Structure, morphology, thermal and electrochemical studies of electrochemically synthesized polyaniline/copper oxide nanocomposite for energy storage devices

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Abstract
Polyaniline (PANI)/copper oxide nano composite (PCN) was synthesized by electrochemical deposition method. The PCN nanocomposite was characterized by using Fourier transform infra-red (FT-IR) spectroscopy, x-ray diffraction (XRD), UV-Visible absorption spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Impedance analyser and electrochemical workstation methods. The FT-IR analysis shows proper chemical interaction of PANI with CuO nanoparticles. In XRD it is found that the amorphousity increases with increasing CuO concentration. The surface morphology observed changes from granular to rod shape structure and TEM gives the particle size range from 30–70 nm. UV-visible spectra shows increase the absorption and decreased the optical band gap with addition of nano composite concentration. The CV curve exhibits rectangular shape with high current density and specific capacitance ($C_{sp}$) was observed increases with increasing CuO nano concentration at various scan rates from 100–500 mVs$^{-1}$. The highest specific capacitance ($C_{sp}$) value 286.66 Fg$^{-1}$ was obtained for PCN1 nano composite. These results suggest that the PCN nano composite can be used in the energy storage device applications.

Introduction
Polyaniline (PANI) nano composites are broadly investigated due to its unique features like relatively high electrical conductivity, excellent environmental stability, easily synthesis, and promising potential applications. The main application domains are super capacitors, light emitting diodes, rechargeable batteries, electro chromic devices, electromagnetic interference shielding, and sensors [1–5]. PANI is a conjugated conducting polymer; its electrical conductivity depends upon the oxidation/reduction reactions. In the present study, PANI compositied with nano particles may enhance the physical properties. But still there are some unanswered questions like weak mechanical property and solubility are limits to be used in the numerous practical applications [6–8]. To overcome these problems the researchers followed various synthesis techniques like electro spinning, in situ synthesis, electrochemical and irradiation techniques as well as various concentration of monomer, catalysis, composites, nano composites and surfactant are used to obtained the stable material [9, 10]. There is a partial development has achieved so far, still it is essential to progress lot in this direction. As per the electrostatics, the electrochemical deposition is accurate and good quality product and the deposition takes place as per electrostatics [11]. The quality materials are prevented chemical hazards like swelling and shrink during the charges diffuse into electrolyte medium [12]. These polymer nano composites are showing good physical properties such as optical properties, morphology, structural phase and electrical conductivity [13–19]. Supercapacitor was classified into pseudo capacitor [20, 21] and electrical double-layer capacitor based on the energy storage mechanism [22]. In the present study, the PANI/CuO nano composites PCN has synthesized using electrochemical deposition method here the cyclic voltammetry range between the voltage window was −4 to 2 V, with specific capacitance ($C_{sp}$) value is 286.66 Fg$^{-1}$, the observed study of cyclic stability has the
maximum value obtained as compared with all the previous studies for same capacitance value \([23, 24]\). The PANI/CuO nano composites of electrochemically synthesized PANI-nickel oxide hybrid electrode are observed at 263 \(\text{F g}^{-1}\) and the mixed ion-electron conducting polymer PEDOT: PSS and sulfonated lignin has reported result was 230 \(\text{F g}^{-1}\) \([25, 26]\). Present work investigation the optical band gap, electrochemical performances, thermal studies, dielectric constant and dielectric loss, AC conductivity of electrochemically synthesized PANI/PCN nano composites. These obtained results shows the characteristics of energy storage devices, thus PANI/CuO nano composite material can be used in the energy storage device applications.

**Experimental methods**

**Materials**

Aniline monomer (99.9%) was distilled prior to use, copper (II) oxide (CuO), Ammonium per-sulphate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) all chemicals are purchased from Sigma-Aldrich and Hydrochloric acid (HCl), Potassium chloride (KCl) chemicals are purchased from Merck India.

