Effect of conducting polymer incorporated heterostructure morphology of MgCo$_2$O$_4$@PPy nanosheets: a novel cathode material for asymmetric supercapacitor applications

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ABSTRACT

In this study, the facile hydrothermal synthesis of Magnesium-cobaltite MgCo$_2$O$_4$ spinel with different morphologies, such as nanosheets and nanospheres has been investigated. The structural, morphological, textural, and chemical composition of the materials were examined using powdered X-ray diffraction (XRD), scanning electron microscopy (SEM), Transition electron microscopy (TEM), N$_2$ adsorption–desorption isotherm and X-ray photoelectron spectroscopy (XPS). The produced materials have heterostructure morphology with a nanospherical surface-coated nanosheet-like morphology that is clearly visible in the results of FESEM and TEM. The results of N2 adsorption–desorption reveal that MgCo$_2$O$_4$@PPy has a larger specific area of 103 m$^2$g$^{-1}$ than MgCo$_2$O$_4$, which has a specific area of 73 m$^2$g$^{-1}$. The synthesized electrode material with inventive nanoarchitectures showed attractive electrochemical performance in a variety of applications. The heterostructure MgCo$_2$O$_4$@PPy electrode produced an impressive capacitive retention of 93% at current density 5 Ag$^{-1}$ and a high specific capacitance of 988 Fg$^{-1}$ after 10,000 cycles. The assembled ASC cell MgCo$_2$O$_4$@PPy//AC provided remarkable high capacitance retention of 84% after 10,000 cycles at 5 Ag$^{-1}$, intensely high energy density of 40 Whkg$^{-1}$, and power density of 1544 Wkg$^{-1}$. 

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1 Introduction

New energy and energy storage device development is becoming increasingly vital as environmental pollution and energy density rise [1–3]. As novel energy storage systems, researchers are looking into fuel cells, Li-ion batteries and electrochemical capacitors [4–7]. Due to their high charge/discharge rates, power and energy densities, eco-friendliness and long-term cycling stability, supercapacitors (SCs), micro-supercapacitors (SCs) and batteries have attracted the most attention among electrochemical energy storage devices. While batteries can give high energy densities they often have low power densities, whereas SCs can deliver high power densities at their current phases of development but their energy densities are typically not satisfactory [8]. The new energy storage technology is usually environmentally benign, reusable and efficient in converting energy [9–11]. Electrochemical capacitors (also known as supercapacitors) are becoming increasingly used all over the world. Supercapacitors are utilised in a variety of applications including electric vehicles, computer memory storage systems, intermittent power supplies and audio systems [12–14]. SCs applications need an active electrode with a large surface area that can store a lot of electrolyte ions on the surface. The internal and external characteristics of the electrode materials commonly influence the electrochemical properties of SCs. Due to their affordable production costs and porous interior structures, SC electrode materials are desirable for energy storage systems [15]. The majority of the high energy storage device is made up of electrodes and electrolytes. Supercapacitor development requires extensive materials research [16, 17]. The material selection and electrode design have a significant impact on how well SCs work. Electrical double-layer capacitors (EDLCs) and pseudocapacitors are two separate classes of SCs that differ in terms of how they store charge. Carbon-based electrode materials are preferred for EDLCs because they are affordable and widely accessible in a variety of forms. Examples include reduced graphene oxide (rGO), graphene quantum dots, carbon nanotubes, and activated carbon. EDLCs depend on charge distribution on the surface and charge transfer at the electrode–electrolyte interface to operate without destroying chemical bonds. Research on pseudocapacitors has been focused on nearly doubling the theoretical specific capacitance value, which is higher than that of carbon-based materials. Pseudocapacitors are based on redox reactions that take place swiftly and irreversibly on the electrode surfaces of electroactive materials. Conducting polymers, transition metal oxides/hydroxides, and materials with oxygen or nitrogen functional groups are a few examples of pseudocapacitor electrode materials. Because they enable the transfer of generated electrons from redox targets to conductive materials due to the presence of cations in the interlayer gaps and at the electrode–electrolyte interface, transition metal oxides/hydroxides are the most promising electrode active materials for pseudocapacitors [18–21].

