectra of O1s, Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, Sr 3d$_{5/2}$ and Sr 3d$_{3/2}$, and C1s core levels are shown in Figure 7(a), 7(b), 7(c) and 7(d) respectively, measured binding energies (B.E) summarized in Table 5. The core levels were convoluted using a simple Gaussian function (just to reveal the curves centroid), giving energy peak located at 530.1 eV for O1s; 641.3 eV, 653.2 eV for Mn 2p$_{3/2}$, Mn 2p$_{1/2}$ spin-orbit doublet; 134.2 eV, 135.7 eV for Sr 3d$_{5/2}$, Sr 3d$_{3/2}$ spin-orbit doublet; and finally the main C1s component, related to hydrocarbon air contaminant, was found at 284.6 eV. Interestingly, these binding energy values can be attributed to O1s, Mn2p, and Sr3d core levels from MnO and SrO oxides, in nearly agreement with binding energies found for Li$_2$MnO$_3$ NPs, N-doped/C-coated MnO NPs, TiO$_2$ NPs dispersed in SrO, ZnO doped SrO nanocomposites, whereas the presence of small carbon peak at higher BE results from C-O bonding. These results provided direct evidence of our SrO$_{0.5}$:MnO$_{0.5}$ NPs synthesized sample like similar formation in the core shell via co-precipitation and reduction processes.

### Electrochemical analysis of SrO$_{0.5}$:MnO$_{0.5}$

To investigate the electrochemical performance of the synthesized SrO$_{0.5}$:MnO$_{0.5}$ electrode, electrochemical analysis like, CV, GCD and EIS were conducted in 6.0 M KOH. CV analysis was carried out in potential range of −1 to 0 V at different scan rates ranging from 10 to 100 mV s$^{-1}$. Since aqueous KOH electrolyte was used, maximum working potential for the electrode was restricted to 1.0 V (V vs SCE). Supplemental Figure S8 compares the CV curves at 10 mV/s for Ni foam and synthesized SrO$_{0.5}$:MnO$_{0.5}$ electrode. From the figure it is clear that, the substrate contribution is insignificantly small towards electrochemical performance of the electrode. CV curves of SrO$_{0.5}$:MnO$_{0.5}$ NPs electrode at different scan rate is shown in Figure 8(a). The presence of well-defined peaks at all scan rates establishes that the charge storage of the electrode could be from the pseudocapacitive charge storage process indicating presence of faradaic charge transfer. The area under the CV curve represents total charge stored. As the scan rate was increased, the area of the CV curve also increased, indicating higher charge storage capability and good reversibility of the electrode. Anodic peak around −0.48 V and cathodic peak around −0.59 V mainly because of reversible faradaic reactions of active material and electrolyte. Anodic and cathodic peaks show positive and negative shifts respectively, as the scan rate was increased, due to electrode polarization and internal resistance of
the electrode. In CV, pseudocapacitive material would be characterized by a broad charge transfer peaks which are mirror images of each other during cathodic and anodic scans. However, as can be seen from Figure 8(a) sweep rate, the peak position/potential changes. The anodic peak potential shifts to right and cathodic peak potential shifts towards left slightly. This makes the distinction between pseudocapacitive and ‘battery type’ process blurred. In nanostructured materials, redox sites remain at interface between electrode and electrolyte. At the interface, the geometry of such sites is expected to be more dispersed than in bulk. This leads to capacitor-like electrochemical response. Figure 8(b) shows plot of anodic and cathodic peak currents as function of scan rates for the prepared material. For both $i_{pa}$ and $i_{pc}$ straight line can be observed, indicating a diffusion controlled kinetics. Furthermore, from CV curves, a mathematical relationship between current response ($i$) scan rate ($ν$) can be represented from following equations

