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High-performance Mn_3O_4/onion-like carbon (OLC) nanohybrid pseudocapacitor: Unravelling the intrinsic properties of OLC against other carbon supports

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ABSTRACT

The electrochemical performance of the tetragonal hausmannite Mn_3O_4, when embedded on various carbon materials, onion-like carbon (OLC), carbon nanotubes (CNT), reduced graphene oxide (RGO) and activated carbon (AC) (i.e., OLC/Mn_3O_4, CNT/Mn_3O_4, GO/Mn_3O_4, and AC/Mn_3O_4), has been investigated as electrode material for symmetric and asymmetric pseudocapacitor device. The nanohybrid electrode materials demonstrated higher electrochemical performance (in terms of specific capacitance and rate capability as energy storage devices) compared to the pure Mn_3O_4. The OLC/Mn_3O_4-based symmetric pseudocapacitor device exhibited higher specific capacitance of 195 F g^{-1}, specific energy of 4.3 Wh kg^{-1} and power density of 52 kW kg^{-1} compared to other carbon nanohybrid materials studied. From the symmetric experiments, the best-performing OLC/Mn_3O_4 nanohybrid has been further explored as high-voltage asymmetric pseudocapacitor, with maximum energy and power densities of *ca.* 19 Wh kg^{-1} (at 0.1 A g^{-1}) and 45 kW kg^{-1} (at 10 A g^{-1}) respectively. The high-performance of the OLC-based system compared to the other carbon systems is ascribed to the combined unique intrinsic properties of the OLC; high electrical conductivity, highly accessible outer surface and large interparticle pore volumes. The above properties have ensured OLC/Mn_3O_4 nanohybrid as a suitable candidate for the high-voltage asymmetric pseudocapacitor device.

1. Introduction

Rapid developmental growth of the economy and the dependency on unclean fossil fuel (i.e., having negative environmental impact) across the globe, compel for more innovative ideas on alternative energy sources that are efficient and clean [1,2]. Electrochemical capacitors (ECs) also known by their commercial names, supercapacitors and ultracapacitors, have shown a great promise in curbing such energy challenges. Redox-based electrochemical capacitors called pseudocapacitors are devices that store their energy through Faradaic processes. Unlike their counterparts, the electrical double layer capacitors (EDLC) that store energy through non-Faradaic processes and only use carbon materials as electrode materials, pseudocapacitors employ redox-active materials such as conducting polymers, metal sulphides and metal oxides for energy storage at the electrode/electrolyte interface. Considering energy and power performance, ECs play a key role as intermediate between batteries and electrolytic capacitors [3] and find widespread applications for fast charge/discharge and uninterrupted power supply (UPS) applications as well as in combination with batteries in hybrid systems [4]. The electrochemical performance of the ECs device depend on the morphological properties (i.e., size, shape, surface area, and architecture) of the electrode materials [5]. Thus considerable attention has been devoted to the development of the ECs electrode materials.

Manganese oxide-based electrode materials characterized by their high theoretical specific surface area (1370 m^2 g^{-1}), high theoretical specific capacitance (1100–1300 F g^{-1}), low-cost, abundance and environmentally friendly in nature, have attracted

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significant interest as active electrode materials for ECs [6–13]. Although intensive study has been done on the MnO_2-based pseudocapacitor, recently, a tetragonal hausmannite metal oxide, Mn_3O_4, has received limited attention in ECs application [14]. Hausmannite, Mn_3O_4, is one of the oxides of manganese which contain both the di- and trivalent manganese (Mn^{2+} and Mn^{3+}, respectively). This type of oxide material belongs to the spinel group, and forms a crystal structure of a tetragonal as shown in Fig. S1 [15]. The Mn^{2+} is coordinated by four oxygen atoms situated at the corners of a tetragonal prism. The Mn^{3+} is also coordinated by four oxygen atoms at the equatorial position to show square-planar coordination geometry. The key challenges to the electrochemical application of Mn_3O_4 material as pseudocapacitor relate to its poor electrical conductivity and small specific surface area [16–18].

Carbon materials are the most studied support materials for supercapacitor device due to cost and ease of real-life application. Several carbon materials (carbon nanotubes (CNT), activated carbon (AC), reduced graphene oxide (RGO) and onion-like carbon (OLC)) have been reported in the literature as efficient supports for manganese oxide-based pseudocapacitor devices [19–22]. Carbon materials are characterized by their large specific surface area (SSA), high conductivity, facile availability, and chemical stability [5,23]. Some of the best-performing carbon materials include activated carbon [24], carbon nanotubes (CNTs) [25,26], graphene and graphene oxide [6,27,28], carbon nanofibers (CNFs) [29,30], carbon aerogels [31] and onion-like carbons (OLCs) [22,32]. OLC is an emerging carbon nanomaterial that has begun to attract major research interest in energy storage and conversion [33,34]. OLC is a highly disordered and defective with sp^2-hybridization consisting of multiple concentric fullerene-like carbon shells [35]. Due to their small size of typically below 10 nm, the large external surface area, and high conductivity, OLCs are used for supercapacitor applications [22,36]. Hausmannite Mn_3O_4 is a widely investigated oxide for various applications, including electrochemical energy systems [37] and catalysts. The key challenges to the electrochemical application of Mn_3O_4 as energy storage material are its poor electrical conductivity and small specific surface area. Some of the recent strategies to curb these challenges include: doping with transition metal such as Cr [15] and Sn [38]; doping with metallic oxides such as TiO_2/CuO [39] and ZnO [40]; integration with CNT [41] and RGO [42,43] and graphene [44].