Since mixed transition metal oxides have a variety of oxidation states from each element and because of synergistic effects, they often perform better electrochemical performance than single oxides. In the last few years, the unique crystal structure of spinel-structure oxides has sparked interest in the study. The spinel-type oxides with organised microstructure reveals superior electrochemical performance. The ternary oxide AB2O4 has been extensively studied as a high efficient anode material for supercapacitors [22, 23]. The electrode materials for reaction pseudocapacitance were found to be Te transition metal oxides. There are many charge transfer transitions in this transition metal [24]. The ligand-to-metal charge-transport transitions are common in metal oxides with high oxidation transitions [25–27]. These materials, which include the AB2O4 spinel with two transition metal components, usually have outstanding electrochemical performance. As can be predicted, a lot of study has previously been done on SC electrodes made of complex transition-metal oxides. Co3O4 can create mixed transition metal oxides with the spinel structure when Co is partially replaced by it [28]. Cobaltite is a ternary oxide made up of cobalt and oxygen, as well as positively charged monovalent and divalent elements or groups [29]. The formula for these ternary oxides is [Am] z+[CoxOy] z, where A is commonly an alkali metal (Na–Cs), [NH4]+, or Tl. The A–Co–O ternary system has diverse structural chemistry due to the flexible coordination of cobalt atoms in the system. It can be created with a variety of structures from a variety of precursors [30]. The synthesis of cobaltite and the research of its properties have sparked a lot of attention recently. Better electrode materials for supercapacitors are cobalt-based oxides with an
AB₂O₄ spinel structure, such as NiCo₂O₄ [31], ZnCo₂O₄ [32], and CuCo₂O₄ [33]. The ternary Mg–Co oxide, commonly abbreviated as MgCo₂O₄, is a molecule with numerous applications in lithium-ion batteries and catalysts due to its helpful multifunctional properties, fascinating catalytic and electrochemical features, and widespread use. Magnesium cobalt oxide (MgCo₂O₄) has recently been used successfully as an electrode material for pseudocapacitors because cobalt and magnesium are complementary components. Theoretically stated, MgCo₂O₄—a lithium ion battery anode material—has a higher capacitance than most 'M’Co₂O₄ (M = Cu, Zn, and Ni) [34]. MgCo₂O₄, which has a higher theoretical capacitance (3122 F g⁻¹) than the other MCo₂O₄ and TTMOs electrode components for pseudocapacitors, is a potential contender and has demonstrated great performance as electrode material in Supercapacitors [35, 36]. Recently, Zhiqiang Liu et al. developed a MgCo₂O₄-based Asymmetric device that delivers a huge energy density of 62.33 Wh kg⁻¹ and a power density of 750 W kg⁻¹ [37]. Silambarasa et al. developed MgCo₂O₄ nanorods using the co-precipitation process, which displayed a high specific capacitance of 752 F g⁻¹ at 2 mA cm⁻² [38]. Krishnan et al. synthesized MgCo₂O₄ nanoparticles using molten salt method and its delivers specific capacitance of 321 F g⁻¹ at 0.5 Ag⁻¹ [35]. Gao et al. created MgCo₂O₄@PPy nanoparticles via hydrothermal and in-situ chemical oxidative polymerization. These materials have a high specific capacitance of 1079.6 F g⁻¹ at a current density of 1 Ag⁻¹ [39].

The two main types of materials utilised in pseudocapacitive/battery-type devices are metal oxides and conducting polymers. However, because of the quick growth of material science, bimetallic oxides (from binary to quaternary) have been extensively researched for pseudocapacitors, battery-type SCs. The most extensively studied conducting polymers are polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives. In addition to these, other polymers are also available, such as polydiacetylene and polyindole [40]. Polypyrrole (PPy) is a flexible, environmentally stable, and electroactive conductive polymer with a high doping state conductivity (10–100 S cm⁻¹). As evidenced from the literature, wrapping PPy enhances the conductivity, stability and improved electrocatalytic activity of metal oxides [41]. Furthermore, as compared to other conductive polymers, PPy is less hazardous and easier to make.

In this work, MgCo₂O₄@Polypyrrole nanocomposite was produced by a facile hydrothermal technique that only took one stage and direct chemical polymerization at few hours. This specific technique of synthesis is used to create heterostructures with bundles of nanosheets and nanosphere-like morphologies. The novelty of the work is the prepared electrode materials and embedded ASC devices made of MgCo₂O₄, MgCo₂O₄@Polypyrrole, and MgCo₂O₄@Polypyrrole //Activated carbon, using the Trasatti method to assess the capacitive contribution from electrical double layers and pseudo-capacitive processes. The dopant p-toluenesulfonic acid can partially etch the MgCo₂O₄ heterostructure during the polymerization procedure, and the dissociative Mn/Co ions can function as a crosslinker to form a 2D PPy nanostructure. The electrochemical performance of the manufactured MgCo₂O₄@PPy composite electrode was superior to that of bare MgCo₂O₄. Furthermore, as constructed ASC based on MgCo₂O₄@PPy //AC showed a high energy and power density. These impressive electrochemical displays convincingly demonstrated that the produced MgCo₂O₄@PPy //AC electrode has the potential to be used in high-performance SCs.

2 Experimental procedure

2.1 Chemicals

All the compounds were analytically pure and did not require any additional purification. Cobalt nitrate (Co(NO₃)₂·6H₂O), magnesium nitrate (Mg(NO₃)2·6H₂O), and urea (CO(NH₂)₂ were all supplied by Sigma–Aldrich. Pyrrole Monomer, Sodium p-Toluenesulfonate (p-TSS, C₇H₇SO₃Na), and ammonium persulfate ((NH₄)₂S₂O₈) were all acquired from India by Merk company.

2.2 Synthesis of MgCo₂O₄ nanosheets

Mg(NO₃)₂·6H₂O (1 mmol), 2 mmol of (Co(NO₃)₂·6H₂O), and urea (CO(NH₂)₂ were all dispersed in 50 ml D.I water and stirred continuously for 30 min. After the process, 4 mmol of urea was utilised as the reaction’s fuel agent. Then, the homogenous solution was transferred into 50 ml Teflon lined autoclave for the
hydrothermal process of 180 °C for 12 h. After the reaction, the black product was washed many times with ethanol and D.I water to remove slags. The slag-free product was dried for 8 h at 60 °C. The product was then annealed for 3 h at 400 °C for air.

### 2.3 Synthesis of heterostructure, nanosheet coated nanospherical MgCo$_2$O$_4$@PPy

The MgCo$_2$O$_4$@PPy heterostructure was created using the following steps:

**Step (i)** 1 mmol of C$_7$H$_7$SO$_3$Na and 20 ml of D.I/ethanol was taken and the solution was stirred for a few minutes to ensure uniform mixing. After that, 2 mmol of pyrrole monomer was dispersed to the aforesaid homogeneous solution (Solution A).

**Step (ii)** 4 mmol of ammonium persulfate (NH$_4$)$_2$S$_2$O$_8$ dissolved in 30 ml D.I water and stirred for a few seconds (Solution B).

**Step (iii)** The bundle of Nanosheet MgCo$_2$O$_4$ product was taken in a clean and pure 100 ml beaker. Solution A was then added to the case, one drop at a time. After a few minutes, add solution B to the continuous polymerization process at 0–6 °C for 3–5 h in a dark environment.

**Step (iv)** The polymerization product was then cleaned with ethanol and D. I water for removing certain slags, the slag free heterostructure MgCo$_2$O$_4$@PPy was dried overnight at 60 °C in a hot air oven. Finally, we built a Nanosheet and Nanspherical coated MgCo$_2$O$_4$@PPy nanomaterial. Figure 1 shows the schematic representation of the MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy nanomaterials synthesis procedure.

### 2.4 Instrumentation analysis

The crystallographic structure of prepared materials was analysed using the XRD technique (Bruker model CuK radiation ($\lambda = 1.5406$)). The surface morphology of prepared materials was analysed using the FSEM instrument (JEOL version JSM6390LV). The elements present in the prepared materials were identified using the EDAX technique (JEOL version JED-2300). The surface area and pore size distribution of prepared materials were analyzed using BET and BJH techniques (Nova 2200e model). Electrochemical behaviours of prepared samples were analysed using a Bio-logic sp-350 and Swagelok cylindrical type instrument (TMAX-type cell).

### 2.5 Electrode fabrication

In a three-electrode setup, Ag/AgCl serves as the reference electrode, while platinum serves as the
counter electrode. The working electrodes were MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy. The working electrode was made with active material (80%): conducting carbon (15%): PVDF (5%) was finely ginned, and a few drops of N-methyl 2-Pyrrolidone solution were added to make a slurry, which was then applied to a Ni Foam (1 × 3 cm) substrate and dried at 60 °C in a hot air oven. In a 2 M KOH electrolyte solution, the potential window was 0.0 V to 0.5 V, with diverse sweep rates ranging from 5 mVs$^{-1}$ to 100 mVs$^{-1}$ and varying current densities ranging from 1 Ag$^{-1}$ to 5 A g$^{-1}$. Two electrode systems were employed to analyse the Swagelok cylindrical type instrument (TMAX-type cell): cathode as MgCo$_2$O$_4$@PPy and Anode as activated carbon with 2 M KOH Gel electrolyte solution.

3 Results and discussion

3.1 X-ray results

Figure 2 shows XRD results of pure polypyrrole, MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy composite materials. The aforementioned samples have no extra feature peaks, indicating that they are very pure. The XRD pattern clearly shows that the magnesium cobaltite was formed by inserting magnesium into cobalt oxide, which was made possible at a little higher temperature (400 °C for 3 h). There are seven prominent diffraction peaks in the XRD patterns of material at $2\theta = 31.03^\circ$, 36.81°, 38.27°, 44.60°, 55.19°, 58.89°, and 64.98°, respectively, which correspond to crystalline planes of (220), (311), (222), (400), (422), (511), and (440) according to MgCo$_2$O$_4$ (JCPDS NO. 02-1073). The synthesised MgCo$_2$O$_4$ product is predicted to have exceptional crystal quality, according to the crisp and strong diffraction peaks. The Mg$^{2+}$ and Co$^{3+}$ divalent and trivalent crystallographic arrangements in the MgCo$_2$O$_4$ FCC structure. To use the Scherrer equation [42],

$$D = \frac{K\lambda}{\beta\cos\theta},$$

where $D$ is the average crystallite size, ‘$\lambda$’ is the X-ray wavelength, ‘$\beta$’ is the x-ray peak’s width on the 2θ axis, which is commonly defined as full width at half maximum (FWHM), ‘$\theta$’ is the Bragg angle, $K$ is the Scherrer constant. Size distribution, crystallite shape, diffraction line indices, and the actual definition of $K$, ‘$\beta$’ whether it be FWHM or integral width, all have an impact on $K$ [43, 44]. Using the aforementioned equation, The XRD measurements revealed that the synthesised MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy products had crystal diameters of approximately 25.3 nm and 17.2 nm, respectively. The measured d-spacing for (311) planes was utilised to calculate the lattice properties of the cubic spinel MgCo$_2$O$_4$ nanomaterial. The computed lattice parameter of MgCo$_2$O$_4$ material was found to be 8.07 Å, which agrees well with the value that was previously reported at 8.09 Å [35]. No other external phases could be identified indicating the sample is built purely of MgCo$_2$O$_4$ nanostructures. Further analysis found that the MgCo$_2$O$_4$@PPy electrode exhibited lower values of the crystallographic parameters elastic strain (E), micro strain ($\phi$), dislocation density, and number of unit cells (n) [45] than the bare MgCo$_2$O$_4$ electrode are summarised Table 1.

