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Polymeric Nanomaterials based on the Buckybowl Motif: Synthesis through Ring-Opening Metathesis Polymerization and Energy Storage Applications

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ABSTRACT: Ring-opening metathesis polymerization (ROMP) of buckybowl corannulene-based oxa-norbornadiene monomer is shown to give rise to polymeric nanomaterials with an average pore size of about 1.4 nm and a surface area of 49.2 m²/g. Application in supercapacitor devices show that the corannulene-based nanomaterials exhibit a specific capacitance of 134 F.g⁻¹ (1.0 V voltage window) in a three-electrode cell configuration. Moreover, the electrode assembled from these materials in a symmetric configuration (1.6 V voltage window) exhibits long-term cyclability of 90% capacitance retention after undergoing 10,000 cycles. This work demonstrates that ROMP is a valuable method in synthesizing nanostructured corannulene polymers, and that materials based on the non-planar polycyclic aromatic motif represents an attractive active component for fabrication of devices targeted at electrochemical energy storage applications.

Corannulene, C₂₀H₁₀, is a polycyclic aromatic hydrocarbon (PAH).^{1,4} However, unlike most PAHs, corannulene adopts a bowl-like shape. This is due to the presence of a five-membered ring in the polyaromatic scaffold - which when fused with six-membered rings around it, forces a positive curvature of the structure.^{5,7} It is one of the most simple curved aromatic structures and can be described as a polar cap fragment of the fullerene C₆₀. Therefore, considering its shape and its relationship with C₆₀, corannulene is often referred to as a bucky bowl.

The nonplanarity of the structure endows corannulene with distinct properties that are not found in planar aromatic hydrocarbons such as anthracene or pyrene. For example, corannulene is an electron acceptor.⁸⁻¹¹ It is known to intercalate efficiently with lithium ions.¹² Furthermore, it can complex with fullerene C₆₀ through a ball-and-socket type of supramolecular interaction.¹³⁻¹⁵ Recently, a kilogram-scale synthesis has been developed thus allowing easy access to the corannulene scaffold.¹⁶

In light of the unique structure and properties, and a facile synthetic access, corannulene represents an attractive building block for the synthesis of functional soft materials. One way to realize this goal is through design of polymers based upon the bucky bowl structure. In this context, so far, there are three examples. In these examples, free radical,¹⁷ metal-catalysed,^{18,19} and coordination polymerization²⁰ is used to obtain corannulene polymers capable of hosting fullerene C₆₀, harvesting solar energy, and redox activity. Here, we show that ring-opening

metathesis polymerization is a valuable new route to bucky bowl-based polymeric nanostructures. Furthermore, we show, for the first time, that such corannulene-

Figure 1. Ruthenium-catalyzed ring-opening metathesis polymerization (ROMP) of corannulene-encoded oxa-norbornadiene monomer.

encoded polymers exhibit remarkable electrochemical energy storage properties through their use in supercapacitor devices.

This latter aspect is of significance because although the history of corannulene is rich and extends over a period of 50 years, promising real-life applications and devices made from this motif remain scarce.^{21,22}

Ring-opening metathesis polymerization (ROMP) is an important synthetic method that allows for facile preparation of a large variety of functional polymers.^{23,25} In the present context, we envisaged that placing an oxanorbornadiene group onto the corannulene nucleus will allow for application of this powerful synthetic tool to access polymers bearing corannulene group as the polymer side-chains. To test this hypothesis, initially, corannulene is brominated to give mono-bromocorannulene **1** (Figure 1).²⁶ Treatment of **1** with sodium amide generates a corannulyne that can be trapped with furan through a Diels-Alder cycloaddition reaction to give monomer **2** in an isolated yield of 76% over two synthetic steps.^{27,28} This simplicity of the synthesis allows for preparation of monomer **2** on a multi-gram scale.

