

## Cost-Effective Synthesis of rGO/CeNiO<sub>3</sub> Perovskite Nanocomposites for Enhanced and Stable Supercapacitors and Oxygen Evolution Reaction Catalysts

Lakshmanan Kumaresan<sup>1,a\*</sup>, Govindasamy Palanisamy<sup>1,b</sup> and Jintae Lee<sup>b</sup>

<sup>a</sup> Department of Physics, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Saveetha University Chennai 602 105, Tamil Nadu, India.

<sup>b</sup> School of Chemical Engineering, Yeungnam University, 280 Daehak-Ro, Gyeongsan, 38541, Republic of Korea

*\*Corresponding author*

*E-mail address: [kumaresh.msc55@gmail.com](mailto:kumaresh.msc55@gmail.com) (L. Kumaresan)*

*1-These authors contributed equally*

### 1. Synthesis of Graphene oxide

Graphene oxide (GO) was synthesized using a modified Hummer's method [1,2]. The procedure began by combining 2 grams of graphite flakes with 2 grams of sodium nitrate in 50 milliliters of concentrated sulfuric acid within a 1000-milliliter round-bottom flask. This mixture was vigorously stirred for 2 hours while placed in an ice bath, ensuring the reaction temperature remained between 0 and 5°C to control the exothermic nature of the reaction. Following this initial phase, 6 grams of potassium permanganate (KMnO<sub>4</sub>) was gradually introduced to the reaction mixture under constant stirring. The slow addition of KMnO<sub>4</sub> prevented rapid temperature fluctuations and ensured a controlled oxidation process. As the reaction progressed, the color of the solution transitioned from dark brown to green, with the temperature maintained at approximately 15°C. After removing the ice bath, the reaction was allowed to continue with stirring at 35°C for 24 hours. During this period, the color of the mixture shifted to a distinctive pastry brown, indicating the progression of the oxidation process. To complete the oxidation, 100 milliliters of water was cautiously added to the reaction mixture, causing the temperature to rise to 98°C. Adding water triggered a rapid exothermic reaction, resulting in a brown-colored solution. Subsequently, 200 milliliters of cold water were added, followed by the gradual addition of 10 milliliters of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to terminate the reaction and reduce excess potassium permanganate, ensuring safe handling of the mixture. This step also brightened the solution, turning it a lighter brown, a visual confirmation of the reduction process. To purify the graphene oxide, 10% hydrochloric acid (HCl) was added to the solution to dissolve residual metal ions,

followed by extensive washing with deionized water until the pH reached a neutral level. This neutralization process was crucial to remove any acidic impurities from the GO. The purified GO was then dried in an oven at 60°C, resulting in a stable dry powder form.

## 2. Electrode preparation and electrochemical measurements

Functional electrodes were fabricated using rGO/CeNiO<sub>3</sub> nanocomposite, carbon black, and polyvinylidene difluoride (PVDF), mixed with N-methyl-2-pyrrolidone (NMP) in an 8:1:1 mass ratio. Before the slurry or active substance coating, the graphite sheet (GS) was cleaned using acetone. The uniformly mixed slurry was applied onto 1 x 1 cm<sup>2</sup> of GS, followed by drying for eight hours at 80°C in a vacuum oven, resulting in approximately 2 mg mass of coated rGO/CeNiO<sub>3</sub> nanocomposite. Subsequently, these electrodes were employed in electrochemical investigations.