$$i_p = aν^b$$

$$\log i_p = \log a + b \log ν$$

where, $a$ and $b$ are adjustable parameters. The slope obtained from a linear relationship between $\log i/p/s$ $\log ν$ yields ‘b’ value which can be used to mathematically signify the charge storage mechanism involved. If the current response is proportional to sweep rate (i.e. $b = 1$), the electrochemical process is believed to be mainly capacitive. If the measured current response is proportional to the square root of scan rate (i.e. $b \leq 0.5$), the process is mainly diffusion controlled faradaic in nature. From equation (6), we calculated the value of ‘b’ considering cathodic current peak with sweep rate ($\log i/v/s \log ν$) plot as depicted in Figure 8(c). The value of ‘b’ found to be 0.33 ($R^2 = 0.98$), denoting that, charge storage was achieved through diffusion controlled Faradaic mechanism. Specific capacitance was calculated from CV curves using the following equation

$$C = \frac{\int_1^0 \Sigma dν}{2 × ν × m × ΔV}$$

The capacitance plotted as function of scan rate is shown in Figure 8(c). Maximum of 180.3 F/g at 10 mV/s was calculated.

The faradaic charge storage mechanism could be due to different reactions at electrode–electrolyte interface. One could be due to intercalation of alkali metal cations ($C^+$), like $K^+$ during reduction and oxidation in electrode

$$SrO_{0.5} : MnO_{0.5} + C^+ + e^- ⇄ SrO_{0.5} : MnO_{0.5}C^+$$

Another possibility could be that cations be adsorbed onto the $SrO_{0.5} : MnO_{0.5}$ electrode surface.
Another possibility is from the redox reaction of the active material itself. The following reactions could be the redox reactions responsible for redox peaks in CV plot. (There are no previous reports available on SrO$_{0.5}$:MnO$_{0.5}$ type bimetallics for supercapacitor applications)

\[
\text{(SrO}_{0.5}\text{:MnO}_{0.5})_{\text{Surface}} + C^+ + e^- \rightleftharpoons [(\text{SrO}_{0.5}\text{:MnO}_{0.5}) - C^+]_{\text{Surface}} \tag{11}
\]

Further electrochemical analysis of the electrode was carried out from GCD tests. Figure 8(d) shows the GCD curves of the electrode at \(-1.0\) to \(0\) V under differing current densities from \(0.15\) A g$^{-1}$ to \(2.0\) A g$^{-1}$. The shape is non-linear with plateaus of nearly constant potential at lower current densities before dropping to linear, suggesting pseudocapacitor behaviour with faradaic charge transfer. At higher current densities, shape is still non-linear but also without any plateau of constant potential (The inset in Figure 8(e)). Specific capacitances were calculated from discharge curves for using formula reported in previous literature for materials with pseudocapacitor behaviour$^{54,55}$ The electrode material exhibited a high specific capacitance of \(392.8\) F g$^{-1}$ at \(0.15\) A g$^{-1}$. The variation of specific capacitance over current density is plotted (Figure 8(f)).