PANI and PANI/CuO nanocomposite synthesized by electrochemical method

0.2M of 1 ml aniline was dissolved in 1M of 40 ml HCl and 0.2M of 2 gm ammonium per sulphate \((\text{APS})\) dissolved in 1M HCl of 40 ml stirred them separately. Using ice bath the freezing temperature was maintained and the APS solution added drop wise to aniline monomer. The CHI-660E electrochemical workstation instrument was used to electrochemically deposit on carbon electrode with applied voltage 2 volt and 900 s time allowed for sample deposition on the working electrode. The resultant precipitation product is PANI emeraldine salt (ES) with dark green in colour. Similar method was followed for different CuO nanocomposite concentrations 0.1, 0.5 and 1 gm and they have coded as PCN0.1, PCN0.5 and PCN1 respectively. The PANI polymerisation takes place through the chemical reaction between the aniline monomers in the organic phase and the APS in aqueous phase. The carbon electrode is used as a working electrode, platinum (Pt) and silver (Ag/AgCl) as reference and counter electrodes respectively.

The PANI sample was collected in a separate beaker and washed several times using distilled water and filtered with whatman paper, then dried at 60 °C in oven for about 24 hours. Finally, the sample was grind using pestle mortar to obtain the powder form. Fabrication of electrode by preparing the PCN nanocomposite paste with ratio (PCN/CuO: PVDF:HFE; Carbon; 80:10:10) using N-Methyl-2-pyrrolidone (NMP) solvent and pasted on stainless steel electrode using doctor blade method and dried at 40 °C hot air oven for about 24 hours. Schematic representation of the PANI/CuO nanocomposite deposited on Anode (+) by using electrochemical deposition method as shown in scheme 1.
Characterization techniques

The chemical interaction was analysed using a Fourier transform infrared (FT-IR) with model ALPHA BRUKER spectrometer in the spectral range of 2400–500 cm\(^{-1}\) and the surface morphology was analysed using a Sigma Zeiss field emission scanning electron microscope (FESEM). RigaKu 600 Miniflex bench top x-ray Diffractometer is used to study the structural change. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) are studied using TA instruments Q-600 heating from 30 to 700 °C at the heating rate of 10 °C min\(^{-1}\) under nitrogen flow rate of approximately 20 ml min\(^{-1}\).

The optical absorbance \((A)\) was measured using a computerized double beam Perkin-Elmer Lambda-35 UV-visible spectrophotometer in the range 190–1100 nm. The dielectric constant, loss and AC conductivity measurement was done using a Wayne Kerr 6500B precision impedance analyzer in the frequency range 40 Hz to 1 MHz at room temperature. The cyclic voltammetry (CV) measurement was done using a CHI-660E electrochemical workstation.

Results and discussion

FT-IR analysis

The FT-IR spectroscopy is used to identify the functional groups present in PANI and PCN nanocomposites. These analyzed PANI and PCN nanocomposites are identified in the given figure 1. The peaks observed at 1218 and 1384 cm\(^{-1}\) [27] are attributed to C–N stretching and C–C ring stretching vibrations of PANI respectively. The band observed at 797 cm\(^{-1}\) of PANI is corresponds to C–H plane bending vibrations [28]. With increasing the CuO nano concentration the wave number have shifts towards higher wave number. The aliphatic C–H stretching vibrations and aromatic stretching vibrations are corresponds from 2355 to 2360 cm\(^{-1}\). In PANI the peaks at 1384 cm\(^{-1}\) and 1218 cm\(^{-1}\) have been shifted to higher bands i.e., for PCN0.1 is (1385, 1389 cm\(^{-1}\)), PCN0.5 (1494 cm\(^{-1}\)) and PCN1 (1218, 1220, 1222 cm\(^{-1}\)) for CuO nano composites. The FT-IR result clearly confirmed the formation of chemical interaction of PCN nanocomposites [29, 30].

