Electrochimica Acta 246 (2017) 484–496

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Stable and robust nanobiocomposite preparation using aminated guar gum (mimic activity of graphene) with electron beam irradiated polypyrrole and Ce-Ni bimetal: Effective role in simultaneous sensing of environmental pollutants and pseudocapacitor applications

Nathiya Dhananjayan[a], Muthukumaran Palanisamy[a], Wilson Jeyaraj[a,*], Gurunathan Karuppasamy[b]

[a] Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi, India
[b] Department of Nanoscience and Technology, Alagappa University, Karaikudi, India

ARTICLE INFO

Article history:
Received 6 April 2017
Received in revised form 12 June 2017
Accepted 14 June 2017
Available online 16 June 2017

Keywords:
irradiated polypyrrole
modified guar gum
cerium-nickel bimetal
hydroquinone
catechol
resorcinol
nitrite
biosensor
pseudocapacitor

ABSTRACT

We report a novel sensing platform for biosensor and pseudocapacitor application based on electron beam (EB) irradiated polypyrrole/cerium-nickel@modified guar gum (EB-PPy/Ce-Ni@MGG) nanobiocomposite. The EB irradiated PPy nanospheres (NSs) and Ce-Ni bimetallic NSs prepared are functionalized into the amine MGG matrix film for the improvisation of energy storage as well as charge transfer mechanism. MGG film also found to be an effective conducting material in composite formation like reduced graphene oxide (r-GO) with excellent electrocatalytic activity. The nanobiocomposite was confirmed by SEM, EDAX, XRD, Raman and FT-IR analysis. Interestingly, the EB-PPy/Ce-Ni@MGG modified glassy carbon electrode exhibited an excellent electrocatalytic activity towards the simultaneous sensing of hydroquinone, catechol, resorcinol and nitrite with lower detection limits as 87 nM, 84 nM, 518 nM and 786 nM. Furthermore, EB-PPy/Ce-Ni@MGG modified Ni foam electrode was evaluated in 1 M NaOH by cyclic voltammetry and galvanostatic charge-discharge methods for pseudocapacitor application. The Ce-Ni bimetal NSs in the EB-PPy@MGG shows a significant improvisation of specific capacitance to 605 Fg^{-1} at a current density of 1 Ag^{-1}. The optimized electrolyte concentration, current density, scan rate and cycle stability shows promising results to low cost energy storage with wearable power device fabrication.

1. Introduction

Guar gum (GG) is a natural polysaccharide composed of sugar, galactose and mannose, which has OH^- groups that form epoxy linkage with better stability in pH 5-7. It is widely used in the form of powder as an additive in food, pharmaceuticals, paper, textile, explosive, oil well drilling and cosmetic industry. However, one of the main disadvantages for use of GG is that the branched galactose units sterically encumber the formation of the inter-chain junctions, resulting poor conductivity in energy applications. To address this issue, researchers used the strategies of functionalized polysaccharides and crosslinking with conducting polymer to improve the catalytic activity, stability, solubility, sensitivity, sorbing capacity and better biocompatibility [1,2]. Here, we planned a new strategy using irradiated polymer to fabricate the novel material with amine modified GG which could provide electrosteric stabilization. Generally, irradiated polymer exhibits increase or decrease in conductivity depending on the dosage/conformational changes on the polymer backbone on comparison with pristine. In this presented work, we have done irradiation of polypyrrole nanospheres (PPy NSs) with different dosages of electron beam (EB) and analyzed their behavior electrochemically for the preparation of nanobiocomposite material.

Nanoparticles (NPs) are used to offer enormous advantages over microparticles because of their large specific surface area, aspect ratio and excellent interfacial interactions on polymer branches. Interestingly, bimetallic NPs have superior optical, interfacial, catalytic and antimicrobial properties over single metallic NPs. It is well observed that the dispersion of NPs in the polymer matrix improves the desired properties of parent polymer matrix

* Corresponding author.
E-mail address: wilson.j2008@yahoo.com (W. Jeyaraj).

http://dx.doi.org/10.1016/j.electacta.2017.06.075
0013-4686/

including tensile strength, glass transition temperature, thermal degradation, rheological, conductivity and electrochemical capacitance [3,4]. Among various abundant transition metals cerium plays a vital role in electrocatalytic application with features such as good oxygen storage capacity and redox properties [5]. So different bimetal formation based on cerium and transition metal/metal oxides were reported such as CeO-Au [6], CeO-TiO_2, CeO-ZrO_2 [7], CeO-Cu_2O [8], CeO-Ni [9,10] etc and were employed in catalysis, biosensor, supercapacitor applications. Among them, Nickel has been reported as the stabilized bimetal formation with cerium which also exhibited excellent electrocatalytic activity by adopting the coordination number of 8 and 6 respectively. Hence by combining these two metals could induce new electronic properties and structural perturbation in the host biopolymer composite than other reported bimetals such as Fe-Cr, Zn-Cu oxides [9,10]. In addition the synthesis steps involved in other bimetals were complex and time consuming. To avoid this condition in our paper, we reported a novel, one pot and economically feasible synthesis route of Ce-Ni bimetal. So, cerium-nickel (Ce-Ni) bimetallic NPs are decorated along with EB irradiated PPy (EB-PPy) @ amine functionalized GG (MGG) material to fabricate the EB-PPy/Ce-Ni@MGG nanobiocomposite. Here, MGG could also provide electrosteric stabilization towards EB irradiated PPy and Ce-Ni by increasing the surface charge of NPs [11,12]. The long term stability of the nanobiocomposite is possible by sum of interaction forces such as electrostatic force [4], hydrophillic/hydrophobic, Vander waals force [13].