Having oxanorbornadiene monomer **2** in hand, ring-opening metathesis polymerization using ruthenium-based Grubb's second-generation catalyst was carried out. This led to the formation of an insoluble precipitate. The monomer to the catalyst ratio was then varied to see if molecular weight had an effect on the solubility of the final materials. However, in all cases, an insoluble solid was obtained (Table-S1). Subsequently, the polymerisation solvent was changed from dichloromethane to tetrahydrofuran and finally to dimethyl formamide. However, none of this had a bearing on the final outcome of the polymerization reaction. This can best be described by a precipitation polymerization process in which initially all the reactants are soluble but as the polymerization proceeds the resulting polymer precipitates out due to insolubility in the reaction medium.²⁹ Typically, such reactions result into the formation of spherical morphology of the formed precipitate. Indeed, field emission scanning electron microscopy (FESEM) examination of the solid precipitate (Figure 2a-d) revealed spherically structured polymer aggregates in the size range of 400-980 nm. To further characterize the materials, transmission electron microscopy (TEM) was employed (Figure 2e-g). These experiments also showed similar structures as were observed through FESEM. At this point, it became crucial to look into the molecular structure of the solid material. The most important question, perhaps, was if the aromatic scaffold remained intact and if the molecular structure of the polymeric material could be deciphered.

Figure 2. FE-SEM (a-d) and TEM (e-g) images of nanoparticles of polymer **3**. FE-SEM: (a) panoramic view of spherical structures resulted from ROMP of corannulene monomer **2**, (b & c) images

at higher resolutions, (d) image recorded using a half-stub showing a single aggregate, and (e-g) TEM images of **3** at different magnifications

To examine this aspect, due to the insolubility of the materials, typical solution-based analytical tools could not be applied. Therefore, a solid-state nuclear magnetic resonance (NMR) technique, ¹³C cross-polarization magic angle-spinning (CP-MAS) NMR was employed. ¹³C CP MAS NMR spectrum of corannulene monomer **2** exhibited signals from alicyclic sp² carbons in the oxanorbornadiene edge (designated C₁ & C₂ in Figure 3a) and aromatic signals from corannulene carbons (designated COR in Figure 3a). After polymerization, signals from the C₂ carbon atoms at 145 and 150 ppm disappeared which indicated the expected polymerization of the olefin bond. The aromatic resonances at 125 to 135 ppm remained unchanged and established that the aromatic segment of the monomer remained intact in the formed polymer. To further examine the molecular structure, another analytical technique that could be employed in the solid state is FT-IR spectroscopy. In this, the signal at 3024 cm⁻¹ (designated iii in Figure 3b) of the monomer **2** and polymer **3** corresponds to alkenyl C-H stretching. The presence of the aromatic signals at 3001-2846, 1620, and 833 cm⁻¹ (i, ii, iii in Figure 3b) in the monomer and polymer confirms that the corannulene nucleus remained undisturbed after the polymerization process. The signal at 1018 cm⁻¹ can be assigned to (C-O-C) bond-stretching frequency in corannulene monomer and the intensity of the peak increases significantly in the polymer. Thus, ¹³C CP-MAS NMR and FT-IR measurements demonstrated that corannulene monomer **2** polymerized successfully through ring-opening metathesis polymerization and the aromatic bowl remained intact after the polymerization process.

Figure 3. ¹³C CP-MAS NMR (a) and FT-IR spectra (b) of corannulene monomer **2** (red) and the polymeric nanostructures **3** (black).

X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (powder XRD), and N_2 adsorption/desorption measurements were then conducted to study the oxidation state of composed elements, crystallinity, surface area, and porosity of the formed polymeric nanostructures. XPS analysis of the polymer (see full spectrum in **Figure S3**) indicates active elemental composition of carbon and oxygen only. The peak obtained for carbon was deconvoluted and identified for the contribution of sp^3 and sp^2 carbons due to the presence of carbon in different covalent environments (**Figure 4a**). The dominant peak at 284 eV is due to corannulene, whereas the second peak at 284.5 eV is assigned to sp^2 carbon atom present in the macromolecular backbone. The third peak at 288 eV is assigned to the carbon attached to oxygen (C-O) at the oxo-norbornadiene group. Similarly, peak at 531 eV shows the inherent oxygen (O-1s) in the polymerized side chain (**Figure 4b**). Further, powder XRD of the polymeric nanostructures (**Figure 4c**) was recorded and yielded a broad peak at $2\theta = 18.5^\circ$ with no signs of other intense crystalline peaks in the region suggesting the amorphous feature of the materials. We then carried out isothermal N_2 adsorption/desorption measurements using the Brunauer-Emmett-Teller (BET) method to calculate the surface area and pore-size distribution of the formed nanostructures. The materials exhibit a type IV isotherm with H3 hysteresis loop (**Figure 4d**) with a surface area of $49.2 \text{ m}^2/\text{g}$ and the pore size distribution analysis (dominant pore size around 1.4 nm, **Figure S5**) shows porous features for the nanostructures. The existence of narrow hysteresis loops indicates the presence of mixed porous and gas adsorption in plate-like assemblies.