X-ray diffraction analysis

The diffraction patterns of PANI and PCN copper oxide nano composites are represented in figure 2. The crystal planes which corresponds to (110) shows broad peaks of PANI at 2\(\theta\) = 25.11° [27, 28]. The broad peak appears at 2\(\theta\) = 25.23°, 25.35°, and 25.51° has been appeared for PCN nanocomposite [31].
The similar peaks of $2\theta$ were observed between PCN nano composites and PANI which represents the intercalation of PANI and PCN nanocomposites. The value of $2\theta$ gives two shifts, right shift of PCN 0.1 at $6.12^\circ$ and $6.03^\circ$ for PANI and left shift at $5.91^\circ$ for PCN 1 nano composites which confirms the intercalation of PCN1 nanocomposites. These variations of peak intensity and the scattering angle confirmed the structural phase alteration and these influenced by the CuO nano composites in PANI [32, 33].
FESEM images
The FESEM images of PANI and PCN nanocomposite shown in the figure 3. The PANI image figure 3(a) shows the small porosity with granular like structure [34]. The image 3(b) shows the granular shape with small rod like structure was observed for 0.1% of CuO nano concentration. In image figure 3(c) it is seen that disappeared the granular structure and randomly morphology was appeared due to addition of 0.5% of CuO nano concentration.

Finally the image 3(d) shows considerable change in morphology occurs due to increases a more concentration, i.e. the shape of the morphology completely changes from granular to nano rod shape structure in PCN1 CuO nano concentration. The significant change in the morphology of PCN nanocomposite reveals the homogenous nano dispersion in the PANI matrix and these morphology clearly noticed that their average diameter of rod is about 70–100 nm [35]. These changes in the structure may confirm the effect of nano in the polymer matrix [30].

TEM photography
The figure 4 shows the TEM photography of PANI and PCN nanocomposite. The PANI morphology shows more portions appears thick dark cloudy region represents the amorphous nature is as shown in figure 4(a). The PCN 0.1 nanocomposite image shows the core–shell structure is as shown in figure 4(b).

The image shows thick dark region due to copper nano particles agglomerated on PANI rod like structure is as shown in figure 4(c), and the increased magnitude dispersion of CuO nano on the PANI matrix is as shown in figure 4(d). The particle size of PANI and PCN nanocomposite are found to be in the range of 30–70 nm. The thick dark region embedded on surface of white background which indicates there is a presence of more number of copper metal ions [36, 37].

TGA/DTA - thermal analysis
Thermal behavior of PANI and PCN nanocomposites are displayed in the figure 5. The thermal decomposition observed in two steps, the water contents on the surface and the moisture contents of the material has been decomposed in the first step about 14.03% in the region 80.01 °C–106 °C.
This attributes the release of residue, organic solvents and moisture entangled in the PCN nano composite. The loss of doping acid and the loss of weight were shifted to higher temperature range at 112 °C–648 °C [38]. In the PANI matrix the concentration of nano composite increases will results in the decrease of degradation temperature. The relatively larger residual rate and the lower degradation rate of PANI nano composite indicate the protective effects in PANI nano composite. The PANI and PCN nano composite of differential thermal analysis are given in the figure 5. The exothermic peaks of DTA curve observed maximum peak value at 93.36 °C.

Figure 5. TGA/DTA curve of (a) PANI (b) PCN0.1 (c) PCN0.5 (d) PCN1 nanocomposite.

Figure 6. DSC curve of (a) PANI (b) PCN0.1 (c) PCN0.5 (d) PCN1 nano composite.
this represents the structural transformations and the removal of external water molecules; these are shifted to the higher temperature range compared to PANI. These variations may be due to the increase in the thermal stability of PANI nano composite [37, 39].

**Differential scanning calorimetry (DSC)**
The differential scanning calorimetry (DSC) is used to study the thermal properties of electrochemically synthesized PANI and PCN nanocomposites. The graph indicates heat flow versus temperature curves of PANI and PCN nano composites in the figure 6.

**UV-visible spectroscopy analysis**
The UV-Visible absorption of PANI, and PCN nanocomposites are shown in figure 7. This study provides the variation in the absorption and its wavelength due to the nano effect. The main phenomenon of the absorbance is $\pi \rightarrow \pi^*$ transition in the aromatic compounds containing carbon as a back bone.

The PANI absorption peak shows at 628 nm in the visible region is shown in the figure 7(a) [40]. As increasing the copper oxide nano concentration into the PANI matrix, the absorption peak for PCN0.1 undergoes blue shift of 586 nm, then PCN0.5 concentration peak shifted towards red shift 613 nm, and finally the peak PCN1 nanocomposite is shifted to higher wavelength in the visible region of 657 nm [41]. These shifts attributed due to change in molecular structure from benzenoid to quinoid excitonic transition [42], and the absorption peaks values are mentioned in the table 1.