High concentrations of nitrite (NO_2) in water, industrial waste water, food products, and soil as result of their use as additives, fertilizers in agriculture and corrosion inhibitors are significant concerns [14]. NO_2 ions can mingle with blood pigments developing metha-hemoglobin in which oxygen availability to the tissues is blocked. Also, the voltammetric detection of NO_2 suffers from interference by other readily oxidizable compounds [15]. Hence, the selective detection of NO_2 is a challenging assignment to scientists. Similarly, another great concern is the monitoring of phenolic compounds. According to U.S Environmental Protection Agency and Journal of European Union, the consumption of phenolic compounds above maximum contaminant level ($MCL = 0.001(mg/L)^2$) leads to the risk of cancer, liver or kidney problems and in case of nitrite concentration above MCL ($1(mg/L)^2$) may cause serious health effects to infants below six months like shortness of breath and blue baby syndrome. Hence, it is highly desired to detect the concentration level of phenol compounds. However, a stable and sensitive electrochemical determination of phenols is a difficult task with most electrode materials because of irreversible adsorption of reaction intermediates which form passivating films. Consequently, significant effort has been dedicated toward identifying new materials with minimal surface fouling effects associated with the oxidation of phenolic compounds. In order to address these issues, number of analytical methods such as spectrophotometry [16], chromatography [17], chemiluminescence [18], pH based flow injection analysis [19] and electrochemical methods have been employed for the determination of nitrite and phenolic derivatives. Among these, electrochemical method has been widely used because of its high sensitivity, good selectivity, fast response, low cost and feasibility [20]. But in case of sensing phenol compounds which contain same electroactive groups resulted severe overlapping in unmodified electrode [21]. One of the alternative strategy to overcome this issue is thus to incorporate advanced materials including nanoparticles [22], tyrosinase entrapped polymers [23], carbon nanotubes [24], mesoporous carbon [25], etc. for the determination of phenol compounds. In the literature GG was employed in enzymatic electrochemical sensors in which the system becomes complex, cost-effectiveness and time consuming [23], whereas in this paper we report an amine functionalized GG with EB irradiated polymer based composite for biosensing and supercapacitor applications non-enzymatically. The induced electronic properties and structural perturbation in the host biopolymer composite is analyzed as an efficient electrocatalyst for the detection of nitrite and phenol compounds simultaneously.

With the ever-increasing power and energy requirements in modern world, recent research and developments have focused on new electrode materials for advanced energy storage devices. There are three major types of electrode materials reported for supercapacitor applications: carbonaceous materials [26], metal oxides/hydroxides [27] and conducting polymers [28]. Here, we present an alternative route by constructing a novel hybrid EB-PPy/Ce-Ni@MGG nanobiocomposite for electrochemical capacitor applications. In the work presented here, we have carried out the simultaneous electrochemical sensing of environmental pollutants as well as supercapacitance studies using EB-PPy/Ce-Ni@MGG nanobiocomposite modified in glassy carbon electrode (GCE) and Ni foam respectively. The detection limits ($S/N = 3$) for simultaneous sensing of hydroquinone (HQ), catechol (CC), resorcinol (RC) and NO_2 are 87 nM, 84 nM, 518 nM and 786 nM respectively and also the real sample analysis of water samples was performed with high selectivity and sensitivity. To the best of our knowledge simultaneous sensing of HQ, CC, RC and NO_2 are performed for the first time and the prepared MGG also mimics the activity of r-GO in composite formation with EB-PPy and Ce-Ni NSs. The specific capacitance for the EB-PPy/Ce-Ni@MGG nanobiocomposite modified electrode was calculated as 605 Fg^{-1} at current density of 1 Ag^{-1} with the capacitance retention of 69% after 1000 cycles.

2. Experimental section

2.1. Reagents and Materials

Hydroquinone, catechol, resorcinol, sodium nitrite, methyl orange (MO), ferric chloride, pyrrole, guar gum, ethylene diamine, HCl, acetone, cerium (III) nitrate hexahydrate, nickel nitrate were purchased from Himedia, Mumbai. 1 mM of $[Fe(CN)_6]^{3-4-}$ in 0.1 M KCl and 0.1 M phosphate buffer solution (PBS) were prepared respectively. 10 mM of HQ, CC, RC and NO_2 solutions were freshly prepared as stock solution prior to its use.

2.2. Instrumentation

The electrochemical behavior of prepared samples was analyzed by CHI 6005D electrochemical workstation (Austin, USA). The electrochemical cell consists of Ag/AgCl as reference electrode, platinum wire as counter electrode and GC (0.07 cm^{-2}) as working electrode. Nanobiocomposite was drop casted on the surface of GCE and dried at room temperature. The supercapacitance studies were analyzed by SP-150 potentiostat using a cell containing Hg/HgCl as reference electrode, platinum wire as counter electrode and Ni foam working electrode. The electrochemical charge discharge behavior was carried out in NaOH buffer solution. The electron beam irradiation on PPy NSs was done by 8 MeV Microtron instrument, Mangalore University. The SEM images were obtained using Zeiss instrument operating at 21.00 kV. The XRD patterns were obtained using Bruker Germany D8 advance instrument ($\lambda = 1.5418$ Å) operated at 30 mA, 40 kV and using Cu kα radiation. The Raman spectrum was obtained using an imaging spectrograph laser Raman spectrometer (SEKI Japan). The amine modification in GG films were analyzed using Thermo Nicolet 200 FTIR spectrometer. The samples were mixed with KBr and pressed to form pellets. The pellets were analyzed in a single beam mode, with an average of 4 scans and 2 cm^{-1} resolution.