3.2 Morphology analysis of MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy

FESEM, TEM and SAED results of MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy composite materials are shown in Fig. 3. With various magnifications, the FESEM result of bare MgCo$_2$O$_4$ nanomaterials exhibits a bundle of nanosheet like morphology (Fig. 3a, b). FESEM pictures of MgCo$_2$O$_4$@PPy composite material are
shown in Fig. 3c, d. The MgCo₂O₄@PPy composite material has heterostructure morphology similar to that of a surface coated (Nano-spherical) nanosheet. The nanosheets were surface coated on nanospherical after the polymerization process. The heterostructure is a structure that is utilised to improve the electrochemical behaviour of the ion transport process. The EDAX result of MgCo₂O₄@PPy composite material is shown in Fig. 3e, which confirms the identity of Mg, Co, O, and N without any impurities. TEM pictures of MgCo₂O₄ and MgCo₂O₄@PPy composite materials with various magnifications are shown in Fig. 3a, b shows FESEM images of pure MgCo₂O₄ material; c, d shows the FESEM image of MgCo₂O₄@PPy composite material; e shows EDAX result of MgCo₂O₄@PPy composite material; f–h shows TEM images of pure MgCo₂O₄ and MgCo₂O₄@PPy composite material. i Depicts SAED pattern of MgCo₂O₄@PPy composite material.

### Table 1 Kinetic parameters of XRD results

| S. no | Material          | Crystalline size (D) | Elastic strain (E) | Microstrain (ε) × 10⁻³ m | Dislocation density (δ) × 10¹⁵/m² |
|-------|-------------------|----------------------|--------------------|--------------------------|----------------------------------|
| 1     | MgCo₂O₄           | 25.3                 | 0.399              | 0.426                    | 1.562                            |
| 2     | MgCo₂O₄@PPy       | 17.2                 | 0.439              | 0.554                    | 3.380                            |
shown in Fig. 3f–h. The nanosheet and spherical-like morphology are visible in the TEM images. The SAED pattern of MgCo$_2$O$_4@$PPy composite materials is shown in Fig. 3i.

### 3.3 N$_2$ adsorption and desorption

The surface area and pore size distribution were determined using Burner–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) analyses. The surface area and pore size distribution of MgCo$_2$O$_4$ and MgCo$_2$O$_4@$PPy materials are shown in Fig. 4a. Based on IUPAC classifications, the plot clearly shows that both electrodes are mesoporous, as indicated by the Type IV isotherm with H3 hysteresis loop. This loop’s observed P/Po ranges from 0.6 to 1.0. The bare MgCo$_2$O$_4$ electrode has a BET surface area of 76 m$^2$/g, whereas the MgCo$_2$O$_4@$PPy electrode has a massive surface area of 103 m$^2$/g. The BJH method was used to analyse the pore size values. The pore diameters of pure and composite electrode materials are 20 nm and 9 nm, respectively. Electrodes with a tiny pore size and the high surface area will perform better electrochemically. The porous and broad surface structure will supply a large number of ions or electrons, an excellent interacting electrolyte contact, and a fast faradaic redox reaction [46]. In the MgCo$_2$O$_4$ electrode sample, the polypyrrole (PPy) coated MgCo$_2$O$_4$ (MgCo$_2$O$_4@$PPy) electrode has a higher surface area than the MgCo$_2$O$_4$ electrode. This is owing to the interconnected nonspherical structure of PPy, which has more nanogap and nanopores. After covering PPy, the 1D spherical reveals the FESEM picture. The hybrid heterostructure (Nanosheets interconnect with nano spherical) provided extensive active sites for the adsorption and desorption processes, as well as ion–electron travel, resulting in good capacitive performance.
3.4 XPS analysis