**Optical band gap study**
The optical band gap of the PANI, PCN0.1 PCN0.5 and PCN1 nanocomposite are shown in figure 8. The PANI and PCN nanocomposite of optical band at various absorption peak value of the absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) was calculated using relation as follows.
Where, $E_g$ be the optical band gap, $A$ constant, $n$ exponent, and $\frac{1}{2}$ value for direct allowed transition. And to determine the alpha value using the formula of absorption coefficient ($\alpha$),

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$$

Where, absorption ($A$) and ($d$) be the area inside the cuvette (one mm). The figure 8 shows direct band gap values of linear portion of $(\alpha h\nu)^2$ versus photon energy (eV) plots [43]. As increasing copper oxide nano the band gap values decrease, which is attributed the delocalization of charges [41], thus low optical band gap was obtained [44], and values are tabulated in the table 1.

### Table 1. Optical band gap (eV) and absorption peaks in visible regions of PANI PCN0.1 PCN0.5 and PCN1 nanocomposite.

| Samples   | Absorption peaks in Visible regions (nm) | Optical Band gaps (eV) |
|-----------|-----------------------------------------|------------------------|
| PANI      | 628                                     | 2.84                   |
| PCN 0.1   | 586                                     | 2.69                   |
| PCN 0.5   | 613                                     | 2.67                   |
| PCN 1     | 657                                     | 2.73                   |

$$\alpha = 2.303 \left( \frac{A}{d} \right)$$

Dielectric constant

The dielectric constant of PANI and PCN nano composite are as shown in a figure 9. The dielectric constant graph of PANI and PCN nanocomposites can be calculated by the equation,
Where, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts respectively.

The dielectric parameters of real and imaginary parts of PANI and PCN nano composite as a function of frequency at different temperatures are represented in the figure 9. The dielectric constant shows high in the lower frequency and it rapidly increases with frequency due to response of dipoles with applied field, but the dielectric constant is maintain constant at high frequency because the dipoles could not responded with field [45, 46].

### Dielectric loss

The dielectric loss factor of PANI, PCN0.1, PCN0.5 and PCN1 nano composite are capacitance $C_p$ and $\tan \delta$. The dielectric parameters are dielectric constant ($\varepsilon'$) and loss ($\varepsilon''$) were calculated using the formula.

$$
\varepsilon^* = \varepsilon' - i\varepsilon''
$$

Where, $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts respectively.

$$
\varepsilon' = \frac{C_p d}{\varepsilon_0 A}
$$

$$
\varepsilon'' = \varepsilon' \tan \delta
$$

Where, $C_p$ represents the capacitance value, the thickness of the sample is $d$, $A$ is the electrode area, $\varepsilon_0$ stands the dielectric permittivity in a vacuum the value is given (8.85 $\times$ 10$^{-12}$ Fm$^{-1}$). From the figure 10, it is observed that the dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ are found decreased with increasing frequency, but it seems to be $\varepsilon'$ and $\varepsilon''$ increased with temperature for PCN nano composite because of the segmental motion of charge carriers increases at a higher temperature. The increasing trend of $\varepsilon'$ at different temperature attributes the formation of defects in the band gap [45, 47].

### Electrical modulus

The PANI and PCN nano composite are behave as a function of frequency at different temperatures is as shown in figure 11 and figure 12. From this modulus study, the dielectric process can be understood more accurately and clearly. The electric modulus are calculated from the below mentioned formula.
The electric modulus is,

\[ M' = \frac{\varepsilon'}{(\varepsilon')^2 + (\varepsilon'')^2} \]

\[ M'' = \frac{\varepsilon''}{(\varepsilon')^2 + (\varepsilon'')^2} \]

The electric modulus is,

\[ M^* = M' + iM'' \]

Here, the real (M') and the imaginary parts (M'') are complex, energy dissipation and energy storage corresponds from electric modulus (M*). Where M' approaches zero at lower frequencies has been observed [46].

This indicates the negligible contributions from electrode polarization due to lack of required amount of restoring force that governs the mobility of charge carriers. Hence, these support the long-range mobility that corresponds to electrical conductivity [47].