A supercapacitor study was conducted using an electrochemical workstation (SP 300 Biologic Workstation, France). Various electrochemical procedures, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were performed using a three-electrode arrangement. The graphite sheet functioned as the substrate for the working electrode, onto which approximately 2 mg of rGO/CeNiO<sub>3</sub> nanocomposite were meticulously deposited, effectively covering an area measuring 1 x 1 cm<sup>2</sup>. Platinum thin rods served as counter electrodes, while Hg/HgO electrodes were used as reference electrodes. Cyclic voltammetry was executed within a potential window of -1 to 0.0 V (vs. Hg/HgO) at various scan rates ranging from 5 to 120 mV/s. The capacitance values of the rGO/CeNiO<sub>3</sub> nanocomposite, CeNiO<sub>3</sub> and CeO<sub>2</sub> electrodes were determined through GCD at different current densities ranging from 1 to 6A/g. The gravimetric specific capacitance was calculated using the corresponding GCD curves according to Equation S1[3].

$$Cs = \frac{I\Delta t}{m\Delta V} \dots\dots\dots(S1)$$

Where m is the mass of the active components (rGO/CeNiO<sub>3</sub> nanocomposite, CeNiO<sub>3</sub> and CeO<sub>2</sub> nanoparticles), I and t are the discharge current density (A/g) and discharge time, respectively, V is a potential window and Cs is the specific capacitance (F/g).

### Coulombic efficiency

The coulombic efficiency was calculated using various GCD curves (long cycles) according to Equation S2.

$$\eta = (td/tc) \times 100 \dots\dots\dots (S2)$$

**Overpotential**

The overpotential values of all the catalysts were calculated at a benchmarking current density of 10 mA cm<sup>-2</sup> by employing the following relation:

$$\eta_{10}(\text{OER}) = (E_{\text{obs}} - 1.23) \text{ V versus RHE} \dots\dots\dots (S3)$$

$$\eta_{10}(\text{HER}) = (0 - E_{\text{obs}}) \text{ V versus RHE} \dots\dots\dots (S4)$$

**The Tafel Slope**

The Tafel slope was calculated by fitting the overpotential versus log (j) using the Tafel equation as given below[4]:

$$\eta = b \times \log (j/j_0) \dots\dots\dots (S5)$$

where “b” signifies the Tafel slope value, “j” implies the current density value, and “j<sub>0</sub>” is the exchange current density. Electrochemical impedance spectroscopy (EIS) measurements were done on the frequency ranges from 10<sup>5</sup> to 1 Hz.

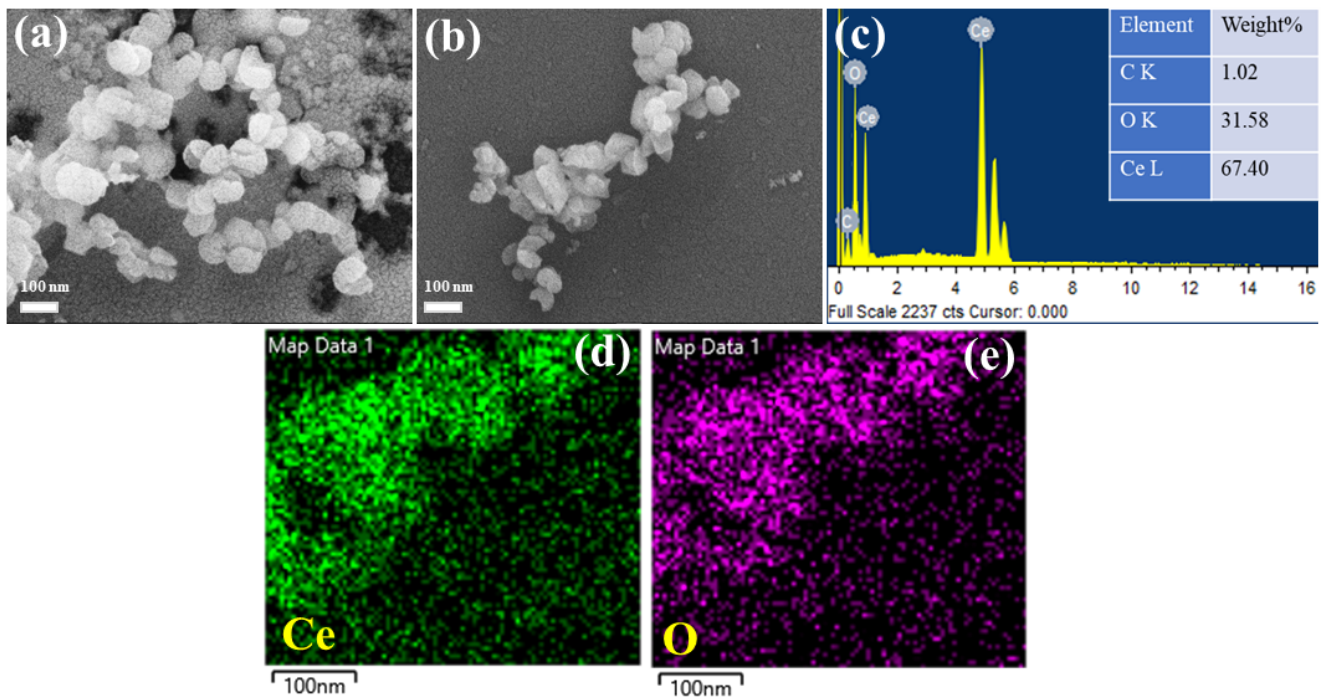
**Electrochemical Active Surface Area (ECSA)**

