

## Polyaniline-cobalt hydroxide hybrid nanostructures and their supercapacitor studies



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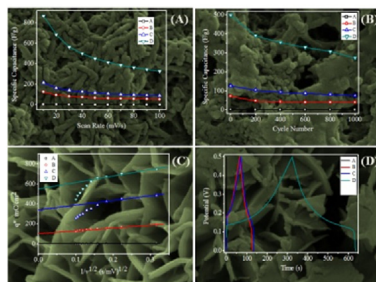
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### HIGHLIGHTS

- Adverse supercapacitive performance in hybrid electrode than pristine is explored.
- Change in structure and morphology of hybrid electrode compared with separate once has been attempted initially.
- Change in supercapacitive performance is explained on the basis of inner and outer charge contributions.
- Obtained results are corroborated using Nyquist spectra.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We attempt to demonstrate comprehensive analysis of experimentally obtained adverse supercapacitive performance of cobalt hydroxide (Co(OH)<sub>2</sub>)-polyaniline (PANI) hybrid nanocomposites (HNs), prepared potentiostatically via electrochemical deposition method, compared to phase pure individual nanostructures. Morphologically amorphous Co(OH)<sub>2</sub>, PANI and HNs are entirely different from one another. The electrochemical properties of the Co(OH)<sub>2</sub>, PANI and HNs electrodes have been investigated by cyclic voltammograms, galvanostatic charge-discharge and electrochemical impedance spectroscopy measurements. The specific capacitances of PANI, HNs and Co(OH)<sub>2</sub> are found to be 3.06F/g, 215F/g and 868F/g, respectively, at a sweep rate of 10 mV/s in 1.0 M NaOH electrolyte, whereas the stabilities and voltammetric charges, assigned to these electrodes, are 47%, 60% & 55% (after 1000 cycles) and 17.22 mC/cm<sup>2</sup>, 836.39 mC/cm<sup>2</sup> and 1128.73 mC/cm<sup>2</sup>, respectively. Obtained adverse (inferior) supercapacitive performance values of HNs electrodes have been demonstrated on occurrence of inner and outer charges concept. Our work demonstrates plausible causes for observed smaller supercapacitor performance in

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hybrid/composite nanostructured electrodes (not a common practice) and useful to researchers working in composite/hybrid symmetric and asymmetric supercapacitor fields.

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## 1. Introduction

Batteries, fuel cells and electrochemical supercapacitors (ESs) are electrochemical energy conversion and storage devices, wherein batteries exhibit lower power and higher energy density and traditional capacitors demonstrate higher power and lower energy density [1]. Therefore, ESs with higher power as compared to batteries, higher energy density than the traditional capacitors, and function as a bridge between batteries and traditional capacitors [2], have attracted considerable attention in portable, reliable and environmentally friendly commercial electrochemical devices [3]. Based on energy storage mechanism, ES are of two categories viz. electrical double layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, the electrostatic charge accumulation occurs at the interface between the surface of electrode and the electrolyte i.e. electroadsorption of electrolyte ions on materials like porous carbon. EDLCs provide relatively higher power and excellent cyclability i.e. durability because of the involvement of non-degradative processes between the electrode and the electrolyte [4]. The performance of EDLCs is determined by the available electrode surface area and the finite charge separation between the electrode and the electrolyte [5]. Cathode materials include metal oxides/hydroxides, polymers or hybrid nano-composites. However, in a pseudocapacitors, the fast and reversible Faradaic reactions taking place near the surface confirm their energy storage capability [6]. Typically, the specific capacitance (SC) of a pseudocapacitor electrode is better than that of an electrode operating as an EDLC [7]. Pseudocapacitors provide higher energy densities but disadvantageously suffer from the durability test and are generally preferred in applications where high capacitance is desired. Polyaniline (PANI) is one the most employed conducting polymers from last four decades due to its low-cost, availability of simple synthesis methods, excellent environmental stability, and competitive redox reversibility by both charge transfer doping and protonation [8–10]. Backbone of *pi*-conjugated chains in PANI is responsible for an electrical conduction where the conjugation is due to overlap of the *pi* ( $\pi$ ) electrons of the carbon atoms and their wave function to form a sequence of alternating double and single bonds, resulting in unpaired electrons delocalized along the backbone chain. The delocalization of *pi*-electrons over the backbone is with low ionization potentials and high electron affinity [11]. The oxidation state of the polymer and its degree of protonation are essentially important during electrical conduction process of PANI [12]. Emeraldine state of the polyaniline, consists of equal proportion of amines ( $-\text{NH}-$ ) and imines ( $=\text{N}-$ ), is highly conducting state among all other existing states [13] whose base is an insulator, but on protonation it changes to the conducting form (emeraldine salt). It is reported that conductivity of emeraldine is due to the formation of polarons and bipolarons at the amines and imines in high acidic medium [14–16]. Similarly, the Faradaic supercapacitive behaviour of the PANI electrode is due to redox reversible electrochemical doping–dedoping of the protons, where PANI can be charged positively or negatively with ion insertion in the polymer matrix and the injected charge contributes to the total capacitance. In the redox reaction of the PANI, oxidation is considered as the de-protonation and reduction is protonation. The protonation and de-protonation processes are

