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Nanostructured multifunctional core/shell ternary composite of polyaniline-chitosan-cobalt oxide: Preparation, electrical and optical properties

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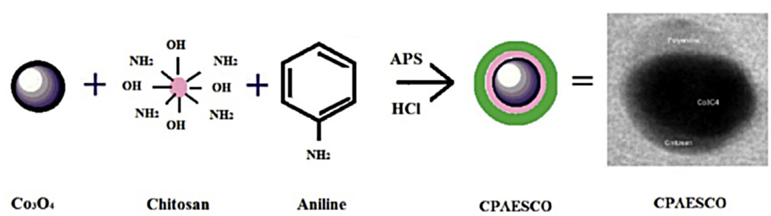
HIGHLIGHTS

- An advanced ternary Core/shellnano compositewith novel properties prepared.
- Small amounts of Nanoparticles to the Polyaniline –Chitosan matrix showed dramatic changes in properties.
- Introduced Multifunctionality to emaraldine salt-Structural, Electrical, optical and Biocompatibility.
- Step wise change in conductivity and band structure modifications are discussed in detail.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper is a report on synthesis and analysis of the structure, morphology, and physicochemical properties of a three-component-Polyaniline/Chitosan/Co_3O_4 – (CPAESCO)-hierarchical core/shell ternary nanocomposite. This was achieved by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Thermo Gravimetric Analysis (TGA), Electrical Conductivity and UV–Visible analysis. The chemical bonding established in the composites were confirmed by using FT-IR. XRD patterns helped analysis of intensity variation of Co_3O_4 peaks, polyaniline (PAES) peaks, Crystallite size (D) and inter-crystallite separation (R) of the composites. Thermal stability increases and electrical property shows a step wise increase with increase in nanoparticle addition. Morphological changes from granular PAES to plate like CPAESCO is visible in SEM. The polaron lattice structures, hypsochromic shift, and crystallite size dependent band gaps in CPAESCO due to energy confinement produced from ligand-metal charge transfer (LMCT) interaction of Co_3O_4 in PAES matrix, are visible in UV–Vis spectra. The improved properties of the composite are as a result of the formation of core/double shell as shown in TEM. This nanocomposite can be used in optoelectronic and biomedical applications, catalysis, chemical and bio sensors, and energy storage devices because of its enhanced properties.

1. Introduction

Polymeric materials can exhibit significant properties if they possess core/shell multi-component phase separated morphology

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at the nanoscale [1]. The nano-domains can constrain the polymer chains or enhance the efficiency of the polymer depending on the type and amount of filler used. So in a ternary composite with two polymers and a nano metal oxide, the extent of improvement is mainly determined by the nano structure represented by the size, shape and homogeneity of it in the polymeric matrix [2]. The main advantages of metal nanoparticles are higher quantum yield in nano scale, higher photoluminescence efficiency, improved optical properties, easy detection of emission spectra, photo-oxidation stability, improved appropriate electronic properties (band gap, band alignment), and finally better structural (lattice mismatch) properties than unlayered particles [3]. As the miniaturization trend of appliances prevails, the synthesis of polymer nanocomposites, their characterization, morphology and property study plays a dominant role in their industrial mass production.

Polyaniline (PANI) is a conjugate conducting polymer with various oxidation states and is recognised as a synthetic metal [4]. The extended π −systems in it are highly affected by chemical and electro chemical method of oxidation or reduction. These processes change PANI's electrical and optical properties, and by controlling the oxidation and reduction, it is possible to control these properties precisely [5]. PANI has wide applications, such as in rechargeable batteries, gas-separation membranes, sensors, corrosion protection of metals, as a matrix for preparation of conducting polymer nanocomposite [6], and super capacitors. PANI bears good chemical, thermal and envFT-IRonmental stability, electrical and optical properties, facile redox and pH-switching behaviour. One of the main qualities of PANI is the rapid switching possibility from the acid doped conducting emeraldine salt (PAES) to the dedoped insulator emeraldine base and vice versa [7].

Chitosan (CS) is a low cost, biocompatible, high molecular weight, branched biopolymer with unique physical and chemical properties. The important advantages are biodegradability, non-toxicity, adsorption, excellent chemical-resistance and electrolytic properties and polymer modification. Unlimited supply of raw materials for the production is an added advantage. The CS is having $-NH_2$ and −OH groups, which offers self doping, one of the chemical advantage to interact with PAES, and enhances its properties. CS is a nontoxic cellulose-like polyelectrolyte polymer which undergoes a large volume change with respect to changes in pH, temperature, or solvent composition and is used in fabrication of artificial muscles. It is used in drug delivery systems and biosensors [8]. Composites have been attempted by incorporating a rigid conducting polymer (such as PAES) into a flexible CS. The nitrogen in the amino and N-acetyl amino groups can establish dative bonds with transition metal ions in selected metal oxide also [9,10].