XPS was used to analyse the oxidation states of elements and chemical compositions of the heterostructure of MgCo$_2$O$_4$@PPy nanocomposite as shown in Fig. 4b–f. The survey spectrum of MgCo$_2$O$_4$@PPy nanocomposites contains Mg, Co, O, and N, as shown in Fig. 4b. Figure 4c shows the XPS spectrum of Mg 1 s and Mg 2p. The Mg 1 s spectrum, which in the image exhibits a binding energy of around 1305.9 eV, serves as evidence of the existence of the Mg element from the MgCo$_2$O$_4$. The peak location of Mg 2p, which emerges around a binding energy of 51.05 eV and indicates the existence of a magnesium element with a $^{2+}$ valence in the MgCo$_2$O$_4$ sample, is shown in an expanded spectrum in Fig. 4c (insert) [47]. The magnified spectrum of Co 2p$_{1/2}$ and Co 2p$_{3/2}$ is clearly shown in Fig. 4d. The two prominent peaks are those of Co 2p$_{1/2}$ and Co 2p$_{3/2}$, which have binding energies of 795.6 and 781.8 eV, respectively [48]. The peak of Co$^{2+}$ and Co$^{3+}$ correspond to the peak at 781.8 eV, which makes up the peak of Co 2p$_{3/2}$ and the peak at 796.4 eV, which makes up the peak of Co 2p$_{1/2}$ respectively. In Fig. 4e, the binding energies for the three oxygen contributions in the O1s spectrum, O1, O2, and O3, are 529.5, 531.8, and 532.4 eV, respectively [49]. Water molecules that are present in the bulk phase or surface of the material are responsible for the very low peak at 532.4 eV (O3). The strongest peak, located at 531.4 eV (O2), is related to crystal imperfections, contaminant levels, an abundance of internal or external hydroxyls, chemical oxygen adsorption, lattice coordination, and intrinsic properties of the materials. The normal metal–oxygen (Mg/Co–O) bonds are compatible with the low intensity peak at 530.5 eV (O1). Figure 4f shows a single N1s signal for polypyrrole at 399.0 eV, which is attributed to the nitrogen ion’s structure (like = N$-$) [50].

3.5 Application studies (electrochemical)

3.5.1 Analysis of cyclic voltammetry (CV)

Figure 5a–c illustrates the electrochemical cyclic voltammetry data of pure polypyrrole, MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy composite electrodes. The cyclic voltammetry analysis of pure polypyrrole, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy composite electrodes were examined using 2 M KOH electrolyte solution at various sweep speeds ranging from 5 to 100 mV s$^{-1}$. The CV curves of the three electrodes show large and visible redox peaks, demonstrating the material’s pseudocapacitive properties. From CV, the specific capacitance values of pure polypyrrole, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy electrodes are 202, 412, and 534 F g$^{-1}$ at 5 mV s$^{-1}$, respectively. The CV investigation involved several sweep rate currents at various diffusion-controlled (faradaic) and surface controlled (capacitive) conduct charge storage systems. A power law [51] governs the relationship between log ip and log v for both behaviours.

\[ i_p = a \cdot v^b. \]  

The charge collected on the surface controls redox processes in electrolyte ions, which explains a statement of Log I propositional log v. The composite electrode b value of anodic and cathodic peaks positioned at 0.45 and 0.57 indicates a semi-infinite diffusive regulated mechanism for faradaic behaviour. The R–S equation [52] describes the link between peak current and sweep rate in a Trasatti technique equation-based diffusion-controlled process. The total capacitance of the MgCo$_2$O$_4$@PPy composite electrode is shown in Fig. 5g. The total capacitance of the MgCo$_2$O$_4$@PPy electrode was examined using the square root of scan rates vs capacitance. The plot shows the total capacitance values of 999 F g$^{-1}$. Figure 5h illustrates the capacitive contribution of MgCo$_2$O$_4$@PPy electrode which exhibits 5.7%, 6%, 8%, 9.4%, 10.8%, 11.9% and 13.8% of 5, 10, 20, 40, 60, 80, and 100 mVs$^{-1}$, respectively.

3.5.2 Analysis of galvanostatic charge–discharge (GCD)

Figure 6a–c displays the GCD results of pure PPy, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy composite electrodes with different current densities of 1 Ag$^{-1}$ to 5 Ag$^{-1}$. The GCD profile clearly shows non-linear curves, which could be related to the electrodes’ pseudocapacitive nature. The specific capacitance values of pure PPy, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy composite electrodes are 137, 692, and 988 F g$^{-1}$, respectively, at a low current density of 1 Ag$^{-1}$, as shown in Fig. 6d–
f. The capacitance retention of MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy electrode materials after 10,000 cycles is shown in Fig. 6g, h. After 10,000 cycles, the capacitive retention of pure MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy electrodes is 79% and 93%, respectively.

