



Haemoglobin/polyindole composites: the novel material for electrochemical supercapacitors

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Abstract. Conducting polymers have recently been employed with metal derivative macromolecules that have led to great improvement in the field of supercapacitor materials. The current work reports on the synthesis of a novel class of haemoglobin/polyindole composites (HPCs) through doping of haemoglobin (Hb) into a polyindole (PIN) matrix. HPCs with enhanced electrocapacitive performance were prepared through a cationic surfactant-assisted dilute solution polymerization of indole (IN) in the presence of Hb at various concentrations ranging from 10 to 30% (w/w) and ferric chloride (FeCl_3) as an oxidant. The HPCs were characterized through Fourier transform infrared spectra, scanning electron microscopy and simultaneous thermogravimetric analysis. Electrochemical capacitance (C_s , F g^{-1}) of graphite-based electrodes fabricated from HPCs over stainless steel in the presence of sulphonated polysulphone as a binder has been investigated in KOH solution (1.0 M) with reference to Ag/AgCl at a scan rate (V s^{-1}) ranging from 0.001 to 0.2. HPCs with 30% (w/w) of Hb have shown the highest C_s of 294.00 as compared with 112.00 for pure PIN at a scan rate of 0.001 V s^{-1} . Successive scans of HPC electrodes show a capacitive decline of $\sim 2\%$ during the first 1000 cycles at a scan rate of 0.1 V s^{-1} in KOH (1.0 M), which indicates the appreciable electrochemical cyclic stability of the HPCs over PIN. Thus, the fabricated HPCs may serve as potential electrode material for development of electrochemical supercapacitors.

Keywords. Polyindole; haemoglobin; electrochemical capacitance; supercapacitors.

1. Introduction

The demand for sustainable and cost-effective energy storage has recently been of prime importance. This led to transformed scientific and commercial attention in advanced supercapacitor electrode material. In recent years, polymer composites (PCs) have attracted considerable attention worldwide due to their technological applications in electrochemical power sources such as rechargeable batteries, fuel cells, supercapacitors etc. For the best-possible conservation and storage of electrochemical energy, there has been growing demand for PCs derived through doping of transition metal ions into conducting polymers bearing high specific capacitance (C_s), reduced over potential at high charge–discharge rates and high cycling stability over long cycle life [1–3].

Among various conducting polymers, polyindole (PIN) has extensively been considered as an extrapolative material due to its straightforward polymerization [4], thermal stability, high-redox activity [5,6], tuneable conductivity and environmental stability that can be regulated by doping [7]. Modification of PIN with biomolecules has extensively been under investigation over past few decades. PIN functionalized with biomolecules are used as smart biomaterial for tissue

engineering [8]. Recently, PIN has been doped with TiO_2 [9], ZnO [10], NiO [11], CuO [12], Fe_2O_3 [13,14], MgO [15], Co_3O_4 [16] and haemoglobin (Hb) [17]. In this context, macrocyclic Hb-functionalized PIN were used in the development of supercapacitors.

Hb is an important redox respiratory protein in red blood cells. It is composed of four polypeptide chains with each having one iron haem group. Because of its commercial accessibility, judicious cost, high stability and high capability rate, Hb is considered as a perfect model for high electrochemical performance for supercapacitor applications [18]. This has been revealed that the electrically conducting composites derived through doping Hb into PIN display feasible electron transfer between haem sites and the PIN chains [19].

The current investigation provides a pioneer attempt towards development and characterization of the Hb/PIN composites (HPCs) bearing improved electrocapacitive performance and cyclic stability through cetyltrimethylammonium bromide (CTAB)-assisted dilute solution polymerization of PIN in the presence of Hb at concentrations ranging from 10 to 30% (w/w) and ferric chloride (FeCl_3) as an oxidant. This HPC was characterized by Fourier transform infrared spectra (FT-IR), scanning electron

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microscopy (SEM) and thermogravimetric analysis (TGA). The sulphonated polysulphone (SPS)-bound electrodes of HPCs with 30.0% (w/w) of Hb over stainless steel (SS) display a relatively higher C_s of 294.00 at a scan rate of 0.001 V s^{-1} with $\sim 2\%$ electrocapacitive decrease during the first 1000 cycles at a scan rate of 0.1 V s^{-1} in KOH solution (1.0 M) with reference to Ag/AgCl. In this context, at present no consistent attempt has been made at the synthesis and studies on electrochemical supercapacitance behaviour of the proposed HPCs.

