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Authors: Sara Samuei, Zolfaghar Rezvani, Ashkan Shomali, Emine Ulker, and Ferdi Karadas

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Preparation and capacitance properties of graphene quantum dot/NiFe-layered double-hydroxide nanocomposite

Sara Samuei \(^{[a]}\), Zolfaghar Rezvanli \(^{[b]}\), Ashkan Shomali \(^{[c]}\), Emine Ulker \(^{[d]}\), Ferdi Karadaş\(^{[e]}\)  

Abstract: In this work, a new composite from graphene quantum dots (GQDs) and NiFe layered double hydroxide is successfully prepared by the coprecipitation method in the optimal conditions. The nanoparticles of the composite are analyzed by X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and, thermal gravimetric analysis (TGA) to obtain the structure, composition and morphology information. Also, the electrochemical properties are investigated by cyclic voltammetry, galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy. The nanocomposite displays specific capacitance of 712.7 F g\(^{-1}\) and excellent cycle life after 2500 cycles by applying 10 A g\(^{-1}\) of the current density in 1 M KOH electrolyte, which confirms that nanocomposite has superb capacitance retention (\(\sim94.8\%\)) and can be used as a capable supercapacitor. Furthermore, this study provides a desirable procedure for the preparation of novel nanocomposite based on graphene quantum dot, which can be used in energy storage/conversion devices.

Introduction

Recently by increasing the energy crisis in the world and the rapid depletion of various fossil fuels, supercapacitors as energy storage tools have attracted much attention. These storage devices have a high capability and power density, a higher rate of charging/discharging, and a long life cycle [1-4]. Supercapacitors (SCs), which are also called electrochemical capacitors or ultracapacitors, can fall into these categories: Electrical double-layer capacitors (EDLCs) and pseudocapacitors[5-7]. The performance mechanism of electrochemical double-layer capacitor is relying on the charge separation between the electrode and electrolyte interfaces[8]. Mostly fabricated by carbon materials with the high surface area such as activated carbon, CNTs, carbon nanofibers, and graphene sheets that can be used in aqueous and non-aqueous solutions as electrolytes[9]. Nevertheless, because of the low energy densities of this kind of supercapacitors, their vast application has been limited[10]. While, pseudocapacitors electrodes mainly consist of transition metal oxides in several oxidation states, for instance, MnO\(_2\)[11], RuO\(_2\)[12], Co\(_3\)O\(_4\)[13], Ni(OH)\(_2\)[14], NiO[15]. These kinds of materials have higher capacitance because of the redox reactions between the surface and bulk part of transition metal oxides. The other category of materials used for pseudocapacitors electrodes is conducting polymers such as polyaniline, polypyrrole, and polythiophene. According to their mechanism, faradic charges transfer occurs between electrolyte (aqueous solutions) and electrode [1, 16], then the capacitance of pseudocapacitors is higher[17]. Up to now, a great deal of research has been done on the various electrode materials to improve the performance of supercapacitors. Among different transition metal hydroxides[18], Layered double hydroxides (LDHs), as some sort of 2D structure anionic clays, have appealed widespread consideration. Nontoxicity, low cost, high stability, excellent reversibility, and high specific capacitance have provided them to be great candidates for supercapacitor materials[19, 20]. Layered Double Hydroxides (LDHs) are presented as anionic hydrotalcite-like clays with the typical chemical formula: \(\{M^{n+}\_x\_M^{3+}\_y(\text{OH})\_z\}^{x/n}\_\alpha\_m\_m\_H_2O\), where \(M^{n+}\) and \(M^{3+}\) are defined as di- and trivalent cations and \(\alpha\_m\) is a variable anion respectively. \(X\) clarified as the ratio of \(M^{n+}/(M^{3+}\_x\_M^{2+}\_y)\). The total charge of the layers depends on the ratio of \(M^{n+}/M^{3+}\) [21-23]. LDHs formed from transition metals contain abundant valence states that can provide excellent redox activity and acceptable cycling stability[24-26]. Previously, many studies tried to investigate the efficiency of LDHs as an electrode material for supercapacitors such as NiCo-LDH[27], NiCoAl-LDH[28], CoAl-LDH[29], NiMn-LDH[30] in basic electrolytes. However, because of having poor electric conductivity and low power performance, their practical applications have been limited [31] to overcome these deficiencies preparing carbon-based nanocomposite can be used as a solution way[32]. For improving the conductivity in some studies, carbonaceous substances like carbon nanotubes, graphene, porous carbon, and carbon fibers have been applied[33]. For example, Wang et al. prepared the NiAl-LDH/graphene composites, which represents a specific capacitance of 781 F g\(^{-1}\) while the pure NiAl-LDH has 566 F g\(^{-1}\) specific capacitance[16]. Also, Zheng et al. investigate that CoAl-LDH/graphene composite has more capability compared to CoAl-LDH with a specific capacitance of 479 F g\(^{-1}\) and 427 F g\(^{-1}\), respectively[34]. One of the novel carbonaceous materials which have been a little-studied so far is graphene quantum dots (GQDs). GQDs exhibit excellent characteristics because of high surface area, abundant surface functional groups which provide a better surface connection with other parts of composite and the fast electron transfer through π-π conjunction; this leads the increases in the catalytic activity of the composites[35].
However, to date, no studies have been performed on the GQDs/NiFe-LDH composite as electrode material for supercapacitors. In the current research work, preparation of the graphene quantum dot /Ni-Fe layered double hydroxide composite by a coprecipitation method has been done for the first time. The GQDs are prepared by pyrolyzing of the citric acid via a bottom-up approach[36], and also a solvent treatment for the separation process performed. Then nanocomposite of GQDs and NiFe-LDH is successfully synthesized by the coprecipitation procedure in the alkaline media. In this study, Fe$^{3+}$ was chosen because compared to the other used ions such as cobalt and aluminum, iron is cheaper and more plentiful[37]. In order to obtain the compositional, morphological, and structural information, the prepared nanocomposite was analyzed by X-ray diffraction, Fourier transforms infrared spectroscopy, thermal gravimetric analysis, and scanning electron microscopy. The supercapacitor properties of the GQDs/NiFeAl-LDH composite as electrode examined by cyclic voltammetry (CV), galvanostatic charge/discharge, and finally, by electrochemical impedance spectroscopy (EIS).

**Results and Discussion**

**XRD analyses**

Fig. 1 shows the XRD patterns of the resultant GQDs/NiFeAl-LDH composite compared with pristine NiFeAl-LDH (JCPDS Card 40-0215) and GQDs. The XRD pattern of the precursor graphene quantum dot (Fig. 1a) represents a broad peak with a relatively low intensity near 27° belongs to the (002) plane. Fig. 1b shows the XRD pattern of pure NiFe-LDH, the symmetric reflection of (003), (006), (110) related to the R3m symmetry (a hexagonal lattice). Also, (113) planes and broad asymmetric peaks such as (009), (015), and (018) planes, belong to the hydrotalcite-like compounds[38]. For the GQDs/NiFe-LDHs composite, the diffraction peaks are similar to those of the pristine NiFe-LDHs. There is no shift in the location of the peaks, so it can be concluded that there is a similarity of the interlayer anions between the pristine NiFe-LDH and composite. Also, there are no other peaks in the spectrum, indicating a lack of impurities in the composite. Just decreases in the intensity of the reflection peaks have occurred, which is associated with the disorder in the condensed structure of the composite compared to pure LDH[39].

![XRD patterns of (a) GQDs, (b) pristine NiFe-LDH, and (c) GQDs/ NiFe-LDH composite.](image)

**FTIR Spectra**

The FT-IR patterns of (a) GQDs, (b) pristine NiFe-LDH, and (c) GQDs/NiFeAl-LDH at ambient temperature are presented in Fig. 2. spectrum 2a belongs to GQDs: As can be seen, there is a distinctive peak located at approximately 1723 cm$^{-1}$, which is specified to stretch of the carboxylic functional group (C=O). The broad peak of O-H is also set at 3550 cm$^{-1}$. In the case of NiFe-LDH, the stretching vibration of the metal-oxygen-metal is observed in the low-frequency area (below 1000 cm$^{-1}$)[40]. Vibration bands centered at 578.61 cm$^{-1}$ and 436.50 cm$^{-1}$ are showing the M–O–H and the O–M–O group respectively[41]. For spectrum b and c, the bands with peak maxima at 1384 cm$^{-1}$ belongs to stretching modes of NO$_3$ anions in the interlayer space and robust broadband centered at 3480.91 cm$^{-1}$ is corresponds to hydroxyl groups stretching vibrations, which exists in the surface of LDH and interlayer water molecules[42]. Hydrogen bonds formed between interlayer water and hydroxyl groups cause the O-H peaks of LDHs, can be seen at low frequencies compared with free water[43]. By comparison of NiFe-LDH and pure graphene quantum dots, it can be observed that the spectrum pattern of composite has additional sharp peaks which are corresponded to characteristic signals of pure LDH and GQDs simultaneously. For example, carbonyl and nitrate peaks that confirm graphene quantum dots are not entered in the interlayer spaces. Though, they exist on the surface of LDH, which SEM analyses confirm this result.

