Dendrimer-functionalized magnetic nanoparticles: A new electrode material for electrochemical energy storage devices

Sudeshna Chandra [a, c, 1], Mumukshu D. Patel [a, 1], Heinrich Lang [b], Dhirendra Bahadur [a, *]

[a] Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India
[b] Inorganic Chemistry, Institute of Chemistry, Technische Universität Chemnitz, D-09107 Chemnitz, Germany
[c] Department of Chemical Sciences, School of Science, SVKM's NMIMS University, Vile Parle (West), Mumbai 400056, Maharashtra, India

HIGHLIGHTS

- Synthesis of redox active NH_2-PAMAM dendrimer for stabilizing and functionalizing Fe_3O_4 to get Fe_3O_4@D-NH_2 nanoparticles.
- Exploring the possibility of using mesoporous Fe_3O_4@D-NH_2 as electrode material for fabrication of energy storage device.
- Fe_3O_4@D-NH_2 exhibited high charge storage and delivery capabilities with optimum capacitance of 70—120 F/g.
- Fe_3O_4@D-NH_2 nanoparticles exhibited enhanced current charging-discharging with improved retention time upto 500 cycles.

GRAPHICAL ABSTRACT
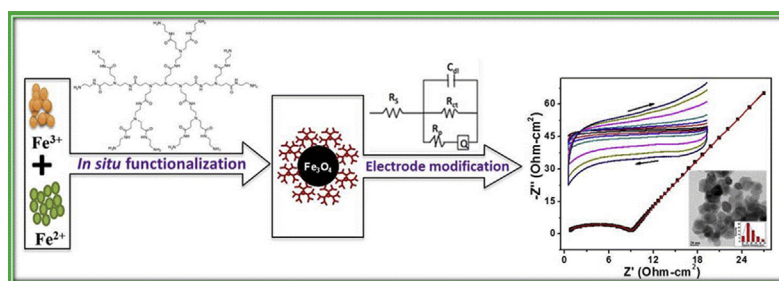
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ABSTRACT

A 10-arm −NH_2 terminated polyamidoamine (PAMAM) dendrimer with a diethylenetriamine core and a redox centre is synthesized using a new protocol. This dendrimer is further used to produce dendrimer-functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2), which are potential electrode and supercapacitor materials for electrochemical supercapacitors. The electron charge transfer mechanism between the core and the branched surface of the dendrimers is ideal for energy storage. Iron oxide nanoparticles with high specific surface area and porosity are looked upon as electrochemically active materials. Combining the advantages from both dendrimers and iron oxide nanoparticles, porous Fe_3O_4@D-NH_2 is of considerable interest due to its large surface area, unique porous structure, diversified composition and excellent electronic conductivity. These extraordinary features enable Fe_3O_4@D-NH_2 to offer high specific capacitance and charge/discharge rate which make them promising candidates as electrode material in supercapacitors, combining high-energy storage densities with high levels of power delivery. The electrochemical behavior of the material is studied by cyclic voltammetry, which shows typical rectangular I−V behavior of an ideal supercapacitor. With a high surface area, the nanoparticles exhibits high charge storage and delivery capabilities possessing optimum capacitance value in the range of 70—120 F/g depending on material loadings in various electrolytes.

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* Corresponding author.
  E-mail address: dhirenb@iitb.ac.in (D. Bahadur).
[1] Both the authors have equal contributions.

1. Introduction

Nanomaterials have been attracting great interest due to their potential use in applications such as energy storage devices, sensors, and solar cells. Electrodes fabricated out of nanomaterials have several advantages in electrochemical technology, such as higher charge–discharge rates due to higher surface to volume ratio and shorter path length for electronic transport and ion transport [1]. Among the energy storage devices, supercapacitors receive a special place in electrochemical technology because they bridge the gap between batteries and conventional capacitors by delivering the stored energy more rapidly than batteries and yielding specific capacitance which are 6–9 orders of magnitude larger than conventional capacitors.

The capacitance and charge storage of electrochemical supercapacitors depend on the electrode materials used. Therefore, developing new materials with high capacitance and improved performance relative to existing electrode materials is very important. There is only a handful of literature on electrode materials inspite of their playing a crucial role in the electrical performance of supercapacitor. Till date, activated carbon (AC) is the most widely accepted electrode material for the supercapacitor because of high specific surface area, porous texture, good electrical conductivity and relatively inexpensive cost [2]. However, there is a discrepancy between the surface area and the capacitance measured; while a high surface area up to 3000 m^2/g is reported but the corresponding capacitance is <15 $\mu F/cm^2$, which indicates that all pores are not utilized for charge accumulation. Therefore, it can be concluded that besides surface area and porosity, electrical conductivity and surface functionalities also play important roles for the electrochemical performance of the cell.