Nanostructured oxides with infinite variety of structural and morphological features exhibit some special surface properties for energy harvesting, conversion, and storage [11].

These electro active nano materials possess better surface properties and balance the electronic and ionic transportation of electrons or ions in the composite [12]. Among the active transition metal oxides, Co_3O_4 has high surface area, good redox and easy tunability of surface, as well as some favourable structural and morphological properties. Therefore it is being studied extensively in heterogeneous catalysis, solid state sensors, magnetic materials and super capacitor applications [13].

The aim of this study is to improve physicochemical properties of PAES by the synthesis of Polyaniline/Chitosan/Co_3O_4 (CPAESCO) ternary nanocomposite through in situ polymerization of aniline in the presence of fixed quantity of CS and varying concentrations of Co_3O_4. Conducting polymer-chitosan-inorganic transition metal oxide composites are expected to improve or complement the optical, electrical, thermal, chemical and structural properties over their individual components. The properties of these new functional materials depend on a number of factors such as concentration of the CS, the dispersant nano material and their morphology, orientation and interfacial interaction of them with the PAES matrix. At a particular concentration CPAESCO (1) the polyaniline nanocomposite attained a core/shell nanostructure and revealed synergism of properties of the initial components.

2. Materials and methods

2.1. Materials

Aniline (Finar chemicals limited, Ahmadabad, India) is distilled under reduced pressure, nano Cobalt oxide < 50 nano meter particle size (Aldrich), Ammonium peroxydisulphate $(NH_4)_2S_2O_8$ (mol. wt.228.20 gm/mol) (Merck), and hydrochloric acid (mol wt. 36.46 gm/mol) is used as received. Chitosan (448877- 50G, Medium molecular weight, Chemie grade, 75–85% deacetylated) was purchased from Sigma–Aldrich. All the chemicals used were of analytical reagent (AR) grade.

2.2. Preparation of polyaniline salt (PAES)

The conducting PAES was synthesized by oxidative chemical reaction method. 0.22 M aniline (5 ml-doubly distilled) was dissolved in 240 ml of 1M HCl and 0.8 M $(NH_4)_2S_2O_8$ (APS) was dissolved in 80 ml 1M HCl solution and the two solutions were then pre cooled to ~ 0 °C by using ice bath. The APS solution was added to the aniline solution drop wise over a period of 2 h with constant stirring to ensure thorough mixing. The mixture was continuously stirred for 24 h and filtered. The residue was exhaustively rinsed with distilled water in order to eliminate the excess of HCl and was finally dried in an oven at 50 °C for 24 h [14,15].

2.3. Preparation of chitosan/polyaniline (CPAES) composites

The CPAES composite was synthesized by using chemical oxidation and precipitation method as per the reported procedure with some modification [16]. In this method, 0.5 g of CS in 4% acetic acid was vigorously stirred for 1 h and filtered to obtained the clear solution, aniline in 1M HCl was added portion-wise for 20 min with constant stirring. The polymerization was carried out by the addition of APS as described earlier. The green sediment was washed several times with distilled water and was oven dried at 50 °C for 24 h, powdered with mortar and designated as CPAES [17].

2.4. Preparation of polyaniline/chitosan/nano Co_3O_4 composites (CPAESCO)

Nano Co_3O_4 (0.4 g) is dissolved in 20 ml distilled water and mixed thoroughly with aniline monomer in HCl. The remaining process is same as stated above in preparation of CPAES. The residue was blackish green which was filtered and dried. The same process is repeated for 0.75 g and 1 g nano Co_3O_4 to get CPAESCO (0.4), CPAESCO (0.75) and CPAESCO (1).

2.5. Characterization methods

The structure of the samples were analysed by Fourier Transform Infrared Spectrometer (FT-IR, Perkin Elmer FT-IR spectro photometer (AIM-8800), using KBr pellets), Ultraviolet–visible absorption spectra (Computer aided double beam spectrometer Perkin–Elmer LAMBDA-35 UV–Vis), XRD by Rigaku miniflex-600 bench top diffractometer with Cu target, Electrical conductivity was done by Wayne Kerr 6500 B Impedance analyser, SEM is done using Carl Zeiss Sigma Variable Pressure Analytical SEM