2. Experimental

2.1 Starting materials

Commercially available Hb (Otto Kemi, India), indole (IN, SD Fine Chemicals), polysulphone (M_n , 26,000, $\rho = 1.24 \text{ g cm}^{-3}$, Aldrich Chemicals), chlorosulphonic acid ($\geq 99\%$, Aldrich Chemicals), CTAB ($\geq 99\%$) and graphite ($\geq 98.0\%$) were purchased from Otto Chemicka-Biochemica. Other chemicals and solvents were of AR grade. All chemicals and solvents were used without further purification.

2.2 Synthesis of HPCs

A series of HPCs for development of supercapacitor electrodes was synthesized. The process of synthesis was executed through CTAB (1.15 g , $3.50 \times 10^{-3} \text{ mol dl}^{-1}$)-assisted dilute solution polymerization of IN (0.12 mol dl^{-1}) in the presence of FeCl_3 (30 ml , $1.85 \times 10^{-2} \text{ mol dl}^{-1}$) along with requisite concentrations of Hb ranging from 10 to 30% (w/w). The contents were under mechanical stirring at the rate of 500 rpm over 24 h at $30 \pm 1^\circ\text{C}$. HPCs were obtained through centrifugation at 5000 rpm over 15 min, followed by filtration, washing and drying at $50 \pm 1^\circ\text{C}/400 \text{ mmHg}$ for over 8 h. PIN was also synthesized under identical reaction conditions and served as the control [20].

2.3 Preparation of SPS

SPS used as a binder and one of the components in the matrix was synthesized through sulphonation of polysulphone resin (PSO) with chlorosulphonic acid in dichloromethane (DCM) as described previously [21]. The precipitated SPS was filtered off and consecutively washed with aqueous solution of sodium hydroxide (10%, w/v) for the removal of unreacted chlorosulphonic acid. Finally, the polymer was washed with distilled water to remove traces of solvent until neutral water was obtained and it was dried at $80 \pm 1^\circ\text{C}$ overnight.

2.4 Fabrication of working electrodes

Prior to use, commercially available 316-SS with 1 cm^2 was de-greased with acetone and subjected to surface oxidation at $50 \pm 1^\circ\text{C}$ for 1 h in a vacuum. The working electrode materials were prepared by mixing an electroactive material

(65 mg), graphite (10 mg) and SPS (5 g dl^{-1}) in *N*-methyl pyrrolidone (NMP). The contents were ultrasonicated for 20 min. The resultant slurry ($100 \mu\text{l}$) was pressed on a SS substrate which acts as a current collector. The treated substrate was dried at room temperature for 5 h, followed by $50^\circ\text{C}/400 \text{ mmHg}$ for 48 h. This has afforded working electrodes with mass thickness of electroactive materials by $0.05 \pm 0.01 \text{ mg}$ over the SS substrate. The electrodes were tested after 24 h of fabrication [20].

2.5 Material characterization and analysis conditions

FT-IR spectra were recorded on a Thermo Nicolet in KBr from 4000 to 500 cm^{-1} in transmission mode. SEM of the gold-coated specimens was performed on a Hitachi S 3700 N at a primary beam voltage of 15 kV. For this purpose, the electrodes were prepared *via* the above-mentioned procedure. The scales of SEM images were between 10 and $30 \mu\text{m}$. The corresponding magnifications ranged from 5.5 to $1.0 \text{ k}\times$.

TGA was performed on an EXSTAR TG 6300 with sample weight ranging from 2.16 to 6.64 mg under N_2 at the rate of 30 ml min^{-1} from ~ 20 to 800°C .

