International Journal of Biological Macromolecules 89 (2016) 89–98

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

Rapid, facile microwave-assisted synthesis of xanthan gum grafted polyaniline for chemical sensor

Sadanand Pandey*, James Ramontja

Department of Applied chemistry, University of Johannesburg, P.O. Box 17011, Doornfontien, Johannesburg 2028, South Africa

ARTICLE INFO

Article history:
Received 29 February 2016
Received in revised form 5 April 2016
Accepted 19 April 2016
Available online 23 April 2016

Keywords:
Biopolymer
Polyaniline
Graft copolymer
Microwave irradiation
Green technology
Chemical sensor

ABSTRACT

Grafting method, through microwave radiation procedure is extremely productive in terms of time consumption, cost effectiveness and environmental friendliness. In this study, conductive and thermally stable composite (mwXG-g-PANi) was synthesized by grafting of aniline (ANi) on to xanthan gum (XG) using catalytic weight of initiator, ammonium peroxydisulfate in the process of microwave irradiation in an aqueous medium. The synthesis of mwXG-g-PANi were confirm by FTIR, XRD, TGA, and SEM. The influence of altering the microwave power, exposure time of microwave, concentration of monomer and the amount of initiator of graft polymerization were studied over the grafting parameters, for example, grafting percentage (%G) and grafting efficiency (%E). The maximum %G and %E achieved was 172 and 74.13 respectively. The outcome demonstrates that the microwave irradiation strategy can increase the reaction rate by 72 times over the conventional method. Electrical conductivity of XG and mwXG-g-PANi composite film was performed. The fabricated grafted sample film were then examined for the chemical sensor. The mwXG-g-PANi, effectively integrated and handled, are NH_3 sensitive and exhibit a rapid sensing in presence of NH_3 vapor. Chemiresistive NH_3 sensors with superior room temperature sensing performance were produced with sensor response of 905 at 1 ppb and 90% recovery within few second.

1. Introduction

The detection of toxic gases has been a major focus of sensor research in recent years. Ammonia is a kind of gas with high toxicity. It is regulated by occupational safety and health administration (OSHA) and has a current permissible exposure limit (PEL) of 35 ppm over 15 min short term exposure limit (STEL). Besides, ammonia concentration at or above 2500 ppm exposures for 30 min are considered immediately dangerous to life and health (IDLH), and may cause induced chemical pneumonitis, burns (eyes, face and mouth), severe local edema, dyspnea, progressive cyanopsis and even death [1]. The human body naturally produces ammonia by various metabolic activities [2]. In medical sector, existence of an excessive amount of ammonia in exhaled human breath can be treated as indications of several diseases related to dysfunctions of liver and kidneys [3,4]. Hence, the detection of ammonia gas/vapor is of paramount importance in terms of both environmental as well as health monitoring sectors.

A wide variety of materials, such as, metal oxides (ZnO, SnO_2, TiO_2, V_2O_5, In_2O_3 etc.), polymers and carbon based materials have been used as sensing elements for various ammonia gas sensor applications [5–7]. However, most of the currently available gas sensors based on these materials, often suffer from more than one drawback such as poor selectivity, influence of humidity, external stimulus such as Joule heating or UV illumination for response/recovery, operation at high temperature (200–500 °C) which lead to high power consumption. Therefore, new sensing materials with low detection limit, high sensitivity and reproducibility, fast response and recovery without any external stimulus, low cost and eco-friendly sensor are expected for gas detection at room temperature.

Polyaniline (PANi) known as intrinsically conducting polymers (ICPs) has attracted specifically consideration in view of its ease of doping, its different chemical forms available depending on acid/base treatment and its substantial stability in ambient atmosphere. All these characteristics clarify, why PANi is contemplate as a moderately effectively prepared and processed ICP for an extensive variety of applications. PANi is pH sensitive and may fulfil the requirements for the development of chemical sensor.

PANi has been utilized as a cost effective conducting polymer [8]. Biological and electronic properties of PANi were altered by doping distinctive types of inorganic nano-materials [9]. Similarly biopolymer has been widely used as a part of sensors because of its biodegradable, biocompatible and non-toxicity [10]. Independently both PANi and xanthan gum (XG) had indicated brilliant properties as conducting and biocompatible material, respectively.

* Corresponding author.
E-mail addresses: spandey.uj@gmail.com, spandey@uj.ac.za (S. Pandey).

http://dx.doi.org/10.1016/j.ijbiomac.2016.04.055
0141-8130/

However XG has restricted conductivity while PANi has limited biocompatibility which has been a subject of in-depth research in last decade or so.

There were a few endeavours to enhance the performance of biopolymer and PANi relies upon alteration in structural and surface chemistry by consolidating nano-metal-oxides [9,11]. Synthesis of metal nano-particles itself is extremely complex process and requires several chemical processes. Thus, the utilization of chemicals for synthesis and non-degradable characteristics of metal oxides can have several environment issues when chemical wastes were disposed. Secondly, oxidative characteristics of nano-materials likewise restrain the stability amid storage and used sensing film in ambient atmosphere.

Taking into consideration these advantage, the objectives of the present work was to develop an appropriate method for metal free conducting biopolymer matrixes by modification of carbohydrate polymers with PANi which may prompt the synthesis of multifunctional electrical conducting composite. It will be the favorable advantages such as technological applications, affinity with environment and biological frameworks, and is financially savvy. The biopolymer selected for the present study is XG. XG is derived from *Xanthomonas campestris*. The structural unit of XG biopolymer consist of backbone of β-(1-4)-D-glucopyranose glucan along with side chains of β-(3-1)-α-linked D-mannopyranose-(2-1)-β-D-glucuronic acid-(4-1)-β-D-mannopyranose on alternating residues [12].

