



An organic route for the synthesis of cationic porous graphite nanomaterial used as photocatalyst and electrocatalyst for dye-sensitized solar cell

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ABSTRACT

An organic synthesis route is proposed to fabricate cationized porous graphite (cpG) for photocatalyst and electrocatalyst nanomaterial. High crystalline structure of graphite possesses few defects and porous channels. In the proposed research, cpG is fabricated by sonicating graphite in cationized enzyme media followed by exfoliating in the activated charcoal filler. The cationic lipase solution distributed positive surface charges over a bare graphitic sheet, and sonication with activated charcoal filler divulges porous channels along graphite exfoliated matrix structure. The charcoal doping in graphite was modified with the different charcoal content percentage ranging from 0 to 100%. The cationized porous graphite (cpG) material possess high surface area, pore volume and conductivity leads to high photoresponse and electrocatalytic reaction. As photocatalyst, the proposed graphite provide fast degradation of methylene blue dye observed by UV–Vis spectrophotometer. As cathode for dye-sensitized solar cell (DSSCs), cpG provides high electrocatalytic activity with low charge transfer resistance ($R_{CT} = 0.95\Omega$) and high photovoltaic performance with 9.59% efficiency. The positive charge distribution over graphite sheet attracts plenty of negative iodide ions present in the electrolyte, provide fast reduction-oxidation reaction. Furthermore, porous charcoal filler doping accepts a large amount of gel electrolyte, and fasten interfacial reaction between electrolyte and CE. This cost-effective cationized porous graphite (cpG) nanomaterial can provide new ways towards sustainable energy resources.

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1. Introduction

Graphite is the two-dimensional layer of sp^2 hybridized carbon atoms having stabilized allotropic crystalline structure [1–4]. Graphite has explored as an efficient catalytic material due to its electronic conductivity, stability, and fast electron transfer ability [5–9]. Graphite is considered as one of the widely used electrode material for various electrochemical applications, such as anode or cathode in the supercapacitor, lithium-ion batteries, and solar cells [10–14]. However, most of the electrochemical application is handicapped by the stacked basal surface nature of graphite causes restricted interactions between the surface functional groups and

the interacting solution media. The allotropic crystalline graphite structure composed of hexagonal sheets are highly stacked together. The extremely oriented basal morphology of graphite stacked sheets restricts the catalytic reaction of graphite electrodes, causing these graphitic planar structures to possess fewer catalytic sites for reduction species in an electrolyte. The electrocatalytic behavior of the graphite electrode is strongly dependent on the surface charge and combination of organic surface compounds composed of carbon and oxygen [15,16].

Various chemical exfoliation treatments of graphite were reported to incorporate functional moieties and porosity by using different compounds such as calcium carbonate ($CaCO_3$), iron carbide (Fe_3C), paraffin wax, amphiphilic polymers, titanium oxide and mesoporous carbon [17–23]. Chemical exfoliation of graphite along with various porous substitute disrupts the electronic structure and introduce many carbonyl ($-CO$) groups, hydroxyl ($-OH$) groups and epoxides on the graphite surface. In order to simplify the

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synthesis of catalytic porous graphite, we combine the effect of non-covalent organic functionalization by means of cationized lipase enzyme followed by a blend of activated charcoal to assist the exfoliation and orientation of charcoal filler into the graphite matrix. Dispersion of graphite in cationic lipase from *Candida rugosa* (triacylglycerol lipase) provide enough positive charge moieties on the hexagonal stacked sheet surface and prevent them from restacking. While ultrasonic exfoliation in mesoporous activated charcoal flakes of 100-mesh size incorporates the porous filler density in the graphitic planar matrix. In this way, a highly electrocatalytic active and conductive graphite nanomaterial can be synthesized for fast electrochemical reactions. Previously various researchers utilized different formulation of salts, polymers, and surfactants to synthesis cationic solutions [24–27]. Concentrated solvents aggregated graphite structure and reduce the conductivity and electron transfer ability of nanomaterial. Therefore, we designed a very sophisticated cationization technique by employing cationized lipase enzyme depends on the facts that enzyme is activated at specific pH or temperature. Lipase from *Candida rugosa* (triacylglycerol lipase) is highly activated when treated with 3–4 pH [28]. For this purpose, acetic acid (CH_3COOH) was used to maintain cationized nature of the enzymatic solution. Introduction of hydroxyl groups present in acetic acid possessing significant hydrating effect due to the presence of hydrogen bond donor and acceptor atoms at the polar active sites of lipase enzyme possibly increases the H_2O generation [29]. Consequently, lipase activity boosts up to an extent suitable to disperse graphite nanomaterials, which is unattainable at neutral enzyme pH. Our proposed system of organic enzymatic cationization technique provide evenly distributed positively charged ions on the graphite sheet and evenly disperses the nanomaterial without affecting its electronic stability. On the other hand, cationic surface enzyme dispersant assists the exfoliation of activated charcoal filler into the graphite matrix. Incorporation of porous charcoal filler in cationized graphite enhances the defect-rich density subsequently trigger the catalytic activity of electrode material. The proposed cationic porous graphite used as the photocatalyst in degradation of methylene blue dye as well as cathode materials for Pt-free dye-sensitized solar cells.