Electrochemical impedance spectroscopy analysis is an effective way to study the fundamental nature of the electrode material. The EIS can be represented by two forms: Nyquist plot and Bode plot. The Nyquist plot obtained from impedance spectroscopy is presented in Figure 9(a). The electrode exhibited a very low equivalent series resistance, \(R_S\) of \(0.48\) Ω, which is the combination of ionic resistance, resistance from substrate and contact resistance between the active material and current collector; obtained from the intersection of \(x\)-axis of the Nyquist plot. Charge transfer resistance, \(R_{CT}\) was found to
be 0.63 Ω obtained from the diameter of the semicircle at high frequency region. Presence of charge transfer suggests the presence of Faradaic mechanism of charge storage.56 The inset in Figure 9(a) depicts the high frequency region. The incomplete not so well formed semicircle and low RCT further confirms the capacitive behaviour of the material. The Bode phase angle plot showing phase angle variation with frequency is shown in Figure 9(b). The phase angle at 0.1 Hz was found to be −77° which is close to ideal capacitor (−90°).57 Real and imaginary capacitances calculated from equations (4) are plotted against frequency Figure 9(c). Relaxation time constant was calculated from the peak of imaginary capacitances and was found to be very less (0.2 s). It signifies that the material can change very quickly from resistive to capacitive behaviour.58 Thus, the synergistic effects of highly conductive SrO 0.5 : MnO 0.5 NPs, flake-like structure of SrO 0.5 : MnO 0.5 resulted in high capacitor performance. Specific capacitance 398.2 F/g at 0.25 A/g for SrO 0.5 : MnO 0.5 electrode was the highest level compared to the previous results of the various electrode systems of MnO 2 NPs and SrO 2 NPs which are summarized in the Table 6. The electrodes were also tested for their stability and cyclability by subjecting to 1000 GCD cycles. Even after 1000 cycles nanostructure retains 73.4% of the initial capacitance, thereby demonstrating excellent cyclic stability and reversibility of the prepared SrO 0.5 : MnO 0.5 NS. Lower impedance values further fulfil the requirement for high-performance super capacitor. Thus, doping is an effective strategy to enhance the energy storage and super capacitive properties of the nanostructures.

| Electrode material | Synthesis method | Electrolyte | Potential window (V) | Specific capacitance (F/g) | References |
|--------------------|------------------|-------------|----------------------|---------------------------|------------|
| SrO/PANI nanocomposites | Sonochemical/physical blending | 1.0 M KOH | 0.6 | 226.36 | [32] |
| Sn doped SrO | Chemical precipitation | 1.0 M H 2SO 4 | 1.0 | 56.49 | [62] |
| SrO/PANI/Graphene | Physical blending | 1.0 M KOH | 0.6 | 296 | [63] |
| rGO/MnO 2 hybrid | Physical grinding followed by electrodeposition | 1.0 M | 1.0 | 288 | [64] |
| Graphene-CNTs-MnO 2 | Spray gun deposition followed by electrodeposition | 1.0 M | 0.9 | 209 | [65] |
| MnO 2-graphene hybrid | Hydrothermal | 1.0 M | 1.0 | 315 | [66] |
| SrO 0.5 : MnO 0.5 | Co-precipitation | 6.0 M KOH | 1.0 | 392.8 | This work |

**Table 6.** Electrochemical comparison of different SrO and MnO based composite structures with SrO 0.5 : MnO 0.5 NS

**Conclusion**

Here, we synthesized flake-like bimetallic nanocomposites of SrO 0.5 : MnO 0.5 and investigated its electrochemical behaviour for application as high performance super capacitor. The synthesised SrO 0.5 : MnO 0.5 NPs was characterized by UV-visible, XRD, SEM and XPS spectroscopic techniques. The SrO 0.5 : MnO 0.5 nanomaterials exhibited optical absorptivity in the UV region (200 nm–325 nm) with optical band gap of 1.74 eV, flake-like structure with orthorhombic crystallinity with average grain size of ~80 nm and binding energies of Mn 2P 3 from 641.3 eV to 653.2 eV and for Sr 3d lie in between 132 eV to 134 eV. The SrO 0.5 : MnO 0.5 achieved the highest capacitance of 392.8 F/g and the long-term cyclic stability of the SrO 0.5 : MnO 0.5 NPs determined by charge-discharge cycles. Even after 1000 cycles nanostructure retains 73.4% of the initial capacitance, thereby demonstrating excellent cyclic stability and reversibility of the prepared SrO 0.5 : MnO 0.5 NS. Lower impedance values further fulfil the requirement for high-performance super capacitor. Thus, doping is an effective strategy to enhance the energy storage and super capacitive properties of the nanostructures.