Previously reports shows that inorganic salt complexes of biopolymer such as gum arabica (GA) act as a superionic electrical conductor [13]. Mostly, addition of conducting polymers, for example, PANi into a flexible matrix of XG ought to result in great processability alongside the electrical conductivity, chemical stability toward dopants and thermal stability.

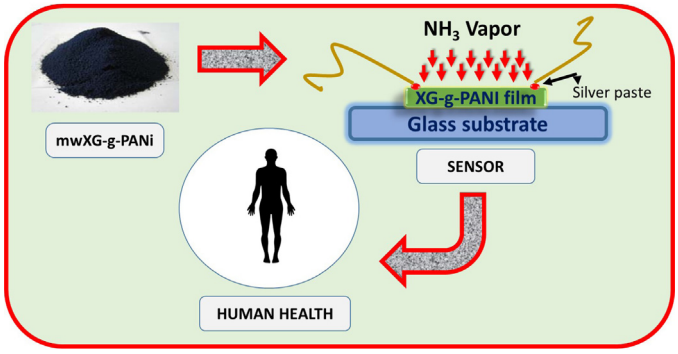
It has been notice presently, that microwave irradiation is rising as effective device for the chemical processing [14] and in different fields of chemistry including polymers. Fundamental point of interest is that it brings about practically rapid 'in core' handling of materials in a homogeneous and specific way. Under microwave irradiation grafting of polyacrylamide, polyacrylonitrile onto potato starch [15,16]; and poly(ethylacrylate) onto XG [17] have been performed in absence or at low concentration of initiator.

In this context, the present work aimed to provides details study of the ammonium peroxydisulfate (APS) initiated synthesis of mwXG-g-PANi under microwave conditions. This study deal with, mwXG-g-PANi optimization, plausible mechanism, different characteristic properties of mwXG-g-PANi such as morphology, conducting, and thermal behavior of the mwXG-g-PANi were explored. Here, we have also reported, a rapid and highly sensitive mwXG-g-PANi composite based chemiresistive sensor for the room temperature detection of ammonia levels in a lower range from 1 parts-per-billion (ppb) to 100 ppb. The sensor is based on the mwXG-g-PANi composite of polysaccharide (xanthan gum, XG) and polyaniline (PANi). Sensor response, temporal response, reproducibility and stability studies reveal excellent ammonia sensing of the mwXG-g-PANi composite. The general schematic diagram of the present work is shown in (Scheme 1).

2. Experimental

2.1. Materials

The biopolymer, XG from *X. campestris* (G1253, Sigma), monomer, aniline (≥99.5%, Sigma-Aldrich; 242284), initiator, APS (≥98.0%, Sigma-Aldrich; 248614), solvent, 1-methyl-2-pyrrolidone (NMP) (Merck; 806072), hydrochloric acid (32% Merck; 100319) and Ammonium hydroxide solution (32.0%, Sigma-Aldrich; V000637) were used.



Scheme 1. Schematic diagram of the present work.

2.2. Graft copolymerization method for synthesis of mwXG-g-PANi composite

During the grafting experiment, XG was dissolve in 25 mL deionized (DI) water. A known amount of ANi and hydrochloric acid (HCl) solutions were included in the container. Further catalytic amount of APS was added in order to initiate the reaction of graft copolymerization. Further, the reaction mixture was exposed to microwave irradiation at definite microwave power and exposure time. After desired time period, the grafted sample was precipitated by pouring the reaction mixture into the NMP. After sought time period, the copolymer were dried in a vacuum oven at 60 °C and weighed. The % grafting (%G), % efficiency (%E) and % homopolymer (%H) were calculated by the following (Eqs. (1)–(3). [18]

$$\%Grafting\,(\%G) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\%Efficency\,(\%E) = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

$$\%Homopolymer\,(\%H) = 100 - \%E \quad (3)$$

2.3. Analysis and characterizations

FTIR spectra of copolymer were perform using PerkinElmer PE1600 FTIR spectrophotometer (USA) in the range of 4000–400 cm^{-1}. The powder XRD patterns of biopolymer and grafted samples was performed by using XRD (Rigaku Ultima IV, X-ray diffractometer) employing CuKα radiation of the wavelength of 1.5406 Å with visible slights at 45 kV/40 mA. The surface morphology of the grafted samples was examined by a scanning electron microscopy (SEM), (TESCAN, VEGA SEM) under a 20 kV electron acceleration voltage by carbon coating of samples. Schimadzu UV-1208 models UV–vis spectrophotometer (Japan) was used for chemical structure and conjugation measurement. Apart from this UV–vis also measure the electronic transition and doping–dedoping behavior of mwXG-g-PANi. Thermal stability of copolymer was determined using thermogravimetric analyzer (TGA) (Perkin Elmer model 4000, USA).The pH measurements were made with OHAUS starter 2100 (USA). Microwave oven LG (Model No. MS-283MC; 1200 W) having 2450 MHz microwave frequency and a power output from 0 to 1200 W was used with constant alteration for utilization. Finally, the sensing properties of the mwXG-g-PANi film are tested against increasing ammonia concentration by monitoring the changes in current through DC current-voltage (I–V) measurement using Keithley 237.

2.4. Measurement of sensing properties

The synthesized mwXG-g-PANi (172 %G) sample was crush in a smooth agate and mortar. The sensing film of XG and mwXG-