Vacuum 93 (2013) 79–83

Contents lists available at SciVerse ScienceDirect

Vacuum

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

Two-step electrochemical synthesis of Au nanoparticles decorated polyaniline nanofiber

Yasir Ali [a], Vijay Kumar [a,*], R.G. Sonkawade [b], M.D. Shirsat [c], A.S. Dhaliwal [a]

[a] *Department of Physics, Sant Longowal Institute of Engineering and Technology, Longowal District, Sangrur-148106, Punjab, India*
[b] *School of Physical Sciences, BBA University (A Central University), Lucknow-226025, India*
[c] *Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431 004, India*

ARTICLE INFO

Article history:
Received 17 December 2012
Received in revised form
2 January 2013
Accepted 9 January 2013

Keywords:
Electrochemical synthesis
Polyaniline nanofiber
Composite
I–V
SEM
XRD
Raman

ABSTRACT

The present work reports the electrochemical synthesis of H_2SO_4-doped polyaniline nanofibers (PANINFs) on conducting ITO substrate. The subsequent dissociation of $HAuCl_4$ in an acidic solution of HNO_3 and deposition of Au particles was carried out by using cyclic voltammetery (CV) to form Au particles decorated PANINFs (Au–PANINFs) composite film. Electrical conductivity of the Au particles decorated PANINFs has been measured by a two-probe method. Scanning electron microscopy (SEM) investigations of PANINFs and Au–PANINFs samples revealed good porous and fibrous structure with identical distribution of gold nanoparticles coupled with the surface of PANINFs. The average diameter of the PANINFs ranges from 184 nm to 210 nm. X-ray diffraction (XRD) and EDAX spectra also supported the formation of Au particles on the surface of PANINFs. The structural analysis was carried out by Raman spectroscopic technique. A possible mechanism for the formation of Au–PANINFs composite has been proposed.

1. Introduction

Composites of conducting polymers and metal particles have dormant competence to combine two leading edge technologies to yield materials with immense application in the domain of material world. Composites significantly covers a large variety of system such as one dimensional, two dimensional and three dimensional, made of distinctly dissimilar components mixed at micro- and nanolevel. A metal containing conducting polymers amalgamates the redox properties of conducting polymer and that of metal ions [1], hence emerges with unique properties that are significant in various applications especially in gas sensing and catalytic application [2,3].

Amongst metal particles, Au has been widely used because of its unique optical and catalytic properties [3,4]. Au particles offer novel opportunities for fabricating electrochemical devices as they can facilitate electron transfer between electro-active species and electrodes [5]. On the other hand PANI is well designed and the most gifted material because of its high capacitive characteristic, low cost and ease of synthesis [6,7]. Electrochromic properties of PANI have made potential in electrochromic devices and is observed in a large number of conjugated polymers [8,9]. Au–PANI composite reveals a combination of the enviable qualities of both components like stability, high conductivity, mechanical strength and the exclusive optical properties of the metal components and easy processing favourable redox properties from conducting polymer part [10]. Liu et al. [2] studied Au nanoparticles decorated polyaniline nanofibers for the detection of volatile sulphur compounds in expired breath. They reported a template-free electrochemical polymerization for the fabrication of PANINFs. The formation of PANI/Au nanoparticles was realized by the redox reaction between the $HAuCl_4$ and the PANI emeraldine salt.

Metal nanocomposites have been fabricated by such as layer by layer, chemical polymerisation using the metal ions as the oxidant and reduction of metal ions and electrochemical deposition of the metal ions over the conducting polymer [11–13]. Various polyaniline-based core shell nanocomposites such as Ag/polyaniline [14,15], Ni/polyaniline [16], Ag–PET [17,18], Au–silica [19] and silica–polyaniline [20,21] have been reported. The preparation of Au–PANI material is reported using preformed polyaniline by exploiting the multi-oxidative states of the polymer [22,23]. Chemical, electrochemical and radiolysis method have been adopted for synthesis of Au–PANI composites but few functional properties like easy synthesis process, adhesivity, stability and homogeneous

---

* Corresponding author. Tel.: +91 1672 253186; fax: +91 1672 280057.
E-mail address: vj.physics@gmail.com (V. Kumar).

0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.01.007

distribution of metal particles on the surface of polymer film are yet to be achieved to surmount the teething troubles in application domain.

In this work, we report a two-step electrochemical synthesis method to prepare well-controlled Au–PANINFs composite. This approach has some advantages that it is simple, cost effective and ensures controlled fabrication of desired structure with optimized process parameters. Such controlled fabrication of Au–PANINFs could modify significantly the sensing or catalytic properties. Interestingly, the polymer component is used for conjugating analytes, while the gold part serves to increase the catalytic affinity/reactivity. The chronopotentiometeric technique is used for fabrication of PANINFs on ITO substrate and later the synthesized surface of fibrous film is modified by the Au particles using cyclic voltammetery which shows strong redox reactivity occurred during synthesis process. These prepared Au–PANINFs are characterized by electrical conductivity, SEM, Raman, XRD and EDAX.

2. Experimental details

Aniline monomer (MERCK, 99.5% purity), H_2SO_4 (MERCK, >99% purity), $HAuCl_4$ (Sigma Aldrich) and HNO_3 (RANKEM) were used in the present investigation. All these reagents were analytical grade reagents (A.R.) and used without further purifications. All the experiments were carried out with double-distilled (DD) water.