The electrochemical active surface areas (ECSA) were measured by determining the electrochemical C<sub>dl</sub> using the following equations:

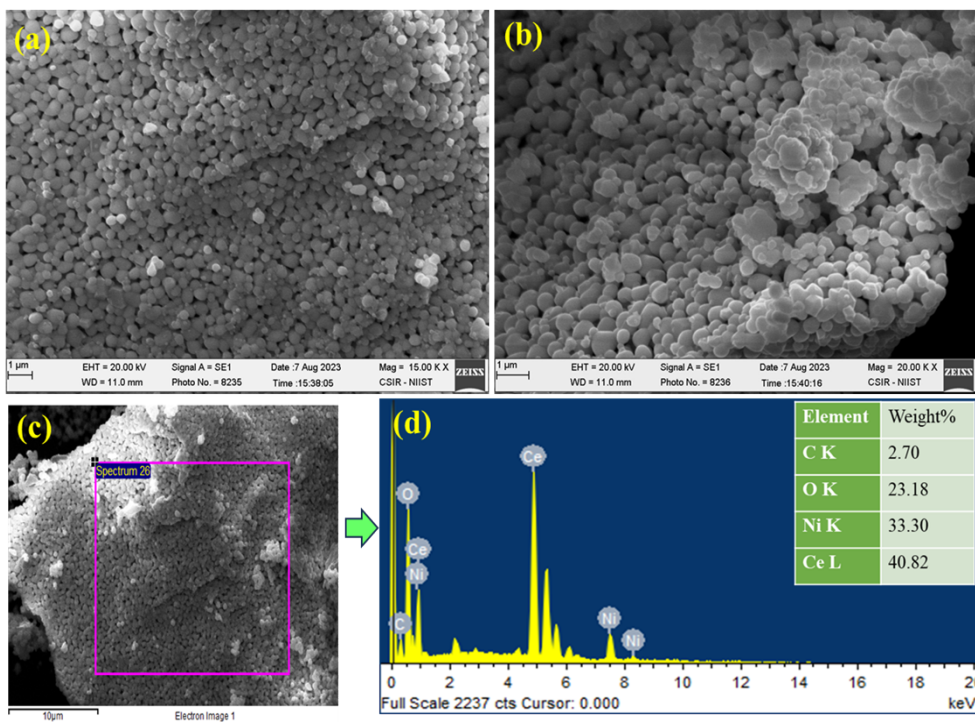
$$i_c = \nu \times C_{dl} \dots\dots\dots (S6)$$