All the electrochemical characterizations were made over the electrodes prepared for supercapacitor applications. Electrodes were electrochemically characterized in KOH (1.0 M) over an IVIUM Potentiostat–Galvanostat (Netherlands) using a three-electrode cell assembly. Ag/AgCl was used as a reference electrode. Pt foil with a 1 cm^2 area was used as a counter electrode. A commercially available SS electrode served as a working electrode. Cyclic voltammetry (CV) was conducted at current compliance of 1 mA in the range of -1.5 – 0.0 V at 0.1 V s^{-1} . All the measurements were performed at room temperature. Specific capacitance (C_s) of the electroactive material was calculated from the voltammetric charges by the CV curve, by means of the below relation:

$$C_s = q_a + |q_c|/2m\Delta V$$

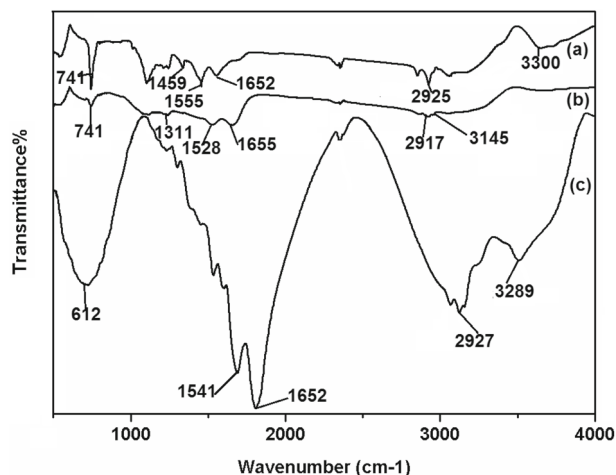


Figure 1. FT-IR spectra of (a) PIN, (b) HPCs and (c) Hb.

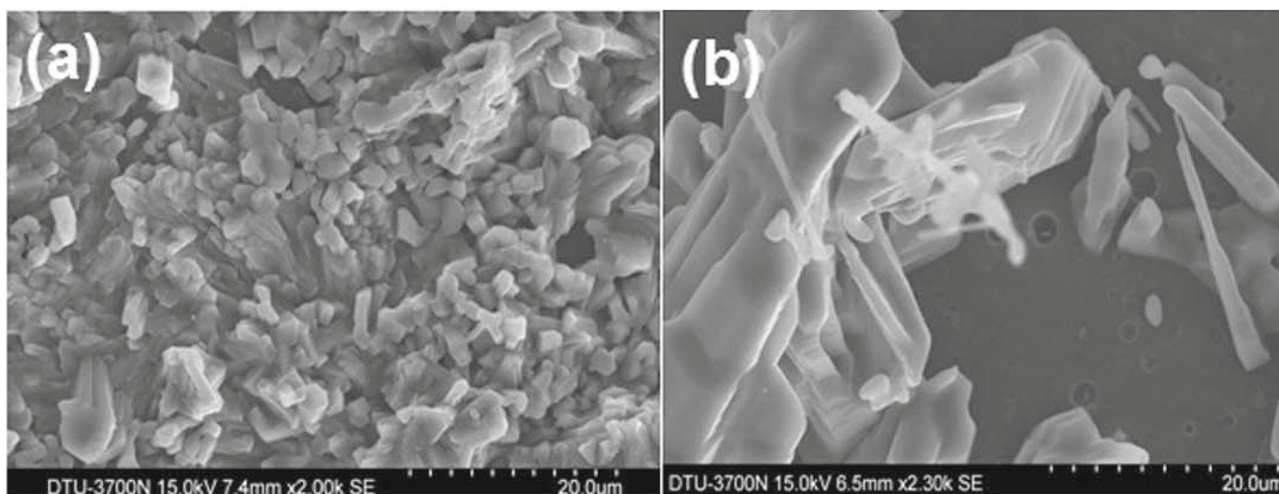


Figure 2. Change in CTAB-assisted polymerization of IN from granular (a) to the flaky morphology of Hb dispersed in the PIN matrix HPC (30%) (b).

where q_a and q_c are the voltammetric charges at anodic and cathodic scans in the capacitive potential region (ΔV) and m being the mass of the electroactive material.

