One-step green synthesis of graphene/ZnO nanocomposites for electrochemical capacitors

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Abstract

A facile, green and efficient approach consisted of a novel liquid phase exfoliation and solvothermal synthesis method has been adopted to prepare graphene/ZnO nanocomposites as electrode material for electrochemical capacitors. Highly pristine graphene was produced from mild sonication treatment of raw highly pyrolytic graphite in a solution at a proper ratio of ethanol and water. The X-ray diffraction (XRD) analysis revealed the formation of pure ZnO structure from the zinc nitrate hexahydrate precursor during solvothermal synthesis. The surface characteristics and elemental composition of the nanocomposites have been studied by means of field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and transmission electron microscope (TEM). The electrochemical properties of the graphene/ZnO nanocomposites were examined by cyclic voltammetry (CV), galvanostatic charge–discharge tests and electrochemical impedance spectroscopy (EIS). The graphene/ZnO nanocomposites displayed an improved capacitive performance of 236 F/g at a scan rate of 10 mV/s, excellent cyclic performance, and an average energy density of 11.80 W h/kg. The improved electrochemical performance of the nanocomposites can be ascribed to the high electrical conductivity of the synthesized pristine graphene and the good electroactive property of ZnO.

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1. Introduction

There are concerns over the limited availability of fossil fuels and its association with global warming and environmental pollution. This growing interest has generated the need for the advancement of renewable energy sources along with new technologies related to effective, facile, and environmental friendly method for energy conversion and storage [1–3]. Energy conversion and storage systems may embrace the technology and systems of an external thermal interface or that of an external electrical interface [4] and they are categorised into groups by the amount of energy and power available for the load [5] which includes batteries, fuel cells, capacitors and supercapacitors [1,5].

Supercapacitors also known as electrochemical capacitors have been a subject to many applications, research and development due to its high power density, environmental friendliness, long shelf life, long life cycle [3,4] and it bridges the energy gap between capacitors (high power output) and fuel cells/batteries (high energy storage) [1,2]. Much research and development have been carried out to improve the overall performance of supercapacitors via the use of carbonaceous compound, metal oxides, conducting polymers and the associated hybrids/ composites as promising electrode materials [1–3,6,7].

Graphene is highly anticipated to be an excellent electrode material due to its notable characteristics such as high surface area to volume ratio, good electrical conductivity, good flexibility, fast electron mobility and good thermal and electrochemical
properties [8–11]. The introduction of graphene and metal oxide composites has demonstrated a better energy density, power density and capacitance for supercapacitors [3,8,12]. The synergetic effect between the metal oxide and graphene clearly indicates that metal oxides play the roles of spaces to expand the surface area of graphene and improves capacitance as a result of the redox reaction while graphene reduces the resistance by providing a conductive pathway for the easy diffusion of ions and movement of electrons [8]. Among the many metal oxides available, zinc oxide (ZnO) has attracted much attention as a promising electrode material for supercapacitors due to its low cost, abundant availability, environmental friendly nature and electrochemical activity [13]. ZnO is a battery active material which attains an energy density of 650 A/g. It has a large exciton binding energy (60 meV) and a wide band-gap (3.37 eV) [14–16]. In addition, it has strong emission of light at room temperature and it is transparent in nature [15].

In view of the outstanding individual properties of graphene and ZnO as electrode materials, the combination of graphene with ZnO nanoparticles as electrodes may result in improved supercapacitor performance. Several methods employed in preparing graphene–ZnO nanocomposites for supercapacitors have been reported. Lu et al. [17] prepared graphene–ZnO nanocomposites via a microwave-assisted system, where the composite compound exhibited an improved electrochemical capacitance of 146 F/g at a scan rate of 2 mV/s. Li et al. [18] reported a hydrothermal technique to grow ZnO nanorods that were distributed homogeneously on the graphene nanosheets. The nanocomposite materials were found to possess a specific capacitance of 156 F/g at a scan rate of 5 mV/s. Zhang et al. [19] synthesised graphene–ZnO composites films for supercapacitors application by depositing ZnO on graphene by ultrasonic spray pyrolysis (USP). They reported that graphene/ZnO composites had demonstrated a better reversible capacitive process than graphene material alone. Wang et al. [3] reported a successful synthesis of graphene nanosheets/ZnO composites prepared by an in situ crystallization method which displayed an improved capacitance of 62 F/g at a current density of 5 mA/cm². However, most of these studies had utilised graphene nanomaterials synthesised via the modified Hummers method, followed by chemical reduction producing the reduced graphene oxide (rGO). By using this conventional method, the graphene produced are less pristine due to the used of harsh acids in the synthesis processes, resulting in many oxygenated groups formed on the graphene surface [20,21]. The presence of these oxygenated groups results in significant compositional and structural defects which affects its electrical properties. Though the reduction process is aimed at removing the oxygen moieties, literatures have indicated that in general, this chemical reduction processes are incomplete and that the oxygenated groups cannot be completely removed resulting in less superior electrical properties or greater crystal defects when compared to the pristine graphene [20–24].