Figure 4. High-resolution XPS spectra of C 1s (a) and O 1s region of the polymeric nanostructures (b). Wide-angle powder XRD patterns (c) and N_2 adsorption/desorption isotherms of the nanostructures (d).

Next, we studied the electrochemical supercapacitor properties of the polymeric nanostructures using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in three-electrode as well as asymmetric configurations. Details of electrode preparation and electrochemical cell set-up are given in the supporting information section S6. Freshly prepared and vacuum dried polymeric material was employed for the study and used as working

electrode with a sweep between 0-1V potential window. First, a three-electrode system was experimented using Pt-strip and standard calomel electrode (SCE) as counter and reference electrode, respectively. **Figure 5a** shows the CV performance of the polymeric nanostructures in 1M H_2SO_4 aqueous electrolyte. A pair of well-defined redox (0.63V oxidation and 0.5V-reduction at 10 mV.s^{-1}) peaks is visible in the CV traces. These peaks could be attributed to the reversible faradic redox behavior (pseudo capacitive) of the sample. The shapes of the redox peaks at all scan rates were similar indicating the high electrochemical reversibility of the process. A simultaneous shift in the oxidation peaks towards the positive position and the reduction peaks towards more negative position with the increase of scan rate from 10 to 100 mV.s^{-1} (**Figure 5a**) - this observed shift in the oxidation/reduction peaks could be attributed to the increased polarisation generated due to internal ion diffusion resistance in the electrode material. In turn, this would reflect in the specific capacitance of the electrode materials and thus an increase of the scan rate decreases the capacitance of the loaded polymeric nanostructures. The specific capacitance of the sample was calculated at different scan rates and a maximum specific capacitance value 111.5 F.g^{-1} is obtained at 10 mV.s^{-1} . However, the cell showed a capacitance of about 84 F.g^{-1} at 100 mV.s^{-1} , which is more than 75% of its initial capacitance. This implied a good rate capability of the polymeric nanostructures.

GCD curves of the polymeric nanostructures at different current rate at a potential window of 0-1V are shown in **Figure 5b**. The charge discharge trend of the polymer redox defined the pseudo-capacitive behavior of the sample and remains consistent with the CV curves. The polymer sample exhibited high capacitance value of about 134 F.g^{-1} at 0.5 A.g^{-1} and also showed an excellent performance with respect to current rate (70 F.g^{-1} at 10 A.g^{-1}). Thus, corannulene-based nanostructures delivered a steady capacitance even at high current rates, which further reveals the good structural strength of the formed polymeric nanostructures.

Figure 5. Electrochemical performances of polymeric nanostructures in a three-electrode system. (a) CV at different scan rates and (b) Galvanostatic charge/discharge profiles of polymeric nanostructures in 1M H_2SO_4 aqueous electrolyte at 0-1V

Further, to understand the charge storage behavior at a practical device configuration, an asymmetric supercapacitor (ASSC) was assembled using polymeric nanostructures. The polymeric material and activated carbon (Norit) were taken as positive and negative electrodes respectively. In an ASSC, the number charge storage on both electrodes might be equal and hence, in the present work the electrode materials loading on both electrodes were subjected to the prior optimisations before

cell assembly. Since, electrodes were prepared using the two different materials possessing different specific capacitance, the ASSC was fabricated mainly by balancing the electrode mass based on the individual electrode's capacitance estimated from the three-electrode system. Thus, commercial activated carbon was used which delivered a specific capacitance of about 80 F/g at a voltage window of 0.8V. Hence, the active mass 1:1.85 (2.15:4 mg) ratio was used in the electrode preparation.