**AC (σ\text{ac}) conductivity**

The ac conductivity of PCN nanocomposites as a function of frequency is shown in figure 13. The ac conductivity varies with frequency and temperature. The ac conductivity increases gradually with frequency due to its disorder characteristic of materials.

AC electrical conductivity is frequency independent at lower frequency due to the free charges and frequency dependent due to the release of activated trapped charges at higher frequency. The ac conductivity (σ\text{ac}) can be calculated using the equation.

\[ \sigma_{\text{ac}} = \omega \varepsilon_0 p d \tan \frac{\delta}{\lambda} \]

Where, sample thickness is (d), area of the electrode (A), vacuum dielectric permittivity is (\varepsilon_0) vacuum (8.85 \times 10^{-12} \text{ Fm}^{-1}), and the angular frequency is (\omega). The ac electrical conductivity values for both PANI and PCN nano composite increases with copper oxide nano concentration and temperature is as shown in figure 13,
because the charge carriers are easily transported by the hopping mechanism and freeing the dipoles present in
the polymer chain at high temperature. Figure 13 reveals that the increase in ac conductivity with increasing in
the CuO nano composite as a resulting is reduced molecular weight at higher concentration. Thus compared to
high molecular weight polymers, the low molecular weight polymers have high conductivity polymers because
of more amorphousity and less crystallinity [47].

Cyclic voltammetry analysis
The cyclic voltammetry (CV) is used to study the electrochemical performance of electrochemically synthesized
PANI and PCN nanocomposite in 1 M aqueous KCl electrolyte solution using three-electrodes system with the
potential window from −4 to 2 V at various scan rates 100–500 mV s⁻¹ are shown in figure 14. The PANI and
PCN electrodes show rectangular CV curve which is a characteristic of pseudocapacitor behavior. The area of
CV curve and current density are found increases with increasing the concentration of copper oxide nano. A
high specific capacitance value was found, because of large surface to volume ratios, which is clearly evidenced by
its unique nano rod like structure, and they are favourable to pseudocapacitor behavior [48, 49].

The specific capacitance (Csp) of cyclic voltammetry curve is calculated using following equation.

\[ C_{sp} = \frac{\int_{V1}^{V2} i(V) dV}{\Delta V \cdot \nu \cdot m} \]

Where, \( \int i(V) dV \) represents the area under the CV curves, \( \nu (V/s) \) indicates the scan rate, \( m (g) \) gives the
electrode mass of material and \( \Delta V (V) \) is voltage window.

The PANI electrode shows specific capacitance of 132.89 F g⁻¹, whereas PCN nanocomposite electrode
shows highest specific capacitance 286.66 F g⁻¹ at scan rate 500 mVs⁻¹ for PCN1 nanocomposite [1, 50–52]. The
calculated specific capacitance values for same scan rates are shown in figure 14, and these values are tabulated in
table 2. From the plot, it is clear that for 500 mVs⁻¹ scan rate, there is an increase in the specific capacitance,
which is due to the redox reaction at high scan rate [44]. At higher concentration PCN1 shows good Csp value
So, this evident that PCN provides significant pseudocapacitance. Therefore, the PCN nanocomposite electrode material could be helpful in the development of energy storage device applications.

Electrochemical impedance spectroscopy

Impedance spectroscopy was used to understand the performance of inorganic-organic junction devices resistance. In this technique the real part of the electrical impedance $Z'$ is plotted as a function of imaginary part of electrical impedance $Z''$ of PANI/CuO nanocomposite device, over a wide frequency range. And to study the capacitance behaviour and electrolyte ion transport of the PANI and PCN nanocomposite electrode, the Nyquist plots is plotted using electrochemical impedance spectroscopy measurements as shown in figure 15. The impedance Nyquist plot of PANI and PCN nanocomposite electrode from 0.01 Hz to 100 kHz frequency range using 1 M KCl electrolyte [53]. High-frequency region of both PANI and PCN electrode consists of a semi-circle and the lower frequency region shows a straight line. The charge transfer resistance of electrode and electrolyte interface can be obtained by the diameter of the semicircle at high frequency region [44, 52], this includes intrinsic resistance occurred from electro active material, resistance from electrolyte ions and electrode interface.