3. Results and discussion

3.1 FT-IR spectra

Figure 1 shows the major assignments of FT-IR spectral absorption concerned with Hb, PIN and representative HPCs synthesized at a Hb concentration of 30% (w/w). FT-IR spectra reveal that most of the assignments of PIN and Hb are retained in the HPC spectra from 500 to 1750 cm^{-1} . Hb shows characteristic absorption (cm^{-1}) at $\nu\text{O-H}$ (3289), which disappeared in the absorption spectra of HPCs, thus confirming the interaction of the carboxylic group of the Hb moiety with the secondary amine group of PIN. The other characteristic absorptions of Hb are $\nu\text{C=O}$ (1652), $\nu\text{C-N}$ (1541), $\delta\text{C-O}$ (612) [22,23] and $\nu\text{C-H}$ (2927). PIN shows characteristic FT-IR absorptions corresponding to $\nu\text{N-H}$ (3300) [24], $\nu\text{C-H}$ (2925) [25], $\nu\text{C=C}$ Ar (1652) [26], $\nu\text{C-C}$ (1459) [26], $\nu\text{C-N}$ (1555) and $\nu\text{C-H}$ out-of-plane deformation (741) [24,27]. HPCs show characteristic absorptions at $\nu\text{N-H}$ (3145), $\nu\text{C-H}$ (2917), the peaks $\nu\text{C=O}$ (1655) and $\nu\text{C-N}$ (1528) cm^{-1} are nearly similar to those of Hb, $\nu\text{C=C}$ (1311) and $\nu\text{C-H}$ out-of-plane deformation (741). Thus, the FT-IR results reveal possibly some interactions of Hb with the matrix of PIN as well as the successful combination of both components.

3.2 Microstructure

To have further insight into the qualitative dispersion of Hb into the PIN matrix, the SEM images have been recorded.

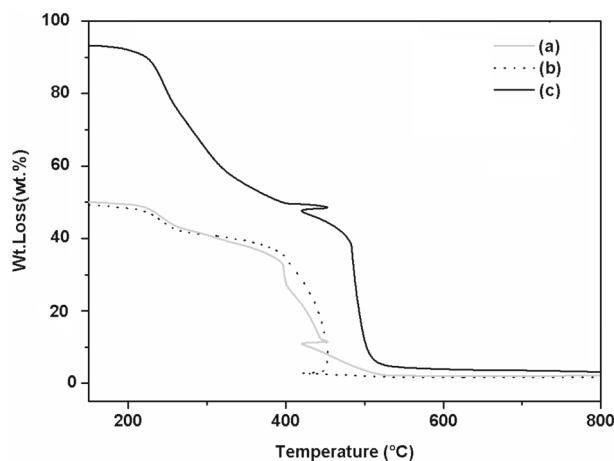


Figure 3. Thermograms of (a) PIN, (b) HPCs and (c) Hb.

Figure 2 shows the SEM images of the electrodes derived from PIN and representative HPCs which were obtained under identical conditions at 15.0 k \times . In agreement with the reported literature, the electrode derived from PIN prepared in the presence of SPS as the binder has delivered the distinctive micro-rod-shaped grains with granular morphology at 20 μm [24,28]. Such rod-shaped micro-sphere formation is the characteristic of PIN irrespective of their adopted method of synthesis under the preparation of electrode (figure 2a). Further increase in magnification is shown in Supplementary figure S4. The SEM of Hb aggregates stabilized into buffers [29] and non-conducting polymers has been well documented [30]. A comparative analysis of such SEM documentation with the current one reveals a similar kind of co-continuous morphology of the Hb electrode used under the current investigation. To the best of our knowledge, no reports have been reported on the morphology of