3.5.3 Analysis of electrochemical impedance spectroscopy (EIS)

Supercapacitor development has depended heavily on impedance spectroscopy measurements. In most impedance data, $Z'$ and $Z''$ represent the real and imaginary components, respectively. The EIS of pure PPy, MgCo2O4, and MgCo2O4@PPy composite electrode materials is shown in Fig. 6i. The intersection of the curve at real part $Z'$ represents the internal resistance ($R_s$), which is the total of the electrolyte’s ionic resistance, active materials’ intrinsic resistance, and contact resistance at the active material-collector interface. The MgCo$_2$O$_4$@PPy, MgCo$_2$O$_4$ and PPy electrodes had internal resistances of 0.3, 3.4 and 6.5 Ω, respectively. The semicircle of the MgCo$_2$O$_4$@PPy electrode has a substantially smaller diameter than the semicircle of the MgCo$_2$O$_4$ and PPy electrode, indicating that the ppy coating improved charge transfer over bare materials. The PPy, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy composite electrodes had charge transfer resistances of 19, 17, and 13 Ω, respectively.
The values of every electrode’s EIS kinetic parameters are shown in Table 2.

### 3.5.4 Fabrication of MgCo$_2$O$_4$@PPy//AC based asymmetric supercapacitor (ASC) applications

The asymmetric supercapacitor of the MgCo$_2$O$_4$@PPy//AC device was built using the Swagelok instrument. The cell was assembled by Cathode material as MgCo$_2$O$_4$@PPy and anode materials like activated carbon with gel type 2 M KOH/PVA electrolyte solution. The comparison CV results of the MgCo$_2$O$_4$@PPy electrode and the activated carbon electrode are shown in Fig. 7a. Figure 7b, c depicts the CV and GCD result of an asymmetric device with various scan speeds ranging from 5 to 100 mVs$^{-1}$ and current density ranging from 1 to 5 Ag$^{-1}$. Figure 7d electrodes with different current densities 1 Ag$^{-1}$ to 5 Ag$^{-1}$; a GCD result Pure Polypyrrole electrode; b GCD result of bare MgCo$_2$O$_4$ electrode; c GCD result of MgCo$_2$O$_4$@PPy electrodes; d-f depicts specific capacitance values of pure polypyrrole, MgCo$_2$O$_4$, and MgCo$_2$O$_4$@PPy material as MgCo$_2$O$_4$@PPy and anode materials like activated carbon with gel type 2 M KOH/PVA electrolyte solution. The comparison CV results of the MgCo$_2$O$_4$@PPy electrode and the activated carbon electrode are shown in Fig. 7a. Figure 7b, c depicts the CV and GCD result of an asymmetric device with various scan speeds ranging from 5 to 100 mVs$^{-1}$ and current density ranging from 1 to 5 Ag$^{-1}$. Figure 7d

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**Table 2** Various EIS parameters of prepared Polypyrrole, MgCo$_2$O$_4$ and MgCo$_2$O$_4$@PPy electrode materials

| Electrode       | $R_s$ (Ω cm$^2$) | $R_{ct}$ (Ω cm$^2$) | CPE (μF/cm$^2$) | Zw | $C_p$ (F/cm$^2$) |
|-----------------|------------------|---------------------|-----------------|----|-----------------|
| Polypyrrole     | 6.5              | 19                  | 2.82            | 9.12 $\times$ 10$^{-11}$ | 2.86 |
| MgCo$_2$O$_4$   | 3.4              | 17                  | 3.38            | 9.74 $\times$ 10$^{-11}$ | 3.12 |
| MgCo$_2$O$_4$@PPy | 0.3             | 13                  | 5.36            | 10.34 $\times$ 10$^{-11}$ | 4.599 |
shows the specific capacitance values of ASC device delivers 98 Fg⁻¹ at a current density of 1 Ag⁻¹.