**Acknowledgements**

Authors are thankful to IIT Kanpur for SEM and XPS analysis, Rani-Chennamma University for XRD and Elemental compositional analysis. One of the author Gurmurthy Hegde acknowledges DST-Nanomission for providing a grant with file No SR/NM/NT-1026/2017. Paola De Padova would like to thank the Mission innovation grant agreement between the Italian Ministry of Ecological Transition and ENEA, Italian National Agency for
New Technologies, Energy and Sustainable Economic Development (ref. agreement: 21A03302 GU n.133 del 5-6-2021).

Declaration of conflicting interests

The author(s) declared the following potential conflicts of interest with respect to the research, authorship, and/or publication of this article: All authors declare that they do not have any conflict of interest.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: Dr Gurumurthy Hegde acknowledges DST-Nanomission, Govt. of India for funding the project ‘Biowaste based porous nano materials for efficient low-cost energy storage devices’ with grant No SR/NM/NT-1026/2017.

ORCID iD

Gurumurthy Hegde  https://orcid.org/0000-0002-1200-5664

Supplemental material

Supplemental material for this article is available online.

References

1. Li N, Zhu X, Zhang C, et al. Controllable synthesis of different microstructured MnO2 by a facile hydrothermal method for supercapacitors. J Alloys Compounds 2017; 692: 26–33.
2. Belanger D, Brousse L, and Long JW. Manganese oxides: Battery materials make the leap to electrochemical capacitors. The Electrochem Soc Interf 2008; 17(1): 49.
3. Rasul S, Suzuki S, Yamaguchi S, et al. Manganese oxide octahedral molecular sieves as insertion electrodes for rechargeable Mg batteries. Electrochimica Acta 2013; 110: 247–252.
4. Rison S, Akshaya KB, Bhat VS, et al. MnO 2 nanoclusters decorated on graphenemodified pencil graphite electrode for non-enzymatic determination of cholesterol. Electroanalysis 2020; 32(10): 2128–2136.
5. Huang M, Li F, Dong F, et al. MnO2-based nanostructures for high-performance supercapacitors. J Mater Chem A 2015; 3(43): 21380–21423.
6. Shin J, Seo JK, Yaylian R, et al. A review on mechanistic understanding of MnO2 in aqueous electrolyte for electrical energy storage systems. Int Mater Rev 2020; 65(6): 356–387.
7. Chabre Y and Pannetier J. Structural and electrochemical properties of the proton–γ-MnO2 system. Prog Solid State Chem 1995; 23(1): 1–130.
8. Biswas S, Sharma V, Mandal D, et al. Hollow nanostructures of metal oxides as emerging electrode materials for high performance supercapacitors. CrystEngComm 2020; 22(9): 1633–1644.
9. Lee H, Park IS, Park YK, et al. Facile preparation of Ni-Co bimetallic oxide/activated carbon composites using the plasma in liquid process for supercapacitor electrode applications. Nanomaterials (Basel, Switzerland) 2020; 10(1): 61.
10. Adnan J, Arfan M, Shahid T, et al. Synthesis of cadmium hydroxide nanostructure via composite-hydroxide-mediated approach. Nanomater Nanotechnology 2019; 9: 1–7.
11. Yadav MS. Metal oxides nanostructure-based electrode materials for supercapacitor application. J Nanoparticle Res 2020; 22(12): 367.
12. Wang XW, Zhu QQ, Wang XE, et al. Structural and electrochemical properties of La0.85Sr0.15MnO3 powder as an electrode material for supercapacitor. J Alloys Compounds 2016; 675: 195–200.
13. Hyun TS, Kim HG, and Kim ID. Facile synthesis and electrochemical properties of conducting SrRuO3-RuO2 composite nanofibre mats. J Power Sourc 2010; 195(5): 1522–1528.
14. Tomar AK, Singh G, and Sharma RK. Charge storage characteristics of mesoporous strontium titanate perovskite aqueous as well as flexible solid-state supercapacitor cell. J Power Sourc 2019; 426: 223–232.
15. Lv J, Zhang Y, Lv Z, et al. Strontium doped lanthanum manganese (LSM) effects on electrochemical performance of LSM/MnO2 composites for supercapacitor. J Mater Sci Mater Electronics 2017; 28(22): 17020–17025.
16. Han Y, Jiao Y, Lv G, et al. High-performance strontium and bismuth bimetallic oxides electrode: combine first-principles calculations with electrochemical testscombine first-principles calculations with electrochemical tests. Mater Today Commun 2020; 24: 100927.
17. Prasankumar T, Ithhaza Aazem VS, Raghavan P, et al. Microwave assisted synthesis of 3D network of Mn/Zn bimetallic oxide-high performance electrodes for supercapacitors. J Alloys Compounds 2017; 695: 2833–2843.
18. Bhat VS, Kanagavalli P, Sriram G, et al. Low cost, catalyst free, high performance supercapacitors based on porous nano carbon derived from agriculture waste. J Energy Storage 2020; 32: 101829.
19. Sharma V, Singh I, and Chandra A. Hollow nanostructures of metal oxides as next generation electrode materials for supercapacitors. Scientific Rep 2018; 8(1): 1307.
20. Bhat VS, Hegde G, and Nasrollahzadeh M. A sustainable technique to solve growing energy demand: porous carbon nanoparticles as electrode materials for high-performance supercapacitors. J Appl Electrochemistry 2020; 50(12): 1243–1255.
21. Athar T. Synthesis and characterization of strontium oxide nanoparticles via wet process. Mater Focus 2013; 2(6): 450–453.
22. Singh VP, Kushwaha HS, and Vaish R. Photocatalytic study on SrB2B2O7 (SrO-Bi2O3-B2O3) transparent glass ceramics. Mater Res Bull 2018; 99: 453–459.
23. Sharma V and Prajapati RC. Synthesis of mixed metal oxide nanoparticles of SrO2 with SrO via sol-gel technology: their structural, optical, and electrical properties. J Sol-Gel Sci Technology 2018; 87(1): 41–49.
24. Lu L, Xu S, An J, et al. Electrochemical performance of CNTs/RGO/MnO2 composite material for supercapacitor. *Nanomater Nanotechnology* 2016; 6: 1–7.