$$\text{ECSA} = C_{dl} / C_s \dots\dots\dots (S7)$$

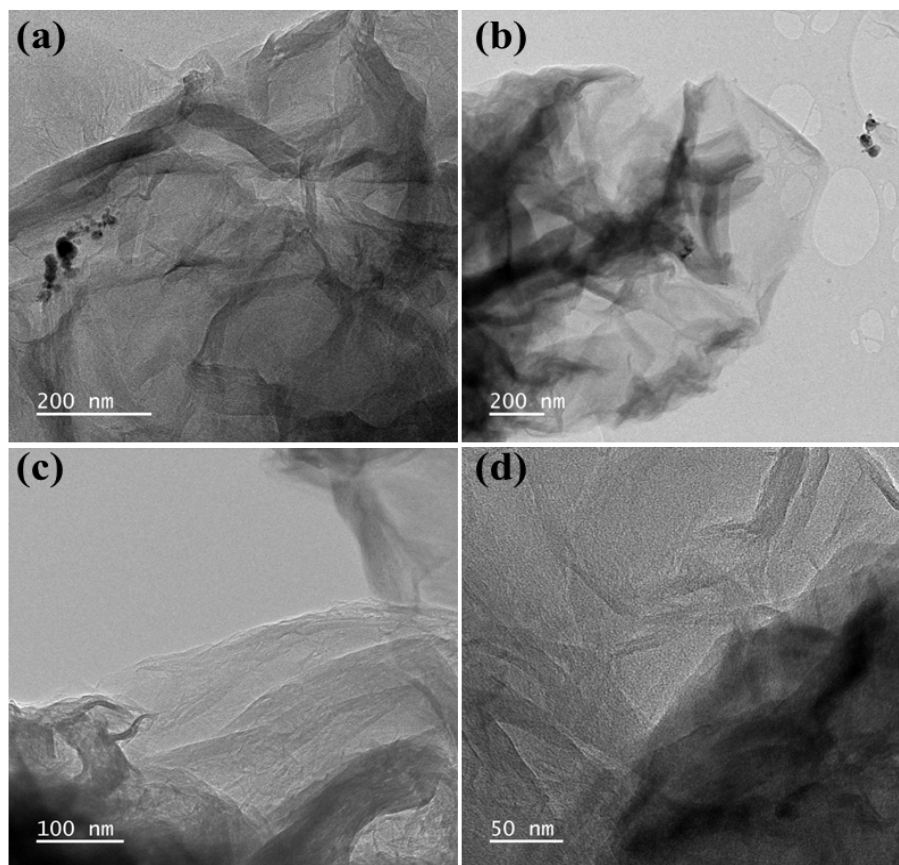
where “i<sub>c</sub>” indicates the double-layer charging current resulting from scan-rates (ν) dependent CVs at non-faradic potential, and “C<sub>s</sub>” denotes a specific capacitance value of 0.040 mF cm<sup>-2</sup> depending on the typical reported values.