Electrochemical synthesis was carried out using a CHI 660D electrochemical workstation under computer control. The standard three-electrode setup was employed in one compartment electrochemical cell. A rectangular conducting ITO sheet of size $20 \times 10 \times 0.7$ mm^3 was used as a working electrode whereas a platinum sheet of size $20 \times 40 \times 0.25$ mm^3 was used as a counter electrode. The reference electrode was an Ag/AgCl electrode. Electrochemical synthesis of PANINFs was carried out on ITO substrate in an aqueous solution of 0.1 M aniline monomer containing 0.5 M H_2SO_4 using a chronopotentiometery technique. The surface modification of synthesized PANINFs was conducted in an aqueous solution of 0.0007 M $HAuCl_4$ containing 0.005 M HNO_3 solution using cyclic voltammetery (CV) between a potential window of 0.4 and 0.7 V at a scan rate of 30 mV s^{-1}.

Scanning electron microscopic images and EDAX spectra were obtained using a JEOL JSM-6490LV microscope at 25 kV after covered with a thin layer (~10 nm) of sputtered gold. The micro-RAMAN investigation was carried out using Renishaw inVia Raman microscope. Argon laser of excitation wave length 514.4 nm was used as an excitation source. XRD pattern of the Au–PANINFs was taken using SHIMADZU XRD-7000 X-ray diffractometer with Cu-K$_\alpha$ radiation (1.54 Å) for a range of Bragg's angle 2θ ($15 < \theta < 55$) at the scan rate of 0.5°/min. I–V characteristics measurements were made using Keithley 2400-C source meter.

3. Results and discussion

3.1. Electrochemical synthesis and characterization

Electrochemical synthesis of aniline on ITO substrate has investigated a function of various parameters such as aniline concentration, dopant, applied current density and deposition time by using chronopotentiometry technique (Table 1). The optimized values were 0.1 M, 0.5 M, 0.65 mA/cm^2 and 800 s, respectively. In this study, PANINFs film (optimized values) was placed into 80 ml aqueous solution of $HAuCl_4$ and HNO_3 for 4-sweep segments of CV to modify the surface of polymer film at 30 mV/s scan rate in a potential range of −0.4–0.7 V (Fig. 1). The scan rate was kept rather high for the four sweep segments for the uniform decoration of Au particles onto the surface of PANINFs. The scan direction of the curve is also included in Fig. 1. The formation of ion exhibits the first order dissociation of $HAuCl_4$ in an acidic solution of HNO_3, the $AuCl4^-$ complex ion formed are attached to the imine sites of PANI film.

Table 1
Optimization of various process parameters for the fabrication of PANINFs.

S. no.	Monomer conc. (M)	Supporting electrolyte conc. (M)	Deposition time (s)	Current density (mA/cm^2)
A	0.05	0.3	800	0.9
B	0.08	0.5	800	0.65
C	0.09	0.55	800	0.7
D	0.4	1.7	800	0.7
E	0.7	1.2	800	0.8
F	0.1	0.25	800	0.5
G	0.1	0.5	800	0.65
H	0.1	0.55	800	0.7

The obtained composite was green with very faint yellow shining. This change in colour can be attributed to the electrochromic process after attachment of Au ion complex or Au nanoparticles on the polymer surface. It is also reported that chloroaurate anions form a strong complex with the protonated imine nitrogen in polyaniline and further the chloroaurate is converted to metallic gold upon reduction at working electrode forming coordination bonding with the polymer film [24]. The changes in redox process occurring during chemical reaction in three-cell compartment are clearly observed in Raman spectrum as the region 1556–1610 cm^{-1} indicates that the PANINFs is in partially oxidised state which is more susceptible for attaching Au nanoparticles. In case of Au–PANINFs composite strong interaction occurs between the polymer and Au–metal particles, which modify the electron transfer rate across the composite [16]. To modify the polymer surface with uniform and isotropic ionic reduction of Au particles the scan rate was kept rather high for less sweep segments. SEM micrographs show efficient embroidery of PANINFs surface with Au–metal particles.

3.2. Scanning electron microscopy (SEM)

For confirmation of experimental results, the PANINFs and Au–PANINF composite was subjected to scanning electron microscopy.

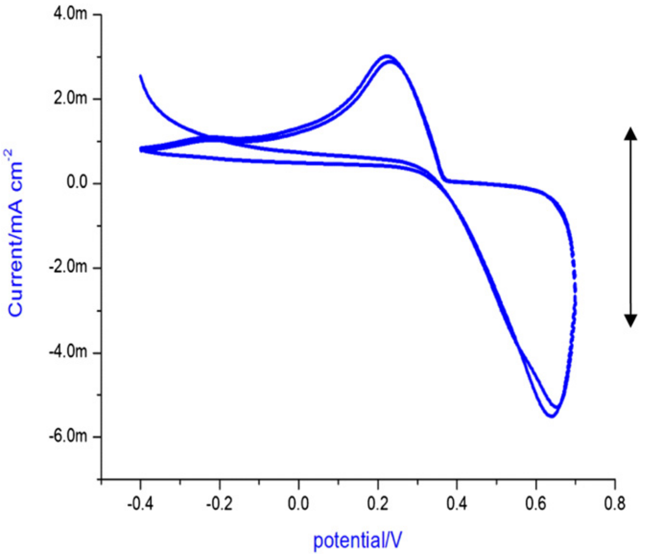

Fig. 1. The cyclovoltgramm Au–PANINF composite between potential windows −0.4 V and 0.7 V in a solution of $AuCl_4 + HNO_3$ in a ratio of 0.0001:0.005 M with scan rate of 30 mV/s for 4-sweep segments.