25. Nemade KR and Waghuley SA. UV-VIS spectroscopic study of one pot synthesized strontium oxide quantum dots. *Results Phys* 2013; 3: 52–54.

26. Seo WS, Jo HH, Lee K, et al. Size-dependent magnetic properties of colloidal Mn3O4 and MnO nanoparticles. *Angew Chem Int Edition* 2004; 43(9): 1115–1117.

27. Pussi K, Gallo J, Ohara K, et al. Structure of manganese oxide nanoparticles extracted via pair distribution functions. *Condensed Matter* 2020; 5(1): 19.

28. Frandsen BA, Brunelli M, Page K, et al. Verification of Anderson superexchange in MnO via magnetic pair distribution function analysis and ab initio theory. *Phys Rev Lett* 2016; 116(19): 197204.

29. Hsieh CT, Lin CY, and Lin JY. High reversibility of Li intercalation and de-intercalation in MnO-attached graphene anodes for Li-ion batteries. *Electrochimica Acta* 2011; 56(24): 8861–8867.

30. Chen JG, Chen CY, Wu CG, et al. An efficient flexible dye-sensitized solar cell with a photoanode consisting of TiO2 nanoparticle-filled and SrO-coated TiO2 nanotube arrays. *J Mater Chem* 2010; 20(34): 7201–7207.

31. Mousavi SV, Bidhendi GN, and Mehrdadi N. Synthesis of graphene oxide decorated with strontium oxide (SrO/GO) as an efficient nanocomposite for removal of hazardous ammonia from wastewater. *Separation Sci Technology* 2020; 55(8): 1462–1472.

32. Iqbal MZ, Alam S, Afzal AM, et al. Binary composites of strontium oxide/polyaniline for high performance supercapattery devices. *Solid State I onics* 2020; 347: 115276.