![FT-IR spectrum of (a) GQDs, (b) pristine NiFe-LDH, and (c) the GQDs/NiFe-LDH composite.](image)

**SEM analyses**

SEM imaging was utilized to investigate the morphology of GQDs/NiFe-LDHs nanocomposite and its comparison with pristine LDH and GQDs (Fig. 3), as can be seen in Fig. 3a, the LDH includes unequal particles with rough surfaces that can conclude agglomeration had occurred. In NiFe-LDH due to partial replacement of Ni$^{2+}$ by Fe$^{3+}$, the self-aggregation of double hydroxide layers had happened, and the electrostatic interaction between composing elements is enhanced, which leads to irregular denser nanosheets of the samples[44]. Fig. 3b represents GQDs morphology, which shows spherical and homogeneous particles with dimensions below 50 nm.
approximately, and have more pores than pure LDH. It is worth to note that the morphology of the composite Fig. 3c is notably different from that of pristine LDHs and GQDs. In the SEM image of GQDs/NiFe-LDH composite, GQDs have covered the entire surface of LDHs, boost the surface area, and augment the more active sites and by increasing pores amount[37].

**Figure 3.** SEM micrographs of (a) pristine NiFe-LDH (b) GQDs, and (c) the GQDs/NiFe-LDH composite.

**Figure 4.** TEM image of GQDs (a), element maps showing the distribution of C(b), Fe (c), Ni (d) elements and EDX result of the GQDs/NiFe-LDH composite (d).

Fig 4a shows the TEM image of synthesized GQDs dispersed in ethanol. The GQDs observed are small and uniform, with an average diameter of 5nm. Fig 4b, c and d show the elemental mapping of the composite. The carbon element of GQDs uniformly distributed on the LDH surface and overlapped with Ni and Fe elements, which are the main constituents of LDH. Fig 4e displays the EDX spectrum of GQD/NiFe-LDH; the result confirms the presence of carbon and oxygen of GQDs with NiFe particles[45, 46].

The Zeta potential of synthesized GQDs is determined -25 mV due to the presence of abundant Oxygen contained functional groups on the surface, GQDs are negatively charged[47]. Table 1 shows Result of zeta potential, Electrophoretic Mobility, and Conductivity of GQDs. Fig 5. Also represents the particle size distribution of GQDs in ethanol. Table 1. zeta potential, Electrophoretic Mobility, and Conductivity of GQDs.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Zeta Potential</th>
<th>Conductivity</th>
<th>Mobility</th>
<th>Field Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>GQD</td>
<td>-25.9 mV</td>
<td>120 uS/cm</td>
<td>2.60 u/s/V/cm</td>
<td>5.0 kV/m</td>
</tr>
</tbody>
</table>

**Figure 5.** Particle size distribution of GQDs in Ethanol.

**Thermogravimetry and differential thermal analysis**

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) patterns for pure NiFe-LDH and GQDs/NiFe-LDH nanocomposite are illustrated in Fig.6. Fig 6a shows that the decomposition of NiFe-LDH has appeared in two steps. The first step is related to the release of water molecules from the LDH surface and interlayer space in the ranges between 100-180°C. The second stage belongs to the dihydroxylation of octahedral layers in LDHs within the ranges of 250-350°C. In the DTA, two peaks can be observed for pure LDH first peak belongs to the removal of water molecules at around 110°C, and the second intense peak corresponds to dehydration of LDH layers around 280°C. Fig 6b is for the GQDs/NiFe-LDH, in which there a remarkable shift to the high temperatures has occurred. The first and second step shifts are quite obvious, which observed at around 250 °C and 380 °C, respectively, and confirm that thermal stability happened in the nanocomposite[48]. Thermal stability can occur because of synergetic effects between two parts of the nanocomposite. As reported in the literature, synergetic effects can improve the properties of each component. This result is corresponds to the presence of the strong interaction between functional groups of each material such as Coulombic electrostatic force and hydrogen bonds[49, 50]. Also, GQDs participation leads to better linkage with the LDH matrix and less residual/unreacted functional groups in both LDH and GQDs [51].