In the field of environmental chemistry, the use of carbon as the photocatalyst has been the focus of recent attention, since its aims the removal of contaminants in air and water. Different carbon materials, ie activated charcoal, mesoporous carbon, carbon nanotubes, graphene and, graphite has been used has low-cost photocatalysts for the degradation of organics in aqueous solution [30–33]. An advantage of carbon materials is that it can absorb the vast spectrum of the solar spectrum due to its defect-rich porous light diffusion property. Pristine graphite materials are restricted due to their low surface area and less catalytic reaction. Their low surface area and porosity are not suitable for the photocatalytic activity. There have been many attempts to produce photocatalytic materials from graphite including doping, introducing defects, constructing composites based on morphology tuning, surface functional modification [34–37]. On the other hand, the photocatalytic efficiency of activated charcoal in practical application is limited by a large band gap of $\sim 3.15\text{eV}$, as well as fast recombination of photogenerated electron-hole pairs. Lower photostability and the wide band gap of activated charcoal only allow to absorbed ultraviolet light ($<387\text{nm}$), which limits the utilization of solar light since UV light represents less than 5% of solar light [38]. To extend the photoresponse of mesoporous carbon materials many modification methods such as metal doping, noble metal deposition, conjugated polymer modified carbon has been used [31,39,40]. Herein, we synthesized a perfect composition of surface area porosity, low band gap (0.01eV), and conductivity to extend

the photoresponse of carbon materials in the visible region. Cationization of graphite followed by ultra-sonication in activated charcoal produce the enormous field of porosity on a graphitic planar surface. Moreover, an electrical conductivity of graphite induce an interesting charge transfer mechanism and enhance degradation of methylene blue dye. The unique electrical, optical, and photoelectric properties of cationic porous graphite (cpG), we expect that the combination of cationization and activated carbon may enhance photocatalytic activity.

In order to broaden the application of our proposed cationized porous graphite, we fabricated dye-sensitized solar cells with our suggested system of carbon cathode. The conventional DSSC is assembled with fluorinated tin oxide (FTO) glass based electrodes, named as photoanode and cathode [41–44]. The photoanodes are fabricated by pasting a mesoporous Titania film adsorbed with N719 dye. The cathodes are fabricated from platinumized FTO glass. Both electrodes are separated by the liquid electrolyte. In DSSCs 30–60% cost is associated with the high temperature ($\sim 400^\circ\text{C}$) thermal annealing and deposition of Pt layer on cathodes. In order to replace Pt, a substituent must be highly conductive, electrocatalytic active and having adequate porosity. Various carbon materials such as carbon nanotubes, activated carbon, carbon fiber fabric, graphite, graphene have been utilized [45–48]. Graphite is the most low cost and highly conductive materials. However, due to its restricted electrocatalytic nature's, its use in cathodes is restricted. Our proposed structure of cationized porous graphite can easily fulfill the needs of an electrocatalytic layer. The synchronized characters of high conductivity and porosity due to an incorporation of charcoal can enhance the reduction mechanism of cathode materials. Furthermore, positive surface charges produced by organic cationization can attract negative iodide and fasten the reduction of triiodide ions. Our proposed system of cationized porous graphite (cpG) proved to be utilized as efficient electrode materials for photocatalytic activity and electrocatalytic activity in broad electrochemical applications.

2. Experimental

2.1. Materials

For synthesis of cationic porous graphite (cpG), Graphite powder (particle size $< 100\ \mu\text{m}$, Asbury Carbon), lipase enzyme from *Candida Rugosa* (type VII, Sigma Aldrich) activated charcoal powder (100 mesh particle size, Sigma Aldrich), ethyl cellulose binder and acetic acid (Junsei chemicals, Japan) were used. For investigation of photocatalytic activity, methylene blue dye was dissolved in deionized water. Cationic porous graphite was deposited and sintered on FTO glass ($8\ \Omega\ \text{cm}^{-2}$, Pilkington Co.) For DSSCs, Photoanodes were prepared by using Titania powder (TiO_2) P25 (main layer, 20 nm) and G2 (scattering layer $< 500\ \text{nm}$) was used. Dye sensitizer D719 cis-di-isothiocyanato-bis (2, 2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) bis (tetrabutylammonium) from Everlight Co. was used. For sealing of DSSCs, two thermoplastic ionomers surlyn ($60\ \mu\text{m}$) purchased from Solaronix was used. For the preparation of quasi-solid-state electrolyte, polyethylene oxide (5%, Mw 300,000) polymer, 1-butyl-3-methylimidazolium iodide (BMII), Iodine (I), Lithium iodide (LiI), 4-tert-butylpyridine (TBP), and anhydrous acetonitrile were purchased from Sigma Aldrich Co. For comparison, Pt. catalyst was also prepared by using Chloroplatinic acid hexahydrate (H_2PtCl_6) from Sigma Aldrich.

2.2. Synthesis of cationic porous graphitic (cpG) nanomaterial

Firstly, a cationized lipase solution was prepared. 0.3 g of lipase-lyophilized powder was thoroughly dissolved in 100 ml ethanol.

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