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Effect of stabilizing agents on the conductivity of Co@TiO$_2$ core–shell nanoparticles

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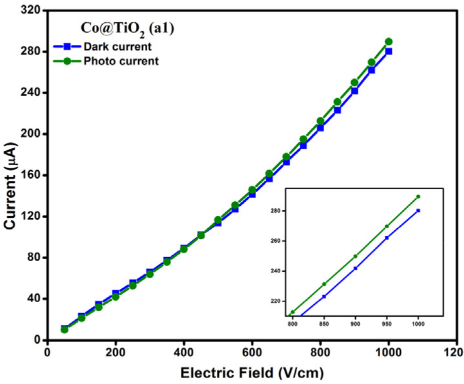
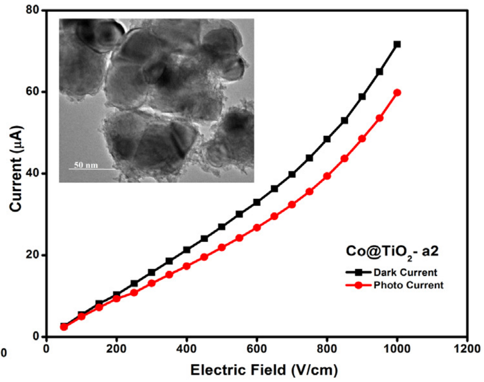
GRAPHICAL ABSTRACT





HIGHLIGHTS

- Synthesis and characterization of PVP/Glycodendrimer stabilized Co@TiO$_2$ core–shell nanoparticles.
- The focus is to study the contribution of stabilizing agents on the conductivity of synthesized nanoparticles.
- PVP stabilized Co@TiO$_2$ nanoparticles shows more conductivity than Glycodendrimer stabilized nanoparticles.

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ABSTRACT

The main focus of this work is to choose a stabilizer which plays a significant role in enhancing the conductivity of Co@TiO$_2$ nanoparticles. Poly Vinyl Pyrrolidone (PVP) and zeroth generation triazolyl Glycodendrimer were the stabilizing agents whose activity on Co@TiO$_2$ nanoparticles has been compared. As a semiconductor with extreme resistivity Co@TiO$_2$ shows good conductivity due to the presence of cobalt at the core which was further improved by suitable stabilizing agent. Being less reactive when exposed to light, glycodendrimer lags behind PVP in the conductivity test results. The results obtained from impedance analysis, UV–Diffuse Reflectance Spectrograph and photoconductivity shows that the

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UV–DRS
Photoluminescence
Photoconductivity

activity of PVP stabilizer is better than glycodendrimer. The structural analysis of the synthesized samples shows that the lattice strain experienced by PVP is less than that of glycodendrimer.

1. Introduction

At the beginning of 20th century, US National Nanotechnology Initiative (NNI) predicted that the development of nanotechnology will be in two fundamental phases, firstly, existing products will be improved by incorporating simple nanostructures and discovering their new nanoscale properties. Secondly, developing new complex nanosystems with the integration of safety and multifunctionality [1–3]. Nowadays, development of nanoparticles and nanostructures is widespread in various levels and its implications are far spread in almost all fields of science and technology viz., material science, optics, electronics, sensors, energy, solar cells, medicine, drug delivery and biological applications [4]. A common way to develop the multifunctionality of nanoparticles is by combining materials in various forms as organic–organic, organic–inorganic, inorganic–inorganic organic–biological as bimetallic nanocomposites or core–shell nanoparticles [5]. Core@shell nanoparticles are successful multicomponent nanomaterials which are desirable for their multifunctionalities [6–8]. The fabrication of such nanostructures may vary widely in different methods [9–11]. The simple and effective method among them is Redox-Transmetalation method [12]. The synthesis of core@shell nanoparticles by this process yields well defined and high quality nanoparticles. Also, additional reducing agent is not required as the shell layer deposits on top of the core layer spontaneously, preventing self nucleation of the secondary metal [13,14].

Stabilizing agents were used during the synthesis of core–shell nanoparticles to prevent the precipitation and agglomeration of metal nanoparticles [15,16]. They are exclusively used to incorporate favourable shell coating by modifying the surface charge and to control the size of nanoparticles. It is important to understand the role of stabilizing agent in influencing the surface properties of the nanoparticles. Most commonly used stabilizer is Poly Vinyl Alcohol (PVA) and Poly Vinyl Pyrrolidone (PVP) [17–20]. By exploiting different stabilizing agents in the synthesis of core@shell nanoparticles, the impact of such capping agents on nanoparticles can be studied.

In order to obtain well defined macromolecules with interesting physical properties, the next generation polymers, called dendrimers are introduced. Dendrimers have rich physical properties and effective applications in various fields [21,22]. Though the science of dendrimers and dentric structures is well established, the use of dendrimers in the synthesis of core@shell nanoparticles is limited. Low generation dendrimers commonly used as stabilizing agents are functionalized by classic reactions whereas high generation dendrimers, which are encapsulators, need special attention as their periphery is bulky [23–25]. Glycodendrimer [26] as capping agent is used in the synthesis of Co@TiO_2 [27] core–shell nanoparticles as it is reported for its effective application in various fields.

Metal/metal oxide nanoparticles, extensively synthesized in the form of core@shell, are one among the important class of compounds. When two different metals or metal oxides are brought closer at its atomic vicinity, it induces electronic charge transfer and affects the electronic band structure [28]. Also, if the difference between the Fermi level of the core and shell nanoparticle is large, then the electrons that diffuse within the shell will be trapped for long period inside the core [29]. Thus, the interaction of TiO_2nanoparticle with other materials is exclusively important in the study of metal oxide nanoparticles [30–33]. They have many promising optical applications ranging from photovoltaics to sensors [34]. Also the TiO_2 based devices are largely influenced by their size at the nanometre scale. Here, in this report we discuss the optical and electrical properties of Co@TiO_2 core–shell nanoparticle synthesized by Redox Transmetalation method using two different stabilizing agents PVP (a1) and glycodendrimer (a2). The proposed research work is to study the conductivity of the oxide based n-type semiconductor (TiO_2) with the ferromagnetic metal (Co) placed at the core, with two different stabilizing agents.

2. Material synthesis

2.1. Chemical reagents

All the chemicals used in this study were of analytical grade and used without further purification. The reactions were carried out under nitrogen atmosphere. Cobalt chloride hexahydrate ($CoCl_2.6H_2O$), Titanium (IV) Oxide (TiO_2), Sodium borohydride ($NaBH_4$) and ethanol were purchased from Sigma-Aldrich Pvt.Ltd. Distilled water was used in all experiments.

2.2. Synthesis of Co@TiO_2 core–shell nanoparticles

Co@TiO_2 core–shell nanoparticles were synthesized by Redox-Transmetalation method. The precursors used are $CoCl_2.6H_2O$ (99%) and Poly Vinyl Pyrrolidone (PVP) (a1) or zeroth generation triazolyl glycodendrimer (a2). The precursors are dissolved in 50 ml of distilled water and stirred for 30 min. 10 ml of the reducing agent prepared (5 ml of 1M NaOH and 10 ml of 2M of $NaBH_4$) was added drop-wise into the solution under nitrogen atmosphere. After stirring for another 20 min, TiO_2(stoichiometric proportions of Co:TiO_2@1:4) was added and stirred at 600 rpm for 10 to 12 h. The sample was collected and repeatedly washed with organic solvents, centrifuged and then dried at ambient temperature. The composite material thus prepared consists mostly of core–shell nanoparticles.

$$\begin{aligned}&2CoCl_2.6H_2O + 2NaOH + 2NaBH_4\\&\quad\rightarrow 2Co^{2+} + 4NaCl + B_2H_6\uparrow + 14H_2O + 3H_2\uparrow\end{aligned}$$

3. Experimental characterization

The surface morphology of the as prepared core–shell nanoparticles were investigated using Powder X-ray Diffractometer (DS Advance Bruker) of CuKα radiation $\lambda = 1.5406$ Å for phase analysis and structure determination. The XRD Pattern is obtained using fine powdered sample of 500 mg for a 2θ range of 10° to 70° . Field Emission SEM images (FEI Quanta FEG 200) of resolution 1.2 nm gold particle separation on a carbon substrate are used to examine the particle size. Energy dispersive X-ray spectrometry (EDX) provides the crystalline information of the synthesized sample. This also confirms the percentage of elemental composition present in the sample. The nanoparticles subjected to High Resolution Transmission Electron Microscope (HRTEM-JEOL 3010 with 200 kV operating voltage) of relative wavelength, $\lambda = 0.0251$ Å were dispersed in ethanol, drop-casted on to copper grid and dried naturally. The HRTEM images provide the size and shape of the synthesized sample. The impedance analysis was done to test the electrical conductivity of the sample using the impedance analyser