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The electrochemical tests were used to explore the electrochemical performance of the nanocomposite. A three-electrode electrochemical system by the Cyclic Voltammetry (CV) method was used to evaluate the super capacitance performance of the GQDs/NiFe-LDH, NiFe-LDH and, GQDs in 1 M KOH aqueous electrolyte in the scan rate of 20 mV s\(^{-1}\) (Fig.7). For this purpose, Ag/AgCl and platinum wire were applied as the reference electrode and the counter-electrode, respectively. The tests were done under similar conditions for evaluation. A pair of redox peaks can be seen in the curve of NiFe-LDH and GQDs/NiFe-LDH nanocomposite, which is related to Ni (III)/Ni(II) couple. A comparison of the electrochemical performance of the GQDs and NiFe-LDH, by the GQDs/NiFe-LDH electrodes, illustrated that the oxidation and reduction peak currents of the Ni (III)/Ni(II) couple for GQDs/NiFe-LDH enhance with the increase of base current by imbalance shape. Also, the distance of a peak to peak (between the anode and cathode peaks) for the nanocomposite modified electrode is less than for the other states. Besides, the Oxidation and reduction peaks of the Ni (III)/Ni(II) couple in the GQDs/NiFe-LDH electrode shifts to the negative potentials and displays high reversibility than the same couple in the pure LDH. Also, the GQDs/NiFe-LDH nanocomposite presented the largest integrated area, compared with the GQDs and NiFe-LDH, indicating that the GQDs/NiFe-LDH had the highest specific capacitance because of the increased surface area\[52\]. It can be clarified that the introduction of GQDs was efficiently prevented the accumulation of LDH and also hindered the loss of the active surface area of the composite. This result indicates that the nanocomposite charge transfer not only relies on the Redox mechanism but is also based on the synergistic effect. The presence of GQDs provides a considerable contribution between two parts of the composite, which can effectively increase the electrical conductivity of the composite. Also, GQDs cause better spreading of the electroactive sites and the surface area. As a result, the electron transfer in the nanocomposite electrode occurs more comfortable and faster than in the pure NiFe-LDH.\[53, 54\] For this reason, the base current of nanocomposite has increased with increasing scan rates and the Oxidation and reduction peaks of the Ni (III)/Ni(II) couple peaks will not be visible gradually.

Fig.8a shows the CV curves of NiFe-LDH in the various scan rates. There is a direct relationship between increasing scan rates and improving the current response of redox peaks, which depicts the pseudo-capacitive behavior of the LDH. Fig.8b represents CV curves of GQDs/NiFe-LDH composite, which can be seen as current response enhanced by increasing scan rates. There are also apparent changes in the shape of the curves. This means the base current and the redox current of active material are enhanced at the same time by providing accelerating charge and electron transfer of the nanocomposite. \(\nu\) represents the potential scan rates (mV s\(^{-1}\)). \(I\) (The current) defines as the current response (A. g\(^{-1}\)) concerning the mass of electroactive material under study. As shown in the figure, the CV curves of the GQDs/NiFe-LDH electrode from -0.2 to 0.7 V (vs. Ag/AgCl) at the scan rates of 20, 400, 80, and 100 mV s\(^{-1}\), have been studied respectively. All CV curves have similar shapes; the quasi-rectangular curves in this study are due to the fast charge/discharge process characteristic, indicating the ideal capacitive behavior of double-layer capacitance.
Fig 8c represents the change of the specific capacitance based on the scan rates for the GQDs/NiFe-LDH electrode. As depicted in Fig, the Cs of the electrode changes from 712.7 to 180 F g⁻¹ with a scan rate from 10 to 200 mV s⁻¹. As a result, by comparing of the Cs at low scan rates, and high scan rates, it can be observed that by increasing the scan rate, a decline in the over-all Cs has occurred. At lower scan rates, electrolyte ions have enough time to enter the pores of the material, which leads to provides more accessible surface for redox reactions[55].