The b value of the ASC device anodic and cathodic values of 0.5 to 0.8 ranges reveal semi-in restricted diffusive behaviour for pseudo-capacitive nature, as shown in image 7 (e). Figure 7, g illustrates the total capacitance and capacitive contribution of the ASC device. For ASC devices, the capacitive contribution ratio for various sweep rate values is 15%, 20%, 27%, 37%, 60%, 63% and 83% for various sweep rates. This ASC device’s cyclic stability is 84% after 10,000 cycles with a high current density of 5 A g⁻¹. The schematic representation of the MgCo₂O₄@PPy//AC charge storage mechanism is shown in Fig. 8a. When compared to the Ragone plot of the newest MgCo₂O₄-based ASC device results in Fig. 8b, the
manufactured ASC device provides a high energy density of 40 W h kg$^{-1}$ and a massive power density of 1544 Wh kg$^{-1}$ at a low current of 1 A g$^{-1}$. These are exceptionally high values when compared with the other MgCo$_2$O$_4$ based ASC devices, such as MgCo$_2$O$_4$ Nanosheet//AC (12.99 Wh kg$^{-1}$; 448.9 Wh kg$^{-1}$) [53], MgCo$_2$O$_4$ THSs//AC (30.6 Wh kg$^{-1}$; 861 Wh kg$^{-1}$) [54], MgCo$_2$O$_4$@PPy//AC (33.4 Wh kg$^{-1}$; 320 Wh kg$^{-1}$) [47], MgCo$_2$O$_4$@NiMoO$_4$//AC (37.5 Wh kg$^{-1}$; 480 Wh kg$^{-1}$) [55], MgCo$_2$O$_4$ SMPs//AC (39.7 Wh kg$^{-1}$; 396 Wh kg$^{-1}$) [56].

4 Conclusion

In this work, the bundle of MgCo$_2$O$_4$ nanosheets and heterostructure of MgCo$_2$O$_4$@PPy materials were synthesized using hydrothermal and chemical polymerization methods. The morphology result of the pure MgCo$_2$O$_4$ sample exhibits a bundle of nanosheets and composite material exhibits heterostructure morphology of nanosphere coated nanosheet. In this heterostructure, morphology improves electrochemical behaviour. XPS data confirm the oxidation state and chemical composition of the MgCo$_2$O$_4$@PPy material. The BET and BJH results show that the MgCo$_2$O$_4$@PPy material has a high surface area of 103 m$^2$ g$^{-1}$ and the smallest pore size of 9 nm in the mesoporous region, implying that they may easily interact with the electrolyte, which is important for obtaining outstanding electrochemical performance. The electrochemical behaviours were analysed using three and two electrode systems. Based on CV results, it can be concluded that the MgCo$_2$O$_4$@PPy electrode exhibits a semi-infinite diffusive controlled mechanism for faradaic analysis. According to the trasati method, the MgCo$_2$O$_4$@PPy electrode has a total capacitance of 999 F g$^{-1}$ and a capacitive contribution of 5.7% at 5 mV s$^{-1}$. In a three-electrode system, the MgCo$_2$O$_4$@PPy electrode delivers high specific capacitance of 988 F g$^{-1}$ at low current 1 A g$^{-1}$ compared with pure electrode materials of PPy, MgCo$_2$O$_4$, respectively. Based on CV results, it can be concluded that the assembled a ASC cell exhibits a semi-in restricted diffusive behaviour for pseudocapacitive nature. According to the trasati method, the ASC cell has a capacitive contribution of 15% at 5 mVs$^{-1}$. The MgCo$_2$O$_4$@PPy //AC ASC cell has a high specific capacitance of 98 F g$^{-1}$ at 1 A g$^{-1}$ and an 84% capacitive retention after 10,000 cycles. The MgCo$_2$O$_4$@PPy //AC ASC cell has a massive energy density of 40 W h kg$^{-1}$ and a power density of 1544 Wh kg$^{-1}$ when fully built. Overall, the synthesized MgCo$_2$O$_4$@PPy proves to be an efficient electrode material for supercapacitor application.

Author contributions

SS, MK, RB, SN and SS study conceptualization and writing (original draft) the manuscript, MP editing the manuscript.
Data availability

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Declarations

Conflict of interest The authors declare they have no conflicts of interest.

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