33. Gholamrezaei S and Salavati-Niasari M. Sonocochemical synthesis of SrMnO3 nanoparticles as an efficient and new catalyst for O2 evolution from water splitting reaction. *Ultrason Sonochem* 2018; 40: 651–663.

34. Astik N, Jha PK, and Sathe V. Temperature dependent raman spectroscopic study of the Fe doped La0.67Sr0.33MnO3 nanoparticles prepared using ball milling method. *Phys Solid State* 2019; 61(4): 618–626.

35. Luo F, Huang YH, Yan CH, et al. Molten alkali metal nitrate flux to well-crystallized and homogeneous La0.7Sr0.3Mn3O nanocrystallites. *J Magnetism Magn Mater* 2003; 260(1): 173–180.

36. Kracker M, Thieme C, Thieme K, et al. Silver-enhanced nucleation and morphology control of surface crystallized Ba0.5Sr0.5Zn2SiO7 from 8 BaO-8 SrO-34 ZnO-50 SiO2 glass. *Ceramics Int* 2019; 45(15): 18760–18766.

37. Kong W, Yan L, Luo Y, et al. Ultrathin MnO2/graphene oxide/carbon nanotube interlayer as efficient polysulfide-trapping shield for high-performance Li-S batteries. *Adv Funct Mater* 2017; 27(18): 1606663.

38. Goudarzi Z, Parvin N, and Sharifianjazi F. Formation of hydroxyapatite on surface of SiO2- P2O5-CaO-SrO-ZnO bioactive glass synthesized through sol-gel route. *Ceramics Int* 2019; 45(15): 19323–19330.

39. Zhang Q, Dai Q, Li M, et al. Incorporation of MnO nanoparticles inside porous carbon nanotubes originated from conjugated microporous polymers for lithium storage. *J Mater Chem A* 2016; 4(48): 19132–19139.

40. Liu G and Zhang S. One-step synthesis of low-cost and high active Li2MnO3 cathode materials. *Int J Electrochem Sci* 2016; 11: 5545–5551.

41. Lim J, Moon J, Gim J, et al. Fully activated Li2MnO3 nanoparticles by oxidation reaction. *J Mater Chem* 2012; 22(23): 11772–11777.

42. Gaire M, Liang K, Luo S, et al. Nanostructured manganese oxide nanoparticles anchored on interconnected graphene ribbons for high-performance lithium-ion batteries. *J Power Source* 2018; 397: 325–333.

43. Liu SY, Xie J, Zheng YX, et al. Nanocrystal manganese oxide (Mn3O4, Mn4O) anchored on graphite nanosheet with improved electrochemical Li-storage properties. *Electrochimica Acta* 2012; 66: 271–278.

44. Hu Q, Wu C, Cao L, et al. A novel TiO2 nanowires/nanoparticles composite photoanode with SrO shell coating for high performance dye-sensitized solar cell. *J Power Source* 2013; 226: 8–15.

45. Harish S, Sabarinathan M, Archana J, et al. Synthesis of ZnO/SrO nanocomposites for enhanced photocatalytic activity under visible light irradiation. *Appl Surf Sci* 2017; 418: 147–155.

46. Thalinger R, Gocyla M, Hegen M, et al. Exsolution of Fe and SrO nanorods and nanoparticles from lanthanum strontium ferrite La0.6Sr0.4FeO3–δ materials by hydrogen reduction. *The J Phys Chem C* 2015; 119(38): 22050–22056.

47. Xia H, Hong C, Shi X, et al. Hierarchical heterostructures of Ag nanoparticles decorated MnO2nanowires as promising electrodes for supercapacitors. *J Mater Chem A* 2015; 3(3): 1216–1221.

48. Gaire M, Liang K, Luo S, et al. Nanostructured manganese oxides electrode with ultra-long lifetime for electrochemical capacitors. *RSC Adv* 2020; 10(28): 16817–16825.