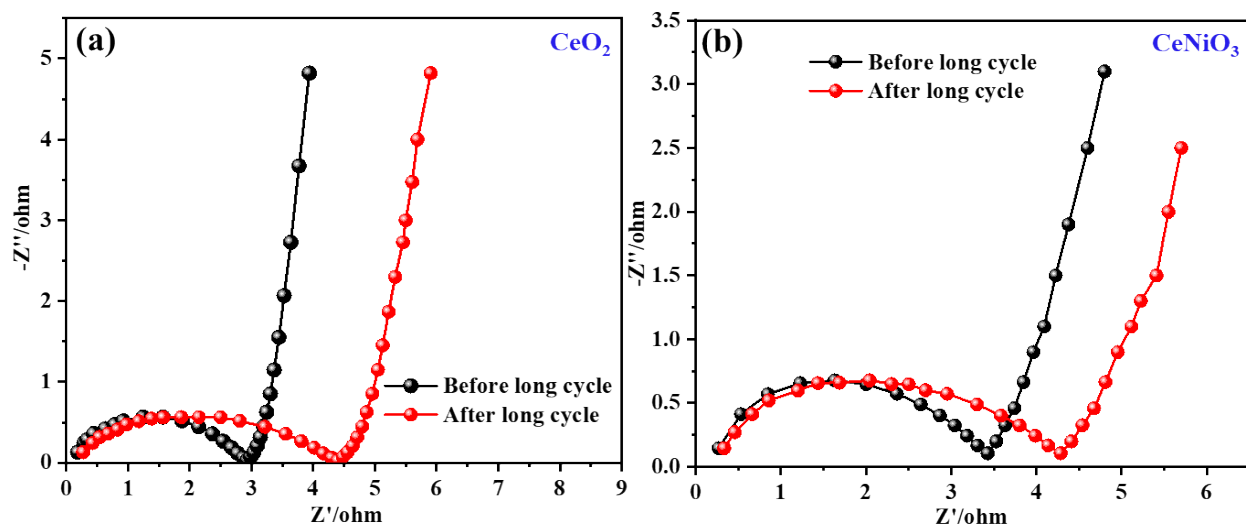
**Figure S1.** Morphology and elemental composition analysis of CeO<sub>2</sub> nanoparticles, (a, b) FESEM images, (c) EDS spectrum, and (d, e) SEM-color mapping images



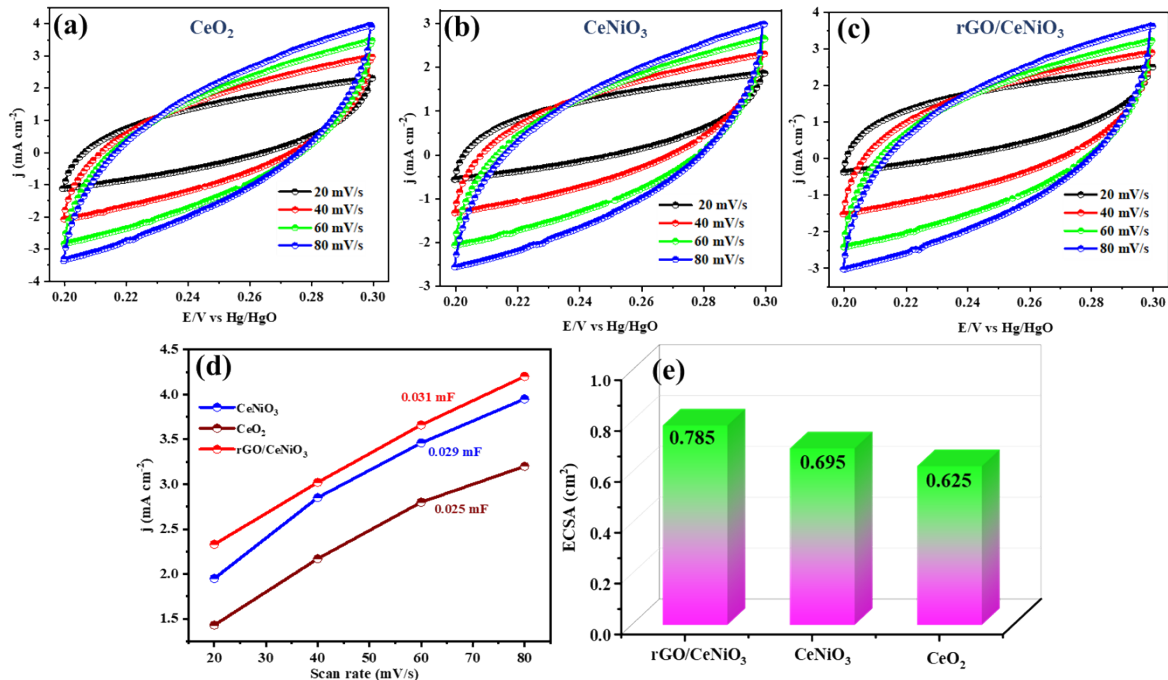
**Figure S2.** Morphology and elemental composition analysis of CeNiO<sub>3</sub> nanoparticles, (a-c) SEM images, and (d) EDS spectrum