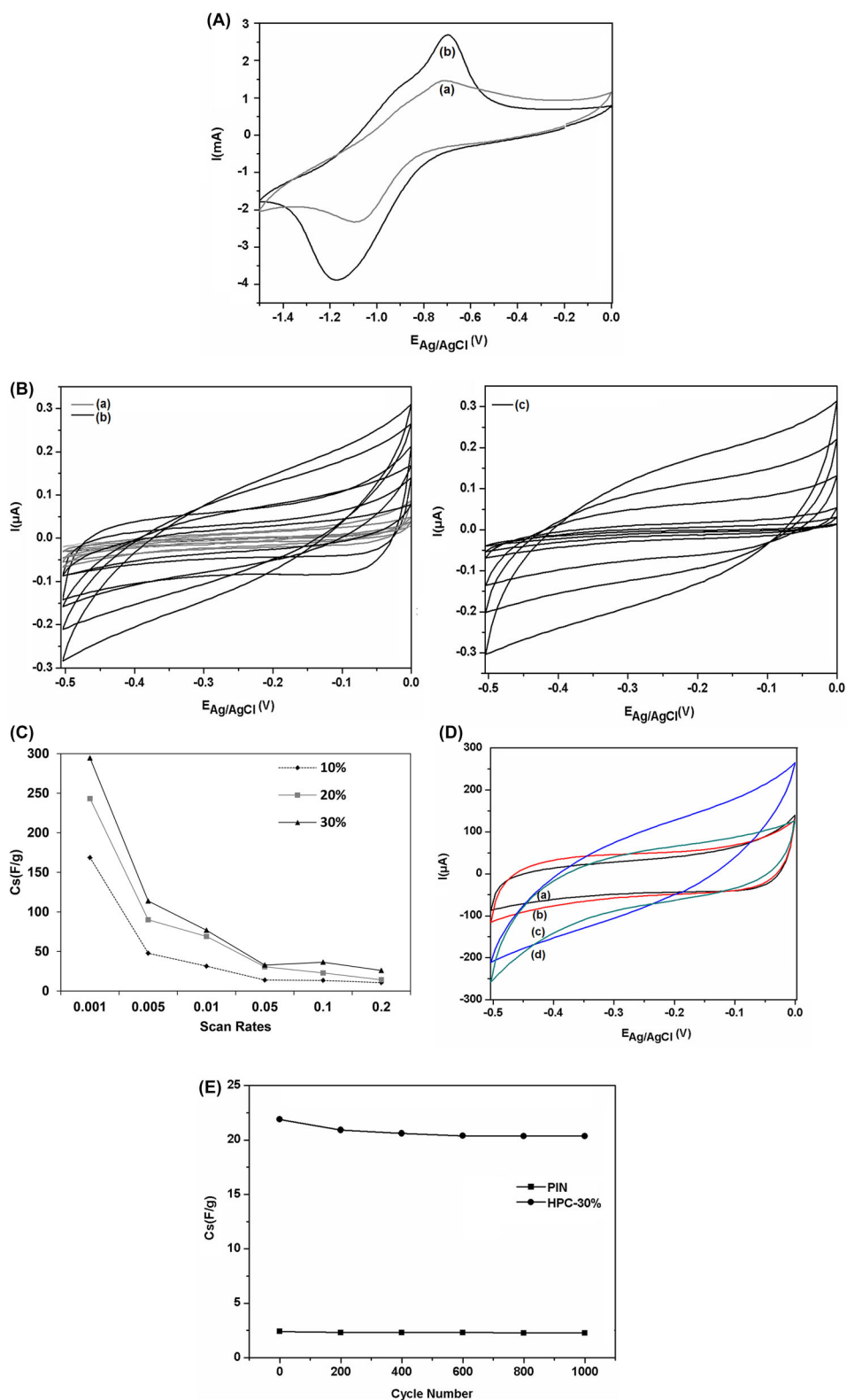


Figure 4. (A) CV of (a) PIN and (b) HPCs showing anodic and cathodic peaks at a scan rate of 0.1 V s⁻¹. (B) CV of (a) PIN, (b) HPCs (30%) and (c) Hb at scan rates of 0.001–0.2 V s⁻¹. (C) Comparative C_s of HPCs 10–30% (w/w). (D) CV of (a) PIN and HPCs with Hb (% w/w) (b) 10, (c) 20 and (d) 30 at a scan rate of 0.1 V s⁻¹. (E) Effect of number of cycles on the C_s and stability.

the composites derived through doping of Hb into conducting polymers. The SEM micrograph of HPCs synthesized at 30% (w/w) of Hb shows a surprising change. The microrods that were observed in the PIN vanished in the presence of Hb and the characteristic non-uniform allocation of the grains that appeared flaky in morphology. Such surface characteristics may be due to the formation of the HPCs [31] (figure 2b). For the amorphous nature, the XRD spectra of Hb, PIN and HPCs are shown in Supplementary figures S1–S3.

3.3 Thermal characteristics

Figure 3 shows the TGA curves of PIN, Hb and HPCs. In the case of PIN, the weight loss was observed in two stages at 201°C (5.1%) and 398°C (30.7%), the first one was due to physisorbed water molecules and volatile impurities while the second one was due to degradation of the unsaturated group in the polymer [10]. In the case of Hb, the first weight loss was observed at 190°C (9.1%), the second weight loss was observed at 339°C (42.6%) and the third weight loss was found at 504°C (50.7%). In HPCs, the first weight loss at 207°C (5.0%) is due to removal of oligomer molecules and the second weight loss up to 411°C (36.8%) is because of degradation of PIN. Thus, due to the presence of Hb, the HPCs are responsible for high-thermal stability compared with the polymer. In order to have further insights into thermal stability of the PIN and HPCs, their differential scanning calorimetry spectra (DSC) were recorded and represented in Supplementary figure S5.