49. Fleischmann S, Mitchell JB, Wang R, et al. Pseudocapacitance: from fundamental understanding to high power energy storage materials. *Chem Rev* 2020; 120(14): 6738–6782.

50. Okubo M, Hosono E, Kim J, et al. Nanosize effect on high-rate Li-Ion intercalation in LiCoO2 electrode. *J Am Chem Soc* 2007; 129(23): 7444–7452.

51. Shin JY, Samuelis D, and Maier J. Sustained lithium-storage rates: emphasis on interfacial storage phenomena. *Adv Funct Mater* 2011; 21(18): 3464–3472.

52. Bhat VS, Krishnan SG, Jayeoye TJ, et al. Self-activated ‘green’ carbon nanoparticles for symmetric solid-state supercapacitors. *J Mater Sci* 2021; 56(23): 13271–13290.
batteries by pre-intercalation of K and Na ions. Scientific Rep 2017; 7(1): 2219.

54. An C, Zhang Y, Guo H, et al. Metal oxide-based supercapacitors: progress and prospectives. Nanoscale Adv 2019; 1(12): 4644–4658.

55. Liang R, Du Y, Xiao P, et al. Transition metal oxide electrode materials for supercapacitors: a review of recent developments. Nanomaterials 2021; 11(5): 1248.

56. Mathis TS, Kurra N, Wang X, et al. Energy storage data reporting in perspective-guidelines for interpreting the performance of electrochemical energy storage systems. Adv Energy Mater 2019; 9(39): 1902007.

57. Ali GAM, Divyashree A, Supriya S, et al. Carbon nanospheres derived from Lablab purpureus for high performance supercapacitor electrodes: a green approach. Dalton Trans 2017; 46(40): 14034–14044.

58. Bhat VS, Supriya S, Jayeoye TJ, et al. Influence of surface properties on electro-chemical supercapacitors utilizing Callerya atropurpurea pod derived porous nanocarbons: structure property relationship between porous structures to energy storage devices. Nano Select 2020; 1(2): 226–243.

59. Park SK, Sure J, Vishnu DSM, et al. Nano-Fe3O4/carbon nanotubes composites by one-pot microwave solvothermal method for supercapacitor applications. Energies 2021; 14(10): 2908.

60. Wang Y, Zhan Y, Yan X, et al. Investigations Ce Doped MnO2/rGO as high performance supercapacitors material. Russ J Electrochemistry 2018; 54(3): 283–291.

61. Kim JH, Choi C, Lee JM, et al. Ag/MnO2 composite sheath-core structured yarn supercapacitors. Scientific Rep 2018; 8(1): 13309.

62. Samuel AJ, Deepi AS, Srikesh Get al. One pot synthesis and characterisation of two dimensional tin doped strontium oxide nanostructured electrode materials for electrochemical supercapacitor applications. Mater Technology 2020; 37: 150–160.

63. Iqbal MZ, Faisal MM, Sulman M, et al. Facile synthesis of strontium oxide/polyaniline/graphene composite for the high-performance supercapattery devices. J Electroanalytical Chem 2020; 879: 114812.

64. Zhao Z, Shen T, Liu Z, et al. Facile fabrication of binder-free reduced graphene oxide/MnO2/Ni foam hybrid electrode for high-performance supercapacitors. J Alloys Compounds 2020; 812: 152124.

65. Rogier C, Pognon G, Bondavalli P, et al. Electrodeposition of MnO2 on spray-coated nanostructured carbon framework as high performance material for energy storage. Surf Coat Technology 2020; 384: 125310.

66. Liu Y, Yan D, Zhuo R, et al. Design, hydrothermal synthesis and electrochemical properties of porous birnessite-type manganese dioxide nanosheets on graphene as a hybrid material for supercapacitors. J Power Sourc 2013; 242: 78–85.