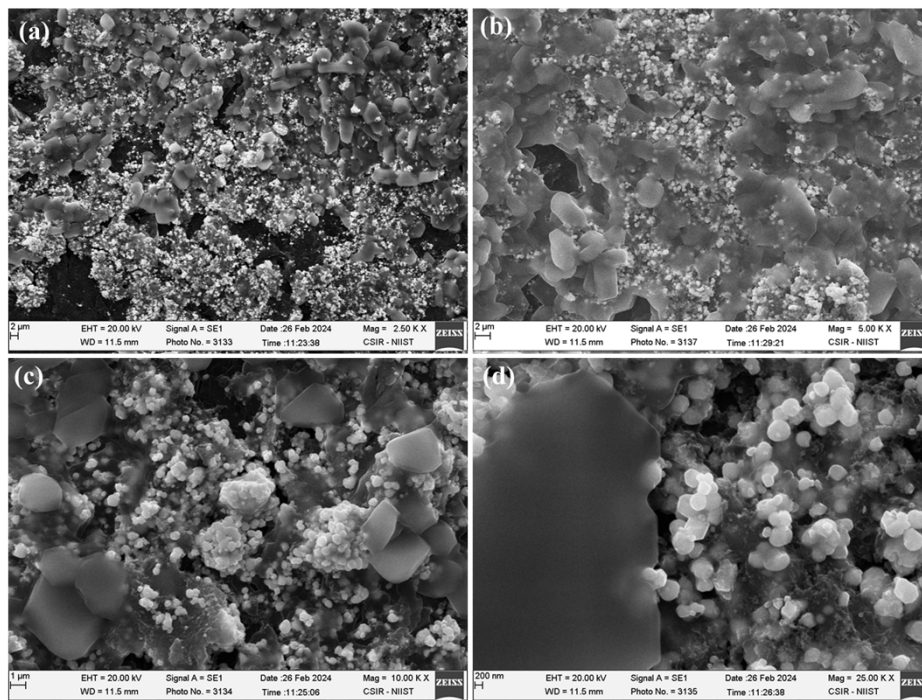
**Figure S3.** Morphological analysis of the rGO sheet, (a-d) TEM images at different magnifications



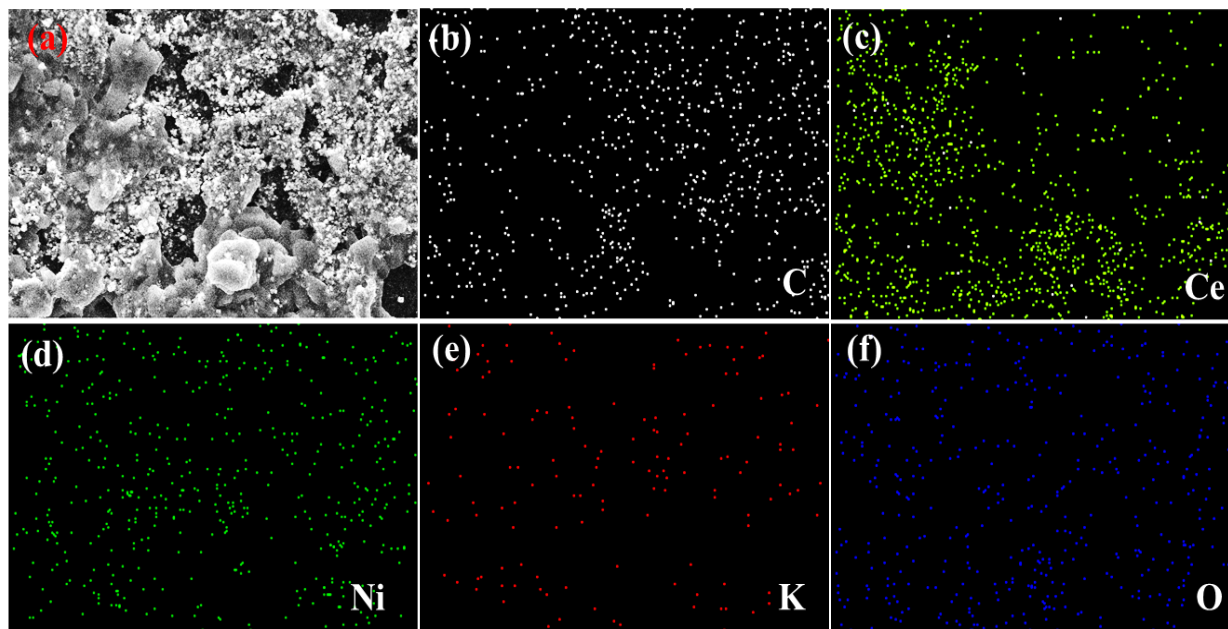
**Figure S4.** EIS spectrum of  $\text{CeO}_2$  and  $\text{CeNiO}_3$  electrodes, (a)  $\text{CeO}_2$  electrode EIS Nyquist plot of before and after long cycles, and (b)  $\text{CeNiO}_3$  electrode EIS Nyquist plot of before and after long cycles