Consequently, the development of a facile green approach for synthesising high-quality graphene is essential and crucial for practical sustainability. Therefore in this work; a novel green synthesis method is used to produce the graphene material. This method involves the liquid phase exfoliation of graphite through the sonication of raw highly pyrolytic graphite flakes in an optimum ratio of ethanol and de-ionized water, as reported in our previous work [25]. Such method does not require strong oxidizing agents (potassium permanganate, sodium nitrate and concentrated sulphuric acid) and reducing agents (hydrazine) thereby making the process simple and fast. The use of a common reagent (ethanol) as the exfoliation medium which has a low boiling point of 78.37 °C for the synthesis of graphene makes the synthesis process relatively safe and preserves the pristine structure of graphene material.

Our composite synthesis method incorporates such simple and green method of synthesising graphene–ZnO nanocomposite material using facile solvent exfoliation and low temperature solvothermal processing approaches. It is our aim to fully harvest the desired high electrical conductivity of graphene and the good electrocatalytic property of ZnO in the nanocomposites material. In this work, the surface characteristics, structural and electrochemical properties of the graphene/ZnO nanocomposites as an electrode material for supercapacitors were evaluated thoroughly.

2. Experimental

2.1. Materials

Commercially available raw highly pyrolytic graphite (HOPG) flakes (99% carbon purity) were purchased from Bay Carbon, zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O (reagent grade 98%) were bought from Sigma Aldrich. Activated carbon ( CH₂-O₂) was purchased from RHE resources, ethanol was obtained from Merck and sodium hydroxide (NaOH) was purchased from R&M Chemicals. All chemicals were used as received without further purification. Deionized water (DI) from the Millipore system was used throughout the experiment.

2.2. Synthesis of graphene

The graphene nanomaterial was prepared via a facile green solvothermal synthesis of graphene and ZnO as illustrated in Fig. 1. Graphite was used as the starting reagent for synthesis of graphene via liquid phase exfoliation method [25]. Typically graphite (50 mg) material was dispersed in 100 ml solution of ethanol and deionized water (2:3 ratio) and sonication treatment was carried out in a conventional ultrasonic bath with working frequency of 50/60 Hz at room temperature for 3 h to form a darkish black suspension. The solution was centrifuged under 1000 rpm for 30 min to remove aggregates and the remaining residue was dried at a temperature of 80 °C for 10 h.

2.3. Preparation of graphene–ZnO composites

Graphene (0.2 g) nanomaterial was then re-dispersed in 50 ml solution of ethanol and deionized water (2:3) under sonication for 30 min. Zinc nitrate hexahydrate was added to
the graphene solution and stirred for 15 min to produce a uniform dispersion. Diluted sodium hydroxide solution was then added to the mixture till a pH value of 12 is obtained and was stirred for 30 min. The mixture was transferred to a 50 ml Teflon stainless steel autoclave and put in an oven for 10 h at 90 °C. The solid precipitation was isolated from the solution by centrifugation, washed repeatedly with excess water and ethanol, respectively and dried overnight at 70 °C in an oven.