Galvanostatic charge/discharge electrochemical studies were performed to investigate the super capacity efficiency of the GQDs/NiFe-LDH electrode. Fig. 8d represents the charge/discharge curves in the potential of -0.8 to 0.7 V for the GQDs/NiFe-LDH electrode in 1 M KOH solutions, at current densities ranging from 1 to 10 A g⁻¹, respectively. As shown in Fig, all of the curves are linear with the shape of triangular, sharp, and symmetric. It also has been explained that the ideal performance of the capacitor versus the time is dependent on the equal charging and discharging process, which specifies the reversible performance and high Coulombic proficiency. The longest charge/discharge time, implying the highest specific capacitance. That shows with the increase of the current density from 1 to 10 A g⁻¹ charge/discharge time decreases. It can be concluded that there is a limitation in the transfer of alkaline ions of electrolyte to the electrode surface during the charge storage process, which causes the charge/discharge time decreases with increasing current density.[56]

Table 2. Comparison of the specific capacitance and cycle retention.

<table>
<thead>
<tr>
<th>Nanocomposite Materials</th>
<th>Cs (F g⁻¹)</th>
<th>Cycle retention</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgFe-hydrrotalcite/polyaniline</td>
<td>593(2A g⁻¹)</td>
<td>87.0% (500 Cycles)</td>
<td>[57]</td>
</tr>
<tr>
<td>NiCo2O4@NiFe-LDH</td>
<td>12.3 (F Cm⁻²)</td>
<td>83.1% (1000 Cycles)</td>
<td>[58]</td>
</tr>
<tr>
<td>MnOOH/NiAl-LDH</td>
<td>1331.11 (F g⁻¹)</td>
<td>82.4% (1000 Cycles)</td>
<td>[59]</td>
</tr>
<tr>
<td>RGO/NiCo-LDH</td>
<td>2130(2A g⁻¹)</td>
<td>72.7% (10000 Cycles)</td>
<td>[60]</td>
</tr>
<tr>
<td>RGO/CoAl-LDH</td>
<td>1492(F g⁻¹)</td>
<td>94.3% (5000 Cycles)</td>
<td>[61]</td>
</tr>
<tr>
<td>NiV-LDH</td>
<td>1581(F g⁻¹)</td>
<td>79% (2000 Cycles)</td>
<td>[62]</td>
</tr>
<tr>
<td>N-doped NiO/NiMn-LDH</td>
<td>1720(3A g⁻¹)</td>
<td>83% (10000 Cycles)</td>
<td>[63]</td>
</tr>
<tr>
<td>RGO/CoAl-LDH</td>
<td>1881(F g⁻¹)</td>
<td>79% (2000 Cycles)</td>
<td>[64]</td>
</tr>
<tr>
<td>CoAl-LDH/graphene</td>
<td>479 (F g⁻¹)</td>
<td>75% (5000 Cycles)</td>
<td>[34]</td>
</tr>
<tr>
<td>NiO/NiMn-LDH</td>
<td>937 (F g⁻¹)</td>
<td>91% (1000 Cycles)</td>
<td>[65]</td>
</tr>
</tbody>
</table>
Fig. 8e shows the performance rate of the GQDs/NiFe-LDH electrode based on various current densities. As can observe, the Cs of the GQDs/NiFe-LDH electrode declines with the rising current density. The Cs of the GQDs/NiFe-LDH electrode was obtained 712.7 F g⁻¹ at the current density of 1 A g⁻¹. Table 2 shows materials that reported the literature for comparison purposes. As can be seen in table 2, Many nanocomposites have been studied in energy conversion and storage applications, but research about developing highly efficient catalysts is still going on. GQDs have unique properties such as more abundant active sites (edges, functional groups, dopants, etc.), large surface area, solubility, and the ability to facilitate charge transfer. Additionally, they can easily form composites with other nanomaterials. This composite was prepared for the first time. Unlike the other Nano carbonic materials, GQDs used for this research were prepared by the simple one-pot method without needing to age in high temperatures or a long time, just in 30 minutes. Also, there is no need to use strong acid-base treatment for purification. In addition to the ease and cost-effectiveness of the preparation method, it is worth to not that it is classified between the efficient capacitor materials because of the excellent cycle life after 2500 cycles and high specific capacitance[66-69].

For the investigation of charge storage capacity during the time, The CCV technique can be applied as the best tool[70, 71]. In this method, the stability of the electrodes evaluated under a long period of potential. The calculated Cs are considered being a function of the cycle numbers presented in Fig 9. As can be seen, The Cs value based on cycle numbers decreases slightly. As a result, after 2500 cycles, at the scan rate of 200 mVs⁻¹, 94.8% of SC value preserved.
This result confirms that GQDs/NiFe-LDH electrode is highly stable during potential cycling tests[72].

Additionally, the EIS is used as a suitable method to evaluate the performance of supercapacitor and impedance of electrode materials. EIS was applied to determine the charge transfer property of materials and diffusion properties of ions[73]. The slope of the curve at low frequencies illustrates the diffusion of ions in the electrolyte over the electrode surface. Fig. 10 demonstrates the Nyquist impedance plot (imaginary part, Z’, versus real factor, Z”) over the frequency range 0.01–100 kHz, for the NiFe-LDH (a) and GQDs/NiFe-LDH electrodes (b) in 1 M KOH solution, at the potential of 0.4 V (about the highest current of the cyclic voltammetry range). The inset of Fig. 10 also compares the Nyquist plots of two electrodes by magnification in the higher frequencies. The EIS curve shows semicircle behavior at higher frequencies and linear behavior in the lower frequencies. The semicircle behavior indicates the presence of a Faradaic charge transfer resistance (Rct). This is correlated to the reaction of the electric double-layer capacitor on the surface of the electrode. As seen in Fig. 10, GQDs/NiFe-LDH electrode (a) displays a higher charge transfer resistance than the NiFe-LDH electrode (b), so as expected, the Rct of nanocomposite is higher than the individual LDH. As can be detected, the width of the semicircle diameter for GQDs/NiFe-LDH is about 2 Ω. In the lower frequencies, the Warburg tail, which appears at about 45°, is related to the capacitor’s diffusive resistance of the electrolyte in the electrode pores and the ion dispersion in the electrode surface. The more the Nyquist plot gets closer to vertical, the more the electrochemical behavior of the electrode, similar to an ideal capacitor[74]. The vast Warburg region (the straight line) of the electrode represents the significant changes in ion diffusion, due to the enhancement of the obstruction in the movement of ions[54, 75]. It is also worth mentioning that the electrode at the higher frequencies represents series resistance (Rs) in the electrode/electrolyte system, which is related to the electrolyte and electronic resistance of the electrode simultaneously. In other words, the difficulty of solution conductivity is determined by Rs value. The Rs of the electrode was achieved from the intersection point of the Nyquist plot for (a) NiFe-LDH electrode, and (b) GQDs/NiFe-LDH electrode is 1.2 Ω and 1 Ω, respectively. These impressive electrochemical properties of nanocomposite can be due to the following reasons: The GQDs/NiFe-LDH structure can provide excess and available active sites, which make the diffusion distance, reduced, and enhance the kinetics of mass transfer. Additionally, increased porosity affects not only the ionic mobility of electrolyte but also keeps more electrolyte molecules in touch with pores during the reversible charging-discharging process.

In summary, we reported the synthesis of novel nanocomposite derived by GQDs and NiFe-LDH. Then electrochemical properties of nanocomposite have been investigated to study the possibility of using this material in the super capacitance application. GQDs/NiFe-LDH electrode exhibits remarkable electrochemical activity, including impressive specific capacity, high rate capability, and excellent cycling stability. Due to the enhancement of the surface area and pore amounts, a vast amount of channels was formed that can provide maximum contact area between compounds and the electrolyte. Also, the synergetic effect between GQDs and NiFe-LDH provides higher conductivity and accelerate the diffusion of ions in the electrode surface in the charge/discharge process. The specific capacitance of GQDs/NiFe-LDH is 712.7 F g⁻¹ at a current density of 1 A g⁻¹ with an excellent cycling life span (~94.8 % capacitance retention after 2500 cycles) determined. It can be concluded that GQDs/NiFe-LDH can be an ideal candidate for application in supercapacitors.
**Experimental Section**

**Materials**

All the required materials such as Ni (NO$_3$)$_2$·6H$_2$O and Fe (NO$_3$)$_3$·6H$_2$O, NaOH, HCl are the Merck factory products and have an analytical grade of purity. All of the synthesis steps performed using double distilled water. The adjustment of pH was achieved by adding various amounts of 0.1 M solution of HCl and 0.1 M solutions of NaOH. Acetylene black and Polyvinylidene fluoride (PVDF) was purchased from Sigma and used without any purification.

**GQDs Preparation**

The GQDs produced by pyrolyzing of the citric acid, as mentioned in the references [26] according to this procedure, 2 g citric acid, were placed into an autoclave, and the temperature reached to 180°C. After half an hour of the pyrolysis process, citric acid molecules converted into carbon nanoparticles, which leads to the formation of pale yellow liquid. Increasing the temperature and increasing the heating will change the color of the solution and yellow color, turning into an orange color, which indicates the formation of the graphene quantum dot has completed. For pH neutralization and bringing it to 7.0, 0.1M NaOH slurry was added gradually into the obtained orange liquid under severe stirring [36]. When the pH setting finished, the solvent treatment and the separation process was done by the same amount of chloroform and distilled water. The aqueous orange solution contains GQDs preserved at 4°C for investigation and further consumption.

**Nanocomposite synthesis**

The coprecipitation procedure was used to synthesize the GQDs-NiFe-LDH nanocomposite. Typically, Ni (NO$_3$)$_2$·6H$_2$O and Fe (NO$_3$)$_3$·6H$_2$O (Ni: Fe = 2:1) were prepared as a 30 ml aqueous solution and added gradually to 20 ml of the sonicated GQDs solution, with severe stirring; pH adjustment at 9.5 is made by adding a 2 M NaOH solution to the metal solutions. The reaction was done under the N$_2$ atmosphere, and the temperature of the solution was kept at 70°C. The final solution was aged for 24 hours. After filtration of slurry by using a centrifuge, the resulted precipitation washed three times with double distilled water and dried completely at 60°C.

**Electrochemical measurements**

The electrochemical tests were done as follows: The prepared nanocomposite was mixed with acetylene black and Polyvinylidene fluoride (PVDF) in a mass ratio of 85:15:5 and dispersed in N-methyl-2-pyrrolidinone (NMP) to form a homogeneous paste. Then the paste was completely at 60°C. After cooling down, the paste was put in a stainless steel grid, and further consumption.

The electrochemical tests were done as follows: The prepared electrode was electrochemical treated to be used as a working electrode, a Pt foil with the area of 1 cm$^2$ and an Ag/AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively; 1M KOH solution used as the electrolyte. A type of electrochemical workstation which used was Autolab PGSTAT 204. Through it, all the electrochemical investigations, including Cyclic voltammetry (CV), Galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were done. The CV tests were obtained between -0.2 and 0.7V (vs. Ag/AgCl) at various scan rates at the range of 10-200 mV/s. Galvanostatic charge/discharge (GCD) was recorded in the potential range of 0.8-0.7 mV at different current densities. EIS measurements were done by applying an AC voltage with 0.4 mV amplitude in the frequency range of 0.01 to 100 kHz.

The specific capacitance of a single electrode can be reckoned through the charge/discharge curve according to the following equation [76, 77]:

$$Cs = \frac{\int i \times \Delta V}{\Delta V \times m \times \mu}$$

Where Cs (F/g) is specific capacitance, m (g) is the mass of the electroactive material coated on the electrode surface, I (A) is the response current, and $\Delta V$ (V) is the potential range, and $\mu$ (mVs$^{-1}$) is the scan rate, respectively. The lower the thickness of the electroactive material on the electrode surface, the less aggregation during the charge-discharge process happens. Additionally, the specific capacitance can be diminished with the increase of mass loading due to self-aggregation, which causes trouble in the electrolyte permeation and electron transfer.[58, 78]

**Physicochemical characterization of nanocomposite**

An advanced diffractometer by the type of Bruker AXS (Germany) with the D8 model was used to record Powder X-ray diffraction (PXRD) spectra of the materials. Cu Ka radiation (λ = 1.54 Å) at 40 kV and 35 mA with a Bragg angle ranging from 3 to 70 was applied. The Bruker (Germany) spectrophotometer was used for FTIR investigation in the range of 400–4000 cm$^{-1}$ and KBr disk used at ambient temperature. Hana pH-meter model 211 was performed in the pH setting. Mettler Toledo TGA 851e device (Germany) recorded the thermogravimetric (TGA) curves with a heating rate of 10°C min$^{-1}$ under the N$_2$ atmosphere. Scanning electron microscopy (SEM; LEO 440i) at 20 keV was also used for the morphology investigation of the samples. The TEM images were obtained by a Zeiss EM10C transmission electron microscope. Zeta potential data was obtained by Nanotrac Wave (Microtrac Company).

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