**Figure S5.** (a-c) are CVs measured at non-faradaic regions at different scan rates to measure the  $C_{dl}$  values of  $\text{CeO}_2$ ,  $\text{CeNiO}_3$ , and  $\text{rGO/CeNiO}_3$ . d) Corresponding calculated  $C_{dl}$  values of  $\text{CeNiO}_3$ ,  $\text{CeO}_2$ , and  $\text{rGO/CeNiO}_3$  and (e) Calculated electrochemical active surface area (ECSA) values.



**Figure S6.** Morphological analysis of after long-cycle in  $\text{rGO/CeNiO}_3$  electrode, (a-d) SEM images at different magnifications and different areas of the electrode



**Figure S7.** SEM color mapping analysis after long-cycle in rGO/CeNiO<sub>3</sub> electrode, (a) SEM image, and (b-f) SEM-color mapping images of different elements

## Reference

- [1] S.N. Alam, N. Sharma, L. Kumar, Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO)\*, *Graphene* 06 (2017) 1–18. <https://doi.org/10.4236/graphene.2017.61001>.
- [2] A.F. Kamil, H.I. Abdullah, A.M. Rheima, W.M. Khamis, Modification of hummers presses for synthesis graphene oxide nano-sheets and graphene oxide /Ag nanocomposites, *Journal of Ovonic Research* 17 (2021) 253–259. <https://doi.org/10.15251/jor.2021.173.253>.
- [3] L. Kumaresan, K.S. Harshini, H. Amir, G. Shanmugavelayutham, C. Viswanathan, Single-step synthesis of Mn<sub>3</sub>N<sub>2</sub>, Mn<sub>x</sub>ON and Mn<sub>3</sub>O<sub>4</sub> nanoparticles by thermal plasma arc discharge technique and their comparative study as electrode material for supercapacitor application, *J Alloys Compd* 942 (2023). <https://doi.org/10.1016/j.jallcom.2023.169121>.
- [4] P. Amarnath, R. Madhu, K. Praveen, S. Govindarajan, S. Kundu, Y. Subramaniam, Phase-Pure High-Entropy Spinel Oxide (Ni,Fe,Mn,Cu,Zn)<sub>3</sub>O<sub>4</sub> via Thermal Plasma: A Promising Electrocatalyst for Oxygen Evolution Reaction, *ACS Appl Energy Mater* 6 (2023) 5899–5911. <https://doi.org/10.1021/acsaem.3c00311>.