Nearly all the studies on Mn_3O_4-based pseudocapacitor have been devoted to the use of half-cell configuration which, unfortunately, does not provide adequate scientific knowledge on the performance of the system when deployed in the real environment [21,41,45–47]. Motivated by the above knowledge gap, this work therefore seeks to understand which of the popular best brings out the pseudocapacitive properties of the highly insulating hausmannite Mn_3O_4. We clearly show that OLC, which is neither as conductive as the CNT nor possesses as high surface area as the AC, confers the best pseudocapacitive properties upon the Mn_3O_4 compared to the MWCNT and AC.

2. Experimental section

2.1. Precursors and synthesis of electrode materials

2.1.1. Onion-like carbon (OLC)

All chemicals were of analytical grade and used as received. OLC was kindly donated by Prof Presser group of INM (Germany). It was synthesized from nanodiamond (ND) powder with a purity of 98–99% (NaBond Technologies) and thoroughly characterized as recently described [48]. Briefly, ND powder was placed in a closed-lid cylindrical graphite crucibles (30 mm in diameter and 20 mm in height) and thermally annealed in a water-cooled high temperature vacuum furnace with tungsten heaters (Model: 1100-3580-W1, Thermal Technology Inc.). The heating and cooling rate were both 15 °C min^{-1} and the chamber pressure ranged between 10 and 100 mPa. The final OLC was annealed at 1750 °C for 3 h.

2.1.2. Graphene oxide (GO)

Graphene oxide (GO) was prepared from expanded graphite powder. The expanded graphite is obtained from the graphite powder using a well-established method [49]. Briefly, a natural graphite powder and conc. H_2SO_4 (98%, Sigma-Aldrich) were first mixed and stirred in the round bottom flask, followed by addition of fuming HNO_3 (Sigma-Aldrich) and the mixture was stirred for 24 h at room temperature. After stirring, de-ionized H_2O was slowly added to the mixture and centrifuged for 10 min at the speed of 4000 rpm. After decanting the supernatant, the solid material was then centrifuged three times (3×) with de-ionized H_2O and dried at 60° C for 24 h to obtain a graphite intercalation compound (GIC) powder. The as-synthesized GIC powder was thermally expanded at 1050 °C for 15 s as to get the expanded graphite (EG). The synthesis of GO was carried out using the well-known modified Hummers method. This approach is outlined as follows: 1.0 g EG was mixed and stirred with 200 mL of concentrated H_2SO_4 (98%, Sigma-Aldrich) in a 500 mL three-necked flask. Followed by a very slow addition of 10 g $KMnO_4$, then the mixture was transferred into an ice bath where 200 mL de-ionized H_2O, and 50 mL H_2O_2 (30%, Sigma-Aldrich) were added slowly resulting in a color change of the suspensions to light brown. After stirring for 30 min, the as prepared GO particles were then washed with an aqueous HCl (35%, Sigma-Aldrich) (9:1 H_2O: HCl by volume), then washed by centrifugation with de-ionized H_2O until the pH is adjusted about 5–6 and dried overnight at 80° C [49,50].

2.1.3. Multi-walled carbon nanotubes (CNT) and activated carbon (AC)

Activated carbon (AC) was purchased from SUPELCO analytical and used as received. CNT was obtained from Nanolab (purity: > 94%, diameter: 10-20 nm, length: 5-20 μm) but was purified using the conventional acid-treatment process, first refluxing in 2.6 M HNO_3 for 48 h, then treating in conc. H_2SO_4/HNO_3 (3:1 ratio) for 24 h, stirring in Piranha solution (H_2SO_4/H_2O_2 (4:1)) at 70° C for 30 min, and finally washing with de-ionized H_2O and drying at 50 °C for 48 h.

2.1.4. Tetragonal hausmannite Mn_3O_4 and carbon/Mn_3O_4

Tetragonal hausmannite Mn_3O_4 nanoparticles were synthesized from Electrolytic Manganese Dioxide (EMD) (Delta EMD (Pty) Ltd) through the annealing process. Briefly, EMD powder was placed in a horizontal tube furnace and ramped from room temperature to 1000 °C at 10 °C min^{-1} in the air and kept at this temperature for 40 h. Carbon/Mn_3O_4 nanohybrid electrode materials (i.e., OLC/Mn_3O_4, CNT/Mn_3O_4, GO/Mn_3O_4, and AC/Mn_3O_4) were obtained by dispersing both carbon precursor (i.e., OLC, CNT, GO and AC) and Mn_3O_4 nanoparticles (1: 1 mass ratio, Carbon: Mn_3O_4) in ethanol. The mixture was ultrasonicated for 24 h using a table-top ultrasonic cleaner (VWR B1500-A MTH, operated at 50 W). After which samples were washed by centrifugation with copious amount of de-ionized H_2O and finally dried at 60 °C overnight.

2.1.5. Structural characterization

Surface morphology characterization of the samples was obtained using a JSM-7500F (JEOL, Japan) scanning electron microscope (SEM) operated at 3.0 kV. Transmission electron microscopy (TEM) samples were prepared by dispersing powders in ethanol and placing the solution over a copper grid with a lacey carbon film.