Table 2. Estimated specific capacitance ($C_{sp}$) from Cyclic Voltammetry for different samples.

| Samples | Specific Capacitance ($C_{sp}$) in F g$^{-1}$ |
|---------|---------------------------------------------|
| PANI    | 132.89                                      |
| PCN 0.1 | 178.79                                      |
| PCN 0.5 | 220.25                                      |
| PCN 1   | 286.66                                      |

286.66 F g$^{-1}$. So, this evident that PCN provides significant pseudocapacitance. Therefore, the PCN nanocomposite electrode material could be helpful in the development of energy storage device applications.

Figure 12. Modulus ($M''$) of (a) PANI (b) PCN0.1 (c) PCN0.5 (d) PCN1 nanocomposite at different temperature.
From the Nyquist plot, PCN nanocomposite electrodes of different resistance charge transfer $R_{ct}$ values are obtained as 48.07 Ω, 49.31 Ω, 33.73 Ω and 54.74 Ω for different voltages 1V, 2V, 2.5V and 3V respectively. They are significantly lower values, which predict fast charge transfer in the electrode material [54].

**Galvanostatic charging-discharging study**

The Galvanostatic charging-discharging (GCD) of PANI and PCN nanocomposite was studied using GCD technique. The PCN samples of long GCD cyclic stability are shown in figure 16. The figure illustrates that charging-discharging curve in the potential windows 0.0 to 0.8 V at constant time of about 1000 s for different samples [55, 56]. From graph it is observed that potential found to be increases from 0.42, 0.63, and 0.74V for PCN 0.1, PCN 0.5 and PCN 1 respectively and this stability was achieved because of the CuO nano concentration.

The charging discharging of PCN nanocomposites samples shows a 2000 cyclic stability. This confirmed that sample having very good storage stability with long durability. Using this formula we can calculate the GCD ($C_{sp}$) values [57].

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m}$$

Where $I$ discharge current, $\Delta t$ be the discharge time, $\Delta V$ is the potential difference in discharge of the material and $m$ is the mass on an electrode [55, 56]. For higher concentration the galvanostatic charging discharging enhanced 2000 cyclic stability. Hence, the combination of PANI/CuO nanocomposite electrode material could be useful in the development of supercapacitor and energy storage device applications [58, 59]. The estimated specific capacitance values from charging/discharging for different samples are mentioned in the table 3.
Figure 14. Cyclic Voltammetry curve of (a) PANI (b) PCN0.1 (c) PCN0.5 (d) PCN1 nanocomposite.

Figure 15. Nyquist plots from electrochemical impedance spectroscopy (EIS) curve for PCN nanocomposite. (a) EIS of PCN nano composite with different voltages (b) Inset image shows enlarged plot of PCN nano composite.

Table 3. The specific capacitances from charging/discharging for different samples are mentioned in the table.

| Samples             | Specific capacitance (F g⁻¹) | [References]       |
|---------------------|------------------------------|--------------------|
| PANI/Cuo/NiO        | 230                          | [23, 24]           |
| Conducting polymer  | 263                          | [25, 26]           |
| PEDOT:PSS           |                              |                    |
| PANI/CuO            | 286                          | Present Work       |
Conclusions

The PANI/CuO nano composite was successfully synthesized using electrochemical deposition method. The chemical interaction, structural phase, thermal behaviour, morphology and structural arrangement are confirmed using FT-IR, XRD, FESEM, TEM, TGA, DTA, DSC, Dielectric constant, loss, AC conductivity, CV, Charging/Discharging and electrochemical impedance spectroscopy (EIS). The nano rod like morphology confirmed the homogeneous dispersion and TEM core structure suggesting the presence of metal ions in the PAN1 matrix. The maximum specific capacitance ($C_{sp}$) value 286.66 F g$^{-1}$ for PCN1 was calculated using electrochemical study of cyclic voltammetry technique. Hence the PCN nanocomposite is a suitable for supercapacitor and other energy storage device applications.

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Figure 16. GCD curves of (a) PCN0.1 (b) PCN0.5 (c) PCN1 nanocomposite.
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