taking place at amine and imine nitrogen groups, respectively. Therefore, protonic (acidic) medium is required for electrochemical behaviour of the PANI. Therefore, at solution  $\frac{[\text{H}^+]}{[\text{P}]} \geq 4$ , the emeraldine salt cannot form and thereby loses its electrical conductivity and also electrochemical activity [17–20].

The extension of electrochemical activity of PANI to high  $\frac{[\text{H}^+]}{[\text{P}]}$  medium is a quite challenging task. One has to introduce either acidic groups into the PANI ring chains or impede the de-protonation. For example in self-doped ring sulfonated polyaniline [21], the self doped *m*-aminobenzoic acid and *m*-aminobenzenesulphonic acid [22], the electropolymerized of poly(aniline) in the presence of poly(vinylsulfonate) counter ions [23], poly(styrenesulfonate) [24], poly-(acrylic acid) [25], camphorsulfonic acid [26], poly-(aniline boronic acid) [27], naphthalenesulfonic acid [28] and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) PAAMPSA [29], the redox activity of PANI has been improved (in neutral and alkaline aqueous solutions). However, its chemical as well as mechanical stabilities are unsatisfactory. By developing hybrid nanocomposites (HNs) of the PANI with other electrochemically active materials, one can improve the supercapacitive performance by the effect of size confinement and additional functionalities [4]. The HNs of the PANI and polypyrrole electrodes have confirmed an enhanced supercapacitive performance in neutral medium with poor stability [30]. The HNs of the PANI with other electrode materials are generally obtained by either mixing physically or by strong chemical bonding, to withstand electrode in alkaline medium. The HN of PANI-with activated carbon [31], carbon nanotubes [32], ordered mesoporous carbon [33] and carbonization of the PANI nanowires [34], three-dimensional graphene [35],  $\text{MnO}_2$  [36,37],  $\text{CoMoO}_4 \cdot 0.75\text{H}_2\text{O}$  [38],  $\text{WO}_3$  [39],  $\text{V}_2\text{O}_5$  [40] and graphene/ $\text{Fe}_2\text{O}_3$  [41] etc., have demonstrated a strong synergistic effect in literature due to which the electrochemical performance in neutral and/or alkaline medium has been considerably boosted.

In this work, we turned our attention to HN film electrodes based on PANI and cobalt hydroxide [ $\text{Co}(\text{OH})_2$ ], which were fabricated by using electro-polymerization of aniline onto a stainless-steel (SS) substrate and electrochemical deposition of  $\text{Co}(\text{OH})_2$  on PANI HNs processes. The electrochemical activities of the  $\text{Co}(\text{OH})_2$  film onto PANI i.e. HNs were investigated and compared with that of the pristine PANI and  $\text{Co}(\text{OH})_2$  film electrodes. Pristine PANI and  $\text{Co}(\text{OH})_2$  electrodes were also used separately for their supercapacitive measurements. To the best of our knowledge, there is no record in the literature of studying the electro-activity of the HN electrodes composed with PANI and  $\text{Co}(\text{OH})_2$  nanostructures in alkaline medium. The focus of the present work was to study electroactivities of pristine and HN electrodes and their comparison with detailed scientific understanding using inner & outer charge, cycling stability, charge-discharge and electrochemical impedance measurement studies.

## 2. Experiment section

### 2.1. Chemicals

All the chemicals were analytical reagent grade of Merck. Aniline monomer (99% pure), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), cobalt nitrate

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