3.4 Electrochemical performance

The electrochemical behaviour of PIN, Hb and respective HPC electrodes synthesized at Hb concentrations ranging from 10 to 30% (w/w) has been investigated for electrochemical supercapacitors. Cyclic voltammogram reveals a proportionality of peak current densities at a scan rate of 0.1 V s⁻¹ in the -1.5 to 0.0 potential range, which indicates the electroactive nature and reversible redox behaviour of PIN and HPCs [20]. The anodic and cathodic peak potentials of PIN and HPCs were almost independent of the scan rates figure 4A. All the materials represent CV curves close to a rectangular shape in the voltage range of -0.5–0.0 V at different scan rates of 0.001–0.2 V s⁻¹ in 1.0 M KOH and there is no current peak caused by a redox reaction, indicating a typical capacitive behaviour with good charge propagation of these materials. Electrochemical studies on PIN, Hb and HPCs give us exciting outcomes which demonstrate HPCs as quite proficient material for preparation and its development as a material for energy storage devices. With scan rate, a regular increase in the peak currents has been observed. In the cases of PIN, Hb and HPCs (30%), the C_s (F g⁻¹) of electrodes has been ranged from 8.39 to 112.00, 3.20 to 0.25 and 26.00 to 294.00, respectively (figure 4B). Figure 4C exhibits the intensification in specific capacitance with an increasing fraction of Hb (i.e., 10–30%, w/w); in the matrix

of the polymer a steady increase was observed in the specific capacitance of HPCs. Figure 4D illustrates the comparative histogram of specific capacitance of PIN and HPCs (10–30%) at a scan rate of 0.1 V s⁻¹, which demonstrates HPCs to be more super capacitive than PIN. These findings indicate that the doping of Hb with the PIN working electrode in KOH medium leads to the formation of conjugates between the carboxylic group of the Hb moiety with the secondary amine group of PIN, which enhance the surface-active sites of the HPCs. Such HPCs subsequently increase the active material usage because of rapid electron transfer in addition to the storage reservoir for ions. This result points towards the doping of Hb into PIN might open new avenues for the fabrication of a new generation of supercapacitors. This has further contributed to a corresponding increase in the C_s of the HPCs, with a capacitive decline of 2% during the first 1000 cycles at a scan rate of 0.1 V s⁻¹ that indicates improved cyclic stability of the HPCs over PIN, making them suitable for development of electrochemical supercapacitors (figure 4E).

4. Conclusions

CTAB-assisted dilute solution polymerization of IN in the presence of FeCl₃ as an oxidant with varying concentrations of Hb ranging 10–30% (w/w) had afforded a series of HPCs. FT-IR and SEM results determine the formation of HPCs. Simultaneous TGA reveals improved thermal stability of HPCs over PIN. Working electrodes derived from PIN and Hb have shown their respective C_s in the range of 112.00–8.39 and 3.20–0.25 F g⁻¹, respectively, at scan rates ranging 0.001–0.2 V s⁻¹ in KOH (1.0 M). With scan rate, a proportionate increase in the peak current densities of PIN and respective HPCs with cyclability of redox behaviour without their significant decomposition has been observed indicating their high electroactive nature and reversible redox behaviour. Working electrodes derived from HPCs with 30% (w/w) Hb rendered C_s of 294.00–26.00 F g⁻¹ at scan rates ranging 0.001–0.2 V s⁻¹. A capacitive retention of ~98% in the specific capacitance of HPC electrodes was observed for the first 1000 successive cycles at the scan rate of 0.1 V s⁻¹, thus illuminating good cyclic stability of the electrode material. The current efforts demonstrate a simple and economical way to synthesize commercial Hb and PIN composites. This shows the application of one of the potential electrode materials for development of electrochemical energy storage devices. The current research reflects its usefulness towards economically viable development of working electrode material for electrochemical supercapacitors.

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