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Synthesis and characterization of Ag_2S/PVA-fullerene (C_{60}) nanocomposites

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ABSTRACT

We present the chemical synthesis of silver sulfide nanocrystals (NCs) in PVA matrix and the extended characteristics of the obtained nanocomposites with fullerene. The samples were prepared with the different concentration of fullerene and PVA for compression of their fraction relation with the optical and phase properties. UV–vis spectra of Ag_2S show sharp excitonic features and a large blue shift from the bulk material. The NCs grain size was determined about 10–15 nm which is confirmed by different techniques such as Scanning electron microscopy (SEM), UV–visible absorption and X-ray Diffractometer (XRD). The SEM images demonstrate that the nanoparticles overlapped and stabilized with a polymer matrix. The EDAX result indicates that the prepared nanocomposites are composed of pure phase Ag, S, C and any other irrelevant mixtures have not been detected.

1. Introduction

Nanoscaled inorganic–organic nanocomposites exhibit unique electrical, electromagnetic, thermal, mechanical and optical characteristics that have attracted high interest due to their considerable technological applications in materials science, such as catalysts, semiconductor sensitized solar cells (SSSCs), photo-conductors, magnetic materials and luminescent materials [1–4].

The semiconductor silver sulfide nanocrystals at nanoscale often have outstanding photoelectric and thermoelectric properties and less toxicity by comparison to other metal-chalcogenides nanoparticles [5]. The silver sulfide nanoparticles in a polymer matrix have been applied in diverse optical and electronic devices, such as photo-conducting cells, IR detectors, solar selective coatings and photovoltaic cells [6].

During the last years, semiconductor quantum dots (QDs) such as CdS, CdSe, PbS, CuS, InAs and InP have been assembled onto porous films, nanotubes, nanowires, and nanoparticles and then used as photocatalysts due to their narrow band gap [7]. In this respect, Ag_2S is an important material for photocatalysis and electronic devices, because of its potential large optical absorption coefficient and a direct band gap of 0.9–1.05 eV, which makes it an effective semiconductor materials [8–11].

Fullerene (C_{60}) is a promising material with large-scale utilization in semiconductor and optoelectronic devices due to individual structural, electrical and optical properties [12,13], however, its coupled mechanism with metal-sulfide nanoparticles in a polymer matrix have not been elucidated properly. In the electron transfer processes fullerene (C_{60}) can expeditiously launch rapid photoinduced charge separation and low charge recombination due to its remarkable acting as an electron acceptor [14]. C_{60}-based materials are among the most important candidates for the expansion of plastic solar cells and renewable sources of electrical energy due to semiconductor band gap energy, about 1.6–1.9 eV [15,16].

There are different approaches for the synthesis of nanodimensional systems, such as the solvothermal method [17], hydrothermal route [18], sonochemical route, single-source precursor routes [19], sol–gel method [20], in-situ [21], and ion-exchange technique [22], etc. In the presented work, we report the synthesis of Ag_2S nanoparticles on PVA polymer matrix and moreover coupled semiconductor Ag_2S/fullerene nanocomposite in PVA with different concentration. Herein, a facile chemical one-pot synthesis method has been applied for the preparation of Ag_2S/PVA–fullerene nanocomposites.

These nanocomposites have unique photoelectric, thermoelectric and photocatalytic properties which are promising materials for diverse applications on photocatalyst, photovoltaic field in the future. One of the advantages of our work: that we have not used the oxidation agent, thus C_{60} takes part in oxidation process

