



Tollen's reagent assisted synthesis of hollow polyaniline microsphere/Ag nanocomposite and its applications in sugar sensing and electromagnetic shielding

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ARTICLE INFO

Article history:

Received 3 March 2014

Received in revised form 10 October 2014

Accepted 16 December 2014

Available online 17 December 2014

Keywords:

A. Composites

B. Chemical synthesis

C. Electrochemical measurements

C. Infrared spectroscopy

C. X-ray diffraction

ABSTRACT

The present study is focused on synthesis of polyaniline hollow microspheres (PnHM) nanocomposites of silver (Ag) i.e., PnHMAg by emulsion polymerization of aniline and Tollen's reagent as a source for Ag nanoparticles. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis of PnHMAg indicated presence of silver nanoparticles dispersed on polyaniline surface. The electrical conductivity of PnHMAg is increased by ~ 6 times compared to PnHM. Cyclic voltammogram of PnHM in sugar sensing exhibits characteristics redox peaks at ~ 0.09 (sugar) and ~ 0.53 V (polyaniline). Interestingly, PnHMAg showed a single peak at ~ -0.18 V with increased intensity (~ 5 times) indicating its high sugar sensing ability. PnHMAg also exhibits high shielding efficiency of 19.5 dB (11.2 GHz) due to the presence of highly conducting Ag nanoparticles. TEM studies confirmed that Ag nanoparticles are well distributed on PnHM. As a result, a continuous electronic path is developed due to enhanced interconnectivity of PnHM.

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1. Introduction

Recently, nanocomposites derived from the metallic or semiconducting material/conducting polymers have been receiving considerable amount of attention [1]. This is mainly attributed to the presence of strong electronic interaction between the nanoparticles and polymer [2]. Simultaneously, the efforts are continuing to control the shape and size of nanocomposites in tuning the electronic band gap, conductivity, light-emission efficiency and many other properties [2]. One such alternatives involved fabrication of nanocomposite derived from conducting polymer hollow spheres of micro to nano dimension. Such nanocomposites possess enhanced properties and wide range of applications in the field of optoelectronics, microcavity resonance, delivery and controlled release of drug, catalysis [3] etc. Polyaniline is one such important conducting polymer due to its light weight, easy processability, flexibility [3,4], good environmental stability [5] and optical properties [6]. The applications in electronic devices, electrochemical sensing, electrocatalysis, electrochromic devices and microwave absorbers of polyaniline have also been attributed to its electronic properties [7–14]. Though, it exists in various types of morphology, the hollow

polyaniline microsphere exhibits superior electrical properties. This is attributed to its enhanced surface to volume ratio and reduced lengths for mass as well as charge transport [15]. Hollow polyaniline microspheres find application in cutting edge technology, such as catalysis, controlled delivery, artificial cells, light fillers, low dielectric constant materials, acoustic insulation, paint industry, and photonic crystals [16]. It may be synthesized by template assisted method [17], self-assembly [18], and chemical process [19]. Interestingly, the template assisted method has widely been used due to its good control over the shape, size and morphology. The properties of hollow polyaniline microspheres could be further enhanced, when it forms composites with other inorganic materials. Though, the formation of SiO_2 [20], Si [21], TiO_2 [22], Au [23], Cu [24] and Ag filled polyaniline composites [25] are reported, only limited contemporary work is reported on the formation of hollow polyaniline microsphere nanocomposite of Au [26–29] and Ag [30]. The choice of silver in this work has mainly been guided by its highest electrical conductivity among all the metals as well as its enhanced catalytic activity, antibacterial properties, good biocompatibility [31–38].

The abnormal proportion of glucose in human cells and blood lipids causes hyper- or hypo-glycaemia and causes severe health problems. Though, a large number of metals have been used for this purpose, no contemporary work is reported using silver-polyaniline composite [39]. Similarly, the EMI shielding is critical

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to the proper functioning of many electronic devices and requires conducting metals e.g., Ni, Cu, Fe [40]. In addition, polyaniline has also been used as conducting filler in various rubber matrixes (NBR, SBR, EPDM, PS, PU) in presence/absence of CNT, graphene and graphite [41–47] etc. However, no such work has been reported so far focusing on both sugar sensing and EMI shielding of PnHMAg. It is anticipated that high conducting silver could further enhance the sugar sensing as well as EMI shielding property due to the presence of continuous electronic path in the polyaniline matrix [30]. All these motivated us to focus our work on polyaniline with special hollow microsphere morphology prepared by ultrasound assisted polymerization process. Subsequently, PnHM is decorated with Ag nanoparticles generated from the reduction of Tollen's reagent. However, smaller size Ag nanoparticles remained a preferred choice in providing relatively much better distribution on the surface of PnHM. Therefore, we followed Tollen's reagent assisted synthesis of Ag nanoparticles in the development of PnHMAg [48]. The as-prepared nanocomposite has been characterized by FTIR, UV-vis, XRD, SEM and TEM analysis and room temperature DC conductivity measurements. Finally, PnHMAg has also been investigated for its applications in sugar sensing and EMI shielding.