Carbon nanotubes (CNTs) and Carbon Aerogels (CAGs) are also being explored as electrode materials for energy storage devices due to their unique pore structure, superior electrical properties, good mechanical and thermal stability [3,4]. However, their capacitance performance have limitations like low specific surface area, high cost and small charge storage capacity due to the internal resistance of the carbonaceous matrix. Several composites of carbon have been explored to improve the capacitive performance of the electrode material for use as supercapacitor [5]. Lu et al. [6] has developed a novel nanocomposite electrode consisting of activated carbon with CNT in an ionic electrolyte. Combination of the two materials helped in achieving a balanced surface area and mesoporosity, which enhance the capacitive performance of the resultant composite (specific capacitance: 188 F/g). Wang et al. [7] investigated a composite film of polypyrrole (PPy) and single-wall carbon nanotubes (SWNT) for supercapacitor applications. Basnayaka and coworkers synthesized graphene-polypyrrole composite materials with a specific capacitance in the range from 267 F/g to 409 F/g at different frequencies in acidic electrolyte [8]. However, the use of graphene sheets is restricted due to the use of highly toxic reagents for its synthesis.

Inorganic metal oxides and sulfides and conducting polymers have been explored as electrode materials [9]. Among these, RuO_2 exhibits higher specific capacitance in an acidic electrolyte. However, its toxicity, low abundance and high cost have necessitated the need to develop other inexpensive materials of comparable performance. As an alternative, many environmentally friendly materials such as MnO_2, Fe_3O_4, NiO etc. whose electrochemical behavior is similar to RuO_2 have been tried as electrode materials [10,11]. Iron oxide, in particular has attracted attention due to its low cost and environmentally safe nature [12,13].

Overcoming the limitations of prior supercapacitor structures and fabrication procedures, the present work showcases the combination of two extremely beneficial materials viz., NH_2-PAMAM dendrimers and iron oxide nanoparticles providing a single device for their use as electrode material for supercapacitors. To the best of our knowledge till date there is no literature available on dendrimer-functionalized magnetic nanoparticles for energy storage devices particularly for supercapacitors. Dendrimers are size- and shape-controlled macromolecules connected from branches to a central core. They also have internal voids and cavities. Dendrimer exhibiting multi photon processes find applications in light harvesting and fluorescence imaging. Ghaddar et al. [14] reported a synthetic dendrimer framework containing a viologen marker as core and array of naphthalene peripheral groups for electron trapping. These dendrimers were capable of performing multiple electron redox events derived from a defined molecular architecture, thus mimicking natural light-collecting antenna systems.

Likewise, PAMAM dendrimers are also conductive in nature as they exist in fully charged state at modest pH levels. Varying polarity of the amine groups present in the dendrimer helps it to undergo protonation in a broad range of pH. At high pH, protonation occurs on the more polar amines, while with lowering of pH, the less polar amines get protonated. With further decrease in pH, the tertiary amines get protonated thereby increasing the internal polarity of the molecule [15].

In the present work, the NH_2-PAMAM dendrimer (D-NH_2) is built with an electron acceptor in the core and electron donors on the branches. The whole dendritic system works like an electron antenna, capturing several electrons and pushing them towards the core where they are stored. Generally, such stored electrons quickly recombine with holes and lose their energy, but dendrimer, due to the presence of long terminal groups, trap these electrons and keeps them separated for longer period of time [14]. The fabricated dendrimer has been used to stabilize and functionalize magnetic nanoparticles and subsequently used as electrode material for assessing the electrochemical performance. The nanoparticles showed higher energy density for supercapacitor than conventional carbon based materials and also exhibit better electrochemical stability than conducting polymeric materials. They exhibit electrochemical faradaic reactions between electrode materials and ions within appropriate potential windows. Further, the nanosystem exhibited good capacitance values and superior rechargeable stability in various electrolytes. To the best of our knowledge, there are no reports where dendrimer functionalized magnetic nanoparticles are used as electrode material for fabricating energy storage devices. Also, the protocol for the synthesis of this PAMAM dendrimer is new.

2. Experimental

2.1. Materials and equipment

Ferric chloride hexahydrate ($FeCl_3.6H_2O$) and ferrous chloride tetrahydrate ($FeCl_2.4H_2O$) were purchased from Sigma Aldrich Chemical Co. All other chemicals were of analytical grade and used as received. X-ray power diffraction (XRPD) of the nanoparticles were analyzed at a scan rate of 48°/min. ranging 2θ from 20° to 80° using PHILIPS pro analytical powder diffractometry (Cu $K_\alpha = 1.54$ Å). The peaks were indexed using the standard patterns from the International Center for Diffraction Data (ICDD) and the average crystallite size were calculated from the Scherrer's formula. Fourier Transform Infrared spectra (FTIR) were obtained using a model 3000 Hyperion Microscope with vertex 80 FTIR system with a spectral resolution of 0.2 cm^{-1}. Transmission Electron Microscopy (TEM) was performed on a CM200 Philips microscope using a Field Emission Gun (FEG) in an operating potential ranging from 20 to