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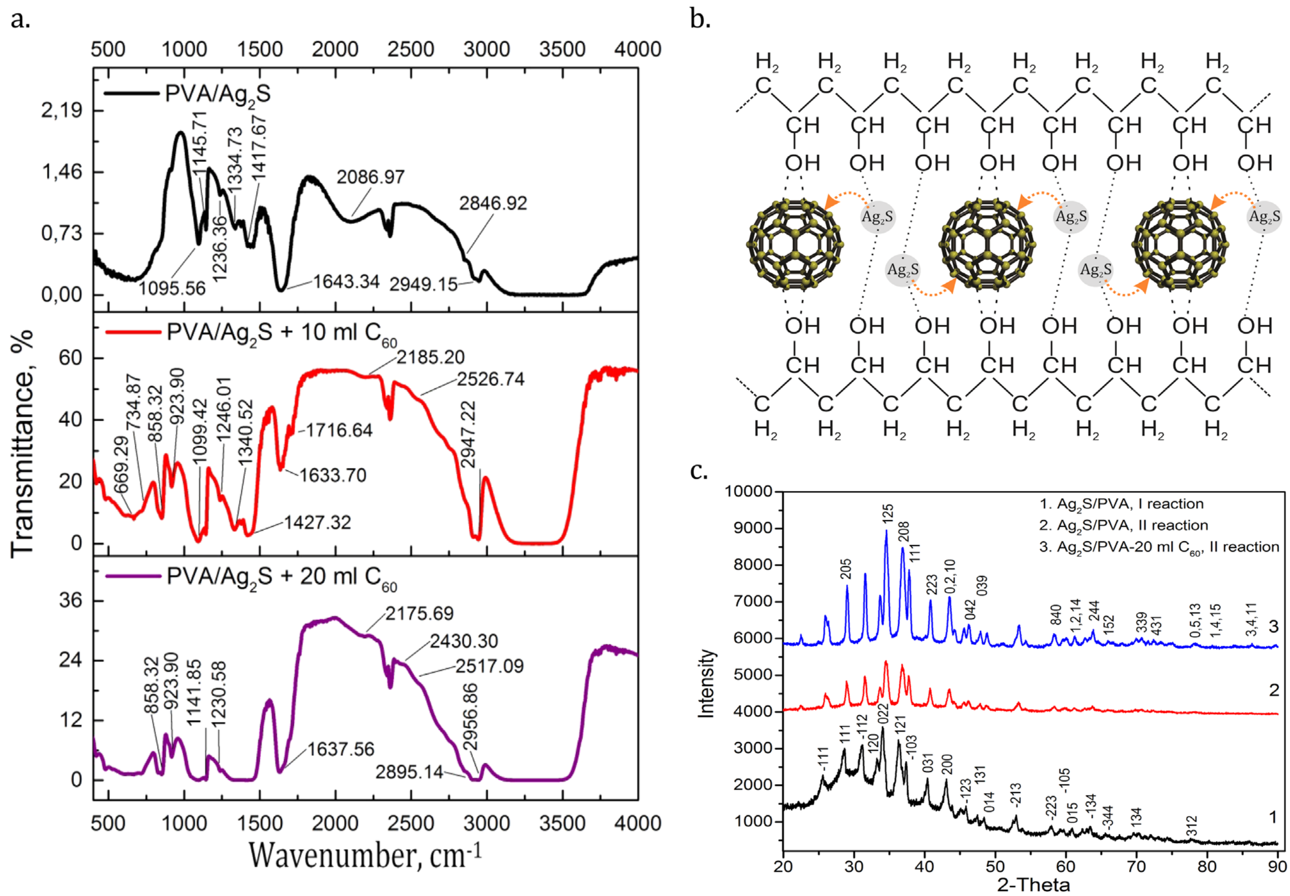

Fig. 1. The FT-IR spectra (a), proposed stabilization process (b) and powder XRD patterns (c) of the obtained nanocomposites.

and PVA stabilizes the nanoparticles due to its functional active groups as a capping agent.

2. Experimental

2.1. 1. Materials and methods

The polyvinyl alcohol (PVA), fullerene (C_{60}), toluene ($C_6H_5CH_3$), thiourea $CS(NH_2)_2$, silver nitrate $AgNO_3$ and hydrazine were all commercial products with the highest purity (99,9%) purchased from Sigma-Aldrich. All initial substances were used without further purification for the preparation of fullerene/metal-sulfide nanocomposites. The obtained nanocomposite material was characterized by several methods. The powder X-ray diffraction spectra of the films and powder specimens were recorded on a Bruker D2 Phaser X-ray diffractometer under Ni filtered CuKα radiation (λ=1.5406 Å). The surface morphology and elemental content analysis were investigated on a Field Emission Scanning Electron Microscope with Energy dispersive spectrometer and Electron Backscattered Diffraction System, respectively. The optical properties of synthesized nanocomposites were measured by UV–vis absorption spectrometer and Fourier transmission infrared spectroscopy (FT-IR).

2.2. Synthesis of Ag_2S/PVA-fullerene (C_{60}) nanocomposites

Chemical synthesis of polymer nanocomposites was carried out in a jacketed four neck round-bottom 250 ml reaction flask equipped with a mechanical stirrer, thermometer and reflux condenser for adjusting the temperature. The reaction went out in the hot water bath and the temperature has been increased gradually up to 373 K.

In the first stage, for the synthesis of polymer capped Ag_2S nanocrystalline, 3 g polyvinyl alcohol was dissolved in 30 ml deionized (DI) water. While the water bath slightly heated up, the polymer mixture was vigorously stirred about 30 min for solving the polymer properly. On the other hand, 0.1 M $AgNO_3$ stock solution was prepared by dissolving in 100 ml distilled water. Similarly, 0,76 g thiourea $CS(NH_2)_2$ was dