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Organic-inorganic hybrid nanomaterials for advanced light dependent resistors

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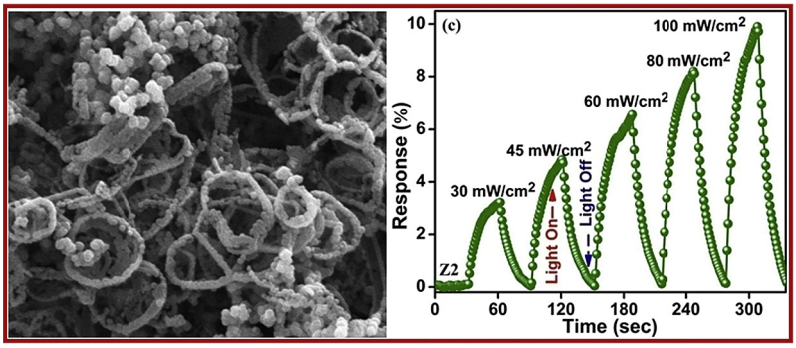
HIGHLIGHTS

- Development of Organic/Inorganic hybrid Nanomaterials for Light Dependent Resistors.
- Designing of Light Dependent Resistors (LDRs) for white/visible light.
- To study the role of ZnO NPs incorporation on the LDR device performance.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the photoconduction behaviour of hybrid organic (polypyrrole) - inorganic (ZnO) nanostructures, synthesized by the surfactant mediated solution based chemical method at room temperature, for the energy saving light dependent resistor (LDR) applications. The formation of organic-inorganic hybrid nanostructures is confirmed by the combination of high resolution transmission electron microscopy and scanning electron microscopy, which revealed creation of cubical shaped wurtzite ZnO nanoparticles with different preferential orientations and transformation of clip-like nanofibres form of pure polypyrrole (PPy) into worm-like nanoribbons having embedded ZnO nanoparticles in it. Given p-type nature of PPy and n-type nature of ZnO, the embedment of ZnO nanoparticles in PPy is expected to create several localized discrete p-n junctions, which is why Raman spectroscopic results reveal the change in molecular structure of PPy due to its nanoscale interaction with ZnO. The photoresponse of PPy is found to continuously enhance from ~4.5 to 10.7% with increase in ZnO concentration from 0 to 10% at the constant illumination intensity of 100 mW/cm^2. The improved photoresponse can be attributed to the formation of localized p-n junctions (p-type PPy/n-type ZnO) in the structure. The

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photoresponse of PPy and its nanocomposites also increases with increase in illumination intensity from 30 to 100 mW/cm^2, which is attributed to the increased number of photo-generated electron-hole pairs.

1. Introduction

Nanoscale hybridization of organic conjugated polymer and inorganic metal oxide semiconductor has received considerable recognition in the field of nanodevice fabrication. Owing to their synergistic effect, these hybrid nanomaterials can open a platform for the development of high performance electronic devices such as transistors, light emitting diodes, gas sensor and solar cells. The efficiency of these devices can significantly depend on the shape and size of the nanomaterials due to increase in surface to volume ratio at nanoscale [1–8]. Today, the generation of renewable and clean energy, like solar energy, is the point of concern to sort out the problems of energy crises and environmental pollution, because the conventional energy sources like coal, petroleum are going to exhaust and their burning generates environment pollutant at high level, resulting into serious health concerns. Apart from the generation of clean and renewable energy, energy saving is also equally important. Unawareness of the energy saving strategies and high cost of automatic switches, which is mainly due to the use of sophisticated and expensive techniques for the fabrication of light dependent resistors (LDRs), seem to be the main reasons for electrical energy wastage. Furthermore, the precursor materials used for LDRs are highly toxic, leaving long term hazardous environmental effects [9]. Thus, the search of new and efficient low cost environment friendly materials for light dependent resistors always remains at the centre of attention.

With the advent of micro/nanomaterials formation techniques, a plethora of nanostructured metal oxides (ZnO, TiO_2, CdO) and metal sulphides (ZnS, CdS, etc.) are exclusively investigated for photoconductors, nanophotodetectors, photoconducting light switches, ultra violet light sensor, field emission and other photonic applications [10–15]. Out of these inorganic materials, ZnO nanostructures have received considerable attention due to their high thermal stability, large optical band gap, high mechanical strength and high resistance against oxidation in callous environments. The optical band gap of ZnO lies in ultra-violet region that makes it suitable for UV- photodetectors [14,15]. On the other hand, polypyrrole (PPy) is recognized as one of the most stable polymeric systems with wide range of applications in gas sensors, super capacitors, batteries, EMI shielding, etc., because of its tuneable optical band gap [16–19]. Although few reports [19–21]are available on PPy and its nanocomposites for photodetectors, most of them were restricted to UV-visible sensors. There is a dearth of data on white light detectors and light dependent resistors for visible light. Moreover, there is lack of data on the parameters like responsivity, detectivity, photocurrent enhancement factor and trap depth, etc., associated with the performance of a photodetector, which are also the centres of attention of the present study. Owing to combined effect and the nanoscale interaction, the organic-inorganic (PPy-ZnO) nanocomposites can show promising light dependent response in the white light region of the spectrum with significant enhancement in nanodevice parameters responsivity, detectivity and photocurrent enhancement factor. These facts have motivated us to carry out the present work. Thus, to investigate the effect of nanoscale hybridization on the performance of white light detectors, nanocomposites of PPy and ZnO were prepared by solution based chemistry method in different morphological forms, towards their non-toxic and cost effective light dependent resistor applications. The nanoscale interaction of ZnO with PPy significantly alters the surface morphology of PPy and resulting in augment photoresponse characteristics.

2. Experimental details

2.1. Synthesis of ZnO nanoparticles and PPy/ZnO nanocomposites

Cubical shaped ZnO nanoparticles were prepared by the surfactant assisted hydrothermal process, the detailed synthetic approach has been described elsewhere [22]. In a typical synthesis process, salt solutions of $Zn(NO_3)_2{\cdot}6H_2O$, capping agent (cetyltrimethylammonium bromide, CTAB), reducing agent (NaOH) were prepared separately in double distilled water. Then these solutions were mixed together under constant stirring and refluxing at a temperature of 90 °C for 2 h in the presence of 1 M ammonia, added to increase the pH value (~9) of the solution. After the completion of the reaction, the solution was allowed to naturally cool down at room temperature, and ZnO nanoparticles were separated out, washed and dried overnight at 60 °C.

2.2. Synthesis of PPy/ZnO nanocomposites

The detailed synthesis process for pure polypyrrole (Z0) and its nanocomposites with 5 wt % (Z1) and 10 (Z2) wt. % of ZnO nanoparticles has been reported elsewhere [23]. In a typical synthesis process, the salt solutions of the capping agent (CTAB) and oxidizing agent ($K_2S_2O_8$) were separately prepared in double distilled water containing 1 M HCl solution and a desired quantity of ZnO nanoparticles (5 wt% or 10 wt %). Then these solutions were well homogenized under constant magnetic stirring. After ensuring the homogenous mixing of above solutions, a desired quantity of double distilled pyrrole monomer was added to it and the reaction was carried out for 12 h. Finally reaction was terminated by adding sufficient amount of methanol and the polypyrrole powder was then separated out, washed and dried at 60 °C for overnight.

2.3. Sample characterization

The morphological analysis of ZnO nanoparticles, PPy and PPy/ZnO nanocomposites was performed using high resolution transmission electron microscopy (HRTEM,FEI, Tecnai G2 F30- STWIN) and scanning electron microscope (SEM Leo Electron Microscope–model LEO 440). Structural analysis of PPy/ZnO nanocomposite was carried out using Raman spectroscopy at Renishaw InVia Reflex micro Raman spectrometer, where air cooled argon laser of wavelength ~514.5 nm is used as an excitation source at a power of 10 mW. The room temperature dc conductivity measurements were carried out using Keithley 2410 SMU on all the samples in sandwich structure (Au/PPy/Au), where gold electrode of 3 mm were deposited on both sides of the pellets of the samples via thermal evaporation technique.

The photoconductivity measurements were performed using Keithley 2410 SMU on the cubical shaped pellets of same sizes (~1 × 10 × 5 mm^3) of the samples in parallel electrode geometry at room temperature and at different illumination intensities. Before performing the experiment, parallel gold electrodes (electrode gap is ~ 2 mm) were deposited by thermal evaporation techniques under high vacuum (~1.2 × 10^{-5} torr) condition. To avoid the heating effect in these samples, a spacing of 25 cm was always