The potential difference between the polymeric nanostructures and activated carbon (AC) electrodes is 1.8 V (polymer; 0–1 V & AC; 0.0–0.8 V) and hence the fabricated cell could work in a voltage window of 0–1.8 V. However, the optimized voltage window (Figure S6) of the cell showed oxygen evolution when the operating potential reaches 1.7 V. Therefore, the operating potential of ASSC was fixed as 1.6V in order to improve the safety and long life of the cell. CV plot of the asymmetric cell at an optimized potential window was evaluated at different scan rates (Figure 6a). When compared to the redox peaks obtained in the three electrode system, a slight shift towards the lower voltage window at 0.36 V (oxidation) and 0.28 V (reduction at 10 mVs⁻¹) followed by the double layer capacitance was observed. In ASSC, a combined effect of both pseudo-capacitive and electric double layer capacitance (EDLC) behavior could be observed which are contributed by redox active polymer and activated carbon, respectively. Similar to the three-electrode system, ASSC exhibited a remarkable response even at high scan rate and the cell delivered a capacitance value of 135 F.g⁻¹ at 10 mV.s⁻¹.

Further, the specific capacitance value of polymeric nanostructures in the ASSC was also estimated from the GCD study. The obtained GCD curves of the sample at different current rate at 1.6V are shown in Figure 6b. The cell showed a high capacitance value about 131.25 F.g⁻¹ at 0.5A.g⁻¹ with good rate capability and stable capacitance retention at high current rates. The ASSC exhibited minimal IR drop, which implied the good conductivity of the electrode materials. During calculation, over-estimation of the capacitance was avoided by calculating the discharge time after the potential drop from the GCD plot. The specific energy and specific power density of the cell was calculated using Ragone plot (Figure 6c). It was noted that the cell delivered the specific energy density of about 46.67 Wh/kg at a power density of 1.6 kW/kg. Whereas, a high specific power of about 19.2 kW/kg at a specific energy density of 34.67 Wh/kg could be observed. This indicates that the ASSC assembled with the polymeric nanostructures showed an excellent performance which balances both high current and high energy even at high current rate (6 A/g). In order to estimate the cycle stability, the cell was tested at 2 A/g at 1.6V window (Figure 6c).

Figure 6. Electrochemical performances of an asymmetric supercapacitor fabricated using polymeric nanostructures. (a) CV at different scan rates from 10 mV.S⁻¹ (black curve) to 90 mV.s⁻¹ (purple curve), (b) GCD curves at different scan rates, (c) capacitance retention from 0 to 10000 cycles, and (d) the Ragone plot showing calculated specific energy and power density of ASSC.

The polymer-loaded ASSC showed good cycle life with the capacitance retention of more than *c. a.* 85% at 11000 cycles. The GCD behavior of the sample at different cycles (each 2000 cycle interval) is given in Figure S7, which clearly reflects the capacitance retention and cycle stability. Electrochemical impedance spectroscopy (EIS) was used to further evaluate the electrochemical performance of the three electrode and asymmetric supercapacitors. The obtained EIS spectra of the samples (Figure S8) showed inclined line observed in the middle frequency region directly related to the pseudo capacitance and the semicircle observed in a higher frequency region is related to bulk resistance and charge transfer resistance of the SCs.

To summarize, ring-opening metathesis polymerization of a buckybowl corannulene-based monomer results into spherically shaped polymeric nanomaterials through a precipitation polymerization process. A systematic and in-depth study reveals that these materials show remarkable energy storage properties through a pseudocapacitive charge storage mechanism. In essence, the findings extend the synthetic methods available to access buckybowl polymers and enhance the repertoire of carbon-rich functional materials applicable in electrochemical energy storage applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available (PDF file) free of charge on the ACS Publications website.

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Author Contributions

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