The addition of NaOH solution in the mixture generates an intermediate hydroxide (Zn(OH)2) colloids upon reaction with Zn(NO3)2·6H2O as stated in Eq. (1), part of the Zn(OH)2 colloids dissolves into Zn2+ and OH− during the hydrothermal process according to Eq. (2). ZnO nuclei are formed when the concentration of Zn2+ and OH− reaches the supersaturation degree of ZnO according to Eq. (3). The possible reactions process can be expressed in the equations as follows:

\[
\begin{align*}
\text{Zn(NO3)2} \cdot 6\text{H2O} + 2\text{NaOH} & = \text{Zn(OH)2} \text{(gel)} + 2\text{NaNO3} + 6\text{H2O} \\
\text{Zn(OH)} \text{(gel)} + 2\text{H2O} & = \text{Zn}^{2+} + 2\text{OH}^- \\
2\text{H2O} & = \text{Zn(OH)4}^{2-} + 2\text{H}^+ \\
\text{Zn(OH)4}^{2-} & = \text{ZnO} + \text{H2O} + 2\text{OH}^- 
\end{align*}
\]

Table 1 shows detailed information of the different ratios of graphene to zinc nitrate hexahydrate which were used to prepare the graphene–ZnO nanocomposites.

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Mass of graphene (g)</th>
<th>Mass of zinc nitrate hexahydrate (g)</th>
<th>Weight ratio of graphene: zinc precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>GZn1</td>
<td>0.2</td>
<td>0.2</td>
<td>1:1</td>
</tr>
<tr>
<td>GZn2</td>
<td>0.2</td>
<td>0.4</td>
<td>1:2</td>
</tr>
<tr>
<td>GZn3</td>
<td>0.2</td>
<td>1.6</td>
<td>1:8</td>
</tr>
<tr>
<td>GZn4</td>
<td>0.2</td>
<td>3.2</td>
<td>1:16</td>
</tr>
</tbody>
</table>

2.4. Characterization

The crystalline structure of the materials were analysed by an X-ray diffractometer (XRD) (Philip XRD) operated at 33 mA and 45 kV with Cu Kα radiation (λ=1.54056 Å) in the range of 10° to 70° with step size 0.03°. The surface characteristics and elemental composition of the composites were analysed using a scanning electron microscope (SEM)
(BT-2000) using the MITS Pro 4.0512.12 software. The cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were also studied in a two-electrode configuration using a VersaSTAT 3 (VE-400) electrochemical working station driven by the V3 studio version 1.0286 software.

3. Results and discussion

The XRD patterns of the prepared graphene–ZnO composites, graphite and zinc oxide are shown in Fig. 2. It can be seen that the ZnO XRD patterns of the nanocomposites with different mass ratios are similar to that of pure zinc oxide, indicating that no other impurity peaks were detected. It can be readily assigned to pure ZnO with hexagonal structure (ICSD No. 98-002-7781) with lattice constants $a = b = 3.2540$ Å, $c = 5.2150$ Å. The peaks at 2$\theta$ values of 32.0, 34.6, 36.5, 47.7, 56.8, 63.0, 66.6 and 68.1 can be indexed to (1 0 2), (1 0 1), (0 1 2), (0 1 4), (2 1 2), (2 0 1) and (2 2 3) crystal planes, respectively. This clearly indicated that ZnO nanoparticles were formed from the precursor. In addition, with the increase in mass loading of ZnO, the increase in intensities of the respective diffraction peaks of the composites were also observed. The two diffraction peaks of graphite at 2$\theta$ values of 26.8 and 54.9° are attributed to the (0 0 2) and (1 −2 0) reflections of graphite (ICSD No. 98-005-2916), and these diffraction maximums were clearly observed for the graphene–ZnO nanocomposites. These results indicate that the crystalline structure of the graphene material was intact and its pristine nature was preserved.