2. Experimental

2.1. Materials

Potassium persulfate ($K_2S_2O_8$), ammonium persulfate, $[(NH_4)_2S_2O_8]$ and aniline were procured from Merck, India. Sodium borohydride ($NaBH_4$) was purchased from Sisco Research Laboratory, Mumbai, India. Dextrose, sodium dodecyl sulfate (SDS) and ethyl acetate were procured from SRL Pvt., Mumbai, India. Silver nitrate ($AgNO_3$), ethanol, and styrene were supplied by Finar Chemicals Limited, Ahmedabad, Hong Yang Chemical Corporation and Jyoti Lab India, respectively.

2.2. Preparation of polystyrene particles and sulfonated polystyrene core

Monodisperse polystyrene particles were prepared according to the method as reported in the literature [30]. According to this, 0.1 mmol styrene monomer was mixed with 140 ml of distilled water under N_2 atmosphere and stirred vigorously for about 20 min to form a white colloidal dispersion. Subsequently, 10 ml of 0.023 mmol $K_2S_2O_8$ was slowly added and magnetically stirred for 24 h at 80 °C. The polystyrene colloidal solution formed earlier was centrifuged and washed 3–4 times with distilled water followed by sulfonation in concentrated sulfuric acid at 50 °C (4 h). Finally, the product was centrifuged and washed with distilled water to obtain sulfonated polystyrene microsphere.

2.3. Preparation of polyaniline hollow spheres

100 mg sulfonated polystyrene particles were dispersed in 10 ml of distilled water followed by addition of 3 mmol of aniline in dilute hydrochloric acid with continuous stirring for 6 h at room temperature. Subsequently, the ultrasound assisted polymerization of aniline was carried out in presence of 1 mmol APS solution for 3 h followed by its termination by the addition of methanol. The green product so formed was centrifuged and washed with distilled water and ethanol several times to remove the unreacted monomers and oligomers and dried in vacuum for 20 h. The resulting polyaniline coated polystyrene was dispersed in ethyl acetate to dissolve the polystyrene core and form hollow polyaniline microsphere. These were subsequently washed with ethanol, centrifuged and dried in vacuum at 50 °C for 30 h.

2.4. Preparation of hollow polyaniline microsphere/Ag nanocomposite (PnHMAg)

Hollow polyaniline microsphere/Ag nanocomposites (PnHMAg) were prepared by depositing Ag nanoparticles on polyaniline hollow microspheres. In this procedure, 0.2 g of PnHM was dispersed into 50 ml of distilled water followed by the addition of 10 ml Tollen's reagent and stirred for 3 h [34]. Subsequently, 5 ml of 1 mmol hydrazenehydrate was added drop wise and the solution was heated in a water bath at 90 °C for 1 h. Finally, the product was washed with distilled water, centrifuged and dried at 50 °C for 24 h.

2.5. Preparation of glassy carbon electrode

Initially, glassy carbon electrodes were polished with 1.0, 0.3, and 0.05 μm size alumina slurry followed by washing with distilled water. After that, 1 mg/ml of PnHM and PnHMAg in deionized water were ultra-sonicated for 30 min to form colloidal dispersion and dropped onto such polished glassy carbon electrode and allowed to dry in vacuum at 50 °C.

2.6. Characterization

X-ray diffraction (XRD) analysis was done at room temperature on a Phillip, Holland instrument with $CuK\alpha$ radiation (0.1541 nm) in the range 20–75°, with scanning rate of 5° per min. FTIR analysis of powder compressed samples (dispersed in KBr) was recorded in the range of 400–4000 cm^{-1} on PerkinElmer FTIR. Spectrometer RXI using Ultraviolet–visible (UV–vis) absorption spectrum was recorded on Varian Cary 5000 UV–vis spectrophotometer. The morphological study of the samples was done by scanning electron microscope (SEM) on JEOL, JSM-5800 scanning microscope instrument operating at 20 kV and field emission scanning electron microscopy (FESEM) on a Carl Zeiss at an accelerating voltage of 20 kV, respectively. Transmission electron micrographs were taken on TECNAI G², SEI (Netherland) instrument operating at 200 kV was used to obtain digitally acquired images on a Gatan multipole charge-coupled device (CCD) camera for the samples placed on carbon-coated Cu grid from dispersion in ethanol. The conductivity was measured by a four-probe method using a digital multimeter (Scientific Equipment Roorkee, Model-LCS-02) at room temperature using the powdered compressed pellets. The electrochemical experiments were performed (HCH Instruments, Electrochemical Analyzer) in a cell containing 20.0 ml of H_2SO_4 (10^{-7} M) solution at room temperature using a coiled platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode and the polyaniline/Ag electrode. Subsequently, cyclic voltammograms (CV) of PnHM and PnHMAg have been recorded in the range of 0.1 to –0.1 V and at a sweep rate of 50 mVs^{-1} at different concentrations of sugar (dextrose). EMI shielding was measured on a compressed pallet of PnHM and PnHMAg (different thickness, diameter: 1.5 cm) in the frequency range of 100 KHz–20 GHz by using ENA Series Network Analyzer, E5071C, Agilent Technology. The S_{11} and S_{12} parameter measurements were carried out in the both S-band and X-band frequency of ISM band with a wave guide of diameter 2 cm. Therefore, the circular pellets of PnHM and PnHMAg of 1 cm diameter were prepared and placed between the respective holders. After that, the sample holder was connected between two coaxial wave guide adaptors and tightened and finally connected to the network analyzer to measure the scattering parameters S_{21} and S_{11} and calculate the reflection coefficient (R), transmission coefficient (T) and shielding efficiency (SE) parameters.

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