The Raman spectra of graphene and graphene/ZnO nanocomposites respectively are shown in Fig. 3. Three distinct peaks are associated with the graphene Raman spectra; namely the G band at $\sim 1580$ cm$^{-1}$ which corresponds to the in-plane vibration of sp$^2$ carbon atoms, the 2D band at $\sim 2719$ cm$^{-1}$
and the D band at $\sim 1351$ cm$^{-1}$ ascribed to the first-order zone boundary phonons, which is absent from defect-free graphene [26]. However, the formation of new edges which can be seen as defects from the exfoliated sheets due to the exfoliation process of graphene from graphite leads to the existences of a D peak [25,27,28]. After the hydrothermal treatment, four peaks indicated as 'X' in the graphene/ZnO spectrum belongs to ZnO. The peak at $\sim 432$ cm$^{-1}$ agrees with the finger signal of the characteristic E$_2$ mode of ZnO wurtzite structure [29], while the peaks at $\sim 327$ cm$^{-1}$ and $\sim 568$ cm$^{-1}$ are well indexed to the transversal optical modes with A$_1$ symmetry and the longitudinal optical modes. The broad peak at $\sim 1127$ cm$^{-1}$ corresponds to 2A1 (LO), 2E1(LO) and 2LO mode of ZnO [26,29]. The D-band, G-band and 2D-band were located at $\sim 1349$ cm$^{-1}$, $\sim 1574$ cm$^{-1}$ and $\sim 2717$ cm$^{-1}$; the shift of the bands are likely due to the doping effects of ZnO [30]. The Raman spectrum after the hydrothermal treatment confirms that the structure of graphene was not destroyed and the graphene/ZnO composites were formed, which is in good agreement with the XRD results (Fig. 2).

Fig. 4a–d shows the FESEM images of graphene–ZnO composites synthesised from different precursor mass ratios. The ZnO nanoparticles formed on the graphene sheets were found to be of spherical to globular structures with diameter around 1500 nm for GZn1 and GZn2 (Fig. 4a and b) and 200 nm for GZn3 and GZn4 (Fig. 4c and d), respectively. The results illustrated that with an increase in the loading mass of Zn precursor, more ZnO nanoparticles will be formed on the surface and edges of the graphene sheets. It was also observed that in GZn1 and GZn2, the ZnO nanoparticles were not uniformly spread on the graphene surface. On the other hand, heavy clusters (agglomerated form) of ZnO nanoparticles were found on the graphene surface of GZn4, and these aggregates tend to form non-conducting layers that can affect its charge storage property [31]. Fig. 4c shows that a uniform and homogenous spread of ZnO nanoparticles were anchored well on the edges and surface of the graphene sheet. The evidence of the formation of ZnO nanoparticles deposited on the surface of graphene is supplemented by images provided by TEM analysis (Fig. 4e and f). The TEM results display the two dimensional structure of graphene and a well spread graphene sheet decorated with ZnO. Fig. 4f illustrates that the ZnO nanoparticles were quasi-spherical in shape and are well deposited on the inside interlayer of the graphene sheet. No free ZnO nanoparticles were observed outside the graphene sheet.

The chemical composition of the composites were analysed by an energy dispersive spectroscopy (EDS). The peaks of C,
O, Zn in the EDS spectrum depict the presence of carbon, oxygen and zinc compounds only, therefore confirming the purity of the composites material (Fig. 4g). The peak corresponding to Si in the EDS spectrum is due to the silicon substrate used for the characterization.

The cyclic voltammograms (CV) tests were carried out within a potential range of −0.1 to 0.5 V at different scan rates varying from 5 to 100 mV/s using 1 M KOH electrolyte. Fig. 5a compares the CV curves of graphene, GZn1, GZn2, GZn3 and GZn4 at a scan rate of 10 mV/s. It can be seen that all the CV curves exhibited a nearly rectangular shape along the current–potential axis indicating good capacitive performance. In comparison to the graphene electrode, the graphene–ZnO composites electrode showed higher integrated area on the current–potential axis, disclosing better charge storage performance. This clearly indicates that the addition of ZnO increases the total capacitance of the electrode. The specific capacitance \( (C_s) \) can be calculated from the CV curves by Eq. (4) below [32]:

\[
C_s = \frac{2I}{s \times m}
\]

where \( I \), \( s \) and \( m \) are the charge current, scan rate and mass of the single electrode respectively. Based on Eq. (4), the calculated \( C_s \) values for these electrochemical capacitors were: 236 F/g (GZn3) > 230 F/g (GZn2) > 188 F/g (GZn4) > 185 F/g (GZn1) > 100 F/g (graphene) at a scan rate of 10 mV/s. From the calculated results, it is noticed that the increase in mass loading of ZnO nanoparticles was not proportional to the improvement in \( C_s \) of the electrochemical capacitors. Sample GZn4 demonstrated lower specific capacitance as compared to GZn3 and GZn2, which can be attributed to excess agglomerations of ZnO nanoparticles on the graphene surface (Fig. 4d). The particle aggregation tends to form non-conducting layers that can increase its intrinsic resistivity and deteriorate the charge storage capacity. In addition, these non-conducting layers on the graphene surface reduces the amount of surface area accessible to the electrolyte ions thereby limiting its capacitive performance [31]. The CV analyses on GZn3 at various scan rates were performed in order to obtain further information on its capacitive performance (Fig. 5b). The CV curves for the composite material exhibited a nearly rectangular shape within a potential window of −0.1 V to 0.5 V signifying good capacitive performance. Generally, it was noticed that an increase scan rate produced an increase in integrated area on the current–potential axis, indicating good storage rate ability, which is similar to previous work reported [18,32,33]. Nevertheless, as clearly indicated in Fig. 5c, a decrease in specific capacitance with increase in scan rate is observed instead. At a scan rate of 5 mV/s, a specific capacitance of 246 F/g was achieved while at higher scan rate of 100 mV/s the recorded specific capacitance was significantly reduced to 112 F/g. The results clearly implies that lower scan rates generally is more favourable, since it allows adequate time for ion adsorption and diffusion within the intrinsic pore structures of the active material, leading to a higher charge storage capacity [33].

The long cycling life is an important requirement for practical applications of supercapacitors [18]. A cycling life test of graphene–ZnO composite electrode (GZn3) was carried out by repeating the CV measurements between −0.1 to 0.5 V at a scan rate of 50 mV/s for 200 cycles. As shown in Fig. 6a, the respective CV curves retained their quasi-rectangular shapes.
The galvanostatic charge–discharge tests were performed by applying a series of charging and discharge currents onto the electrochemical capacitors and measuring the voltage response. The voltage response of graphene, GZn1, GZn2, GZn3 and GZn4 electrodes were studied at a constant current density of 10 mA/g. The energy loss due to internal or equivalent series resistance is shown by the IR drop at the turning point of the charge and discharge curves, as seen in Fig. 7a [34]. From these results, GZn3 sample has the least internal resistance, thereby having the highest capacitance when evaluated with respect to their individual mass. These findings support the results of the calculated specific capacitances obtained from the CV curves earlier (Fig. 5). The IR drop observed in the charge–discharge curve may be due to the internal resistance of the electrodes. Fig. 7b shows the representative galvanostatic charge–discharge measurements of the GZn3 electrode at different current densities of 1, 2, 3, 5 and 10 mA/g under an applied potential between 0 and 1 V. The charge–discharge curves of the GZn3 electrode exhibits near linear and symmetric triangles, indicating good capacitive performance and excellent reversibility [35,36]. The IR drops on all the curves are negligible, implying low resistance and good contact between the collectors and the electrode material. The discharge curves were not straight lines suggesting that the capacitance includes the double-layer and redox capacitance [36]. The specific capacitance of graphene, GZn1, GZn2, GZn3 and GZn4 at different current densities were compared as shown in Fig. 7c. It can be observed that with increase of current densities from 1 to 10 mA/g, there is a corresponding decrease in specific capacitance of the electrode materials. This could be explained by the discrepant insertion–desertion behaviour of ions from electrolyte to electrode material. The rending ions (OH\(^{–}\)) fail to fully occupy the sites at the electrolyte/electrode interface if compared to lower current density because of ions’ limited migration velocity and fixed route in the interface thereby leading to an uncompleted insertion reaction [37]. GZn3 electrode exhibited a drop of 20.8% from its initial capacitance value as the current density increased from 1 to 10 mA/g compared to GZn2, GZn4, GZn1 and graphene which had a drop of 22.7%, 27%, 29% and 60% capacitance values respectively. In order to further evaluate the cycling stability of GZn3 electrode, galvanostatic charge–discharge analysis was performed at a constant current density of 10 mA/g between 0 to 1 V for consecutive 1000 cycles. As displayed in Fig. 7d, the specific capacitance of GZn3 electrode retains 83% of its initial capacitance value, reflecting good electrochemical stability and reversibility upon repetitive charge–discharge process [35].

Electrochemical impedance spectroscopy (EIS) measurements are very essential in assessing the resistive characteristics of the electrode. It shows the response of components performance in the frequency domain [34]. EIS were carried out in a frequency range from 100 kHz to 0.01 Hz in order to evaluate the frequency response of both graphene and graphene/ZnO nanocomposites. The Nyquist plots for the electrodes are depicted in Fig. 8. The EIS data was analysed using Nyquist plots and each data point is at a different frequency. The Nyquist plots consists of two frequency regions, a high frequency region denoted by a semicircle which represents the transfer of charges occurring at the electrode/electrolyte interface and the low frequency region signified by a straight line representing the diffusion of ions in the electrolyte. The equivalent series resistance (ESR) can be obtained from the x-intercept of the Nyquist plot and the charge transfer resistance \(R_{ct}\) can be directly measured as the diameter of the semicircle arc on the real axis [3,34,38]. The ESR and charge transfer resistance \(R_{ct}\) obtained from the Nyquist plot (Fig. 8) are depicted in Table 2.

The ESR and \(R_{ct}\) values of the electrochemical capacitors decreases in the order of graphene > GZn1 > GZn2 > GZn4 > GZn3 which is indirectly proportional to results of the specific capacitance, specifically, the higher the \(R_{ct}\) value, the lower the specific capacitance of the electrochemical capacitor [39].Graphene having the highest ESR and \(R_{ct}\) values affirms that the addition of ZnO to graphene results in an improved charge transfer performance. From Table 2, GZn3 electrochemical capacitor has the smallest ESR and this could be due to the fact that the graphene/ZnO hybrid facilitates the highest accessibility of ions into the surface of graphene sheets made possible by the uniform dispersion of ZnO particles on the graphene surface, as evidenced in the SEM analysis (Fig. 4c).
The average energy density \( E \) and power density \( P \) of the electrochemical capacitors were calculated using the following equations [18],

\[
E = \frac{1000 \times C_s \times \Delta V^2}{2 \times 3600} \tag{5}
\]

\[
P = \frac{E \times 3600}{\Delta t} \tag{6}
\]

where \( E \) is the energy density of the electrode (W h/kg), \( P \) is the power density (kW/kg), \( C_s \) is the specific capacitance of the electrochemical capacitor (F/g), \( \Delta t \) in seconds is the time for a sweep segment and \( \Delta V \) is the voltage range for one sweep segment. The calculated average energy and power densities are tabulated in Table 2.

On the basis of the results provided by Table 2, the graphene/ZnO nanocomposites electrodes showed a higher specific capacitance, improved charge transfer performance.
and a significantly enhanced energy and power densities when compared to the graphene electrode. The resulting specific capacitance of the graphene/ZnO nanocomposites is significantly higher than previous work reported on graphene/ZnO based supercapacitor [3,17,18,33]. The improved electrochemical performance of graphene/ZnO electrodes can be attributed to the following aspects: (i) the pristine nature of the synthesized graphene which improves the electrical conductivity of the hybrid structure. (ii) The electroactive property of ZnO anchored to the graphene sheets provides a three dimensional conductive system which provides more active sites for the formation of electric double layer. This distinctive system also aids the easy diffusion of ions into the inner channels hereby reducing diffusion resistance, similar to those reported in previous studies [31], (iii) The pseudo-capacitance from the ZnO combined with the double-layer capacitance from graphene provides a higher specific capacitance [19,40].

4. Conclusions

In summary, graphene/ZnO nanocomposites as an electrode for electrochemical capacitors was successfully synthesized from highly pyrolytic graphite via a green, facile, effective and scalable solvothermal technique. The structural analysis and electrochemical properties of graphene/ZnO nanoparticles have been studied comprehensively. In comparison with the pristine graphene electrode, the graphene/ZnO nanocomposite electrodes demonstrated an improved electrochemical performance. The graphene/ZnO nanocomposite electrode material with a weight ratio of 1:8 (graphene: ZnO) displayed the highest specific capacitance of 236 F/g at a scan rate of 10 mV/s with energy and power densities of 11.80 Wh/kg and 42.48 kW/kg, respectively. This simple, facile and green synthesis method can be extended for other graphene/metal oxide nanocomposites based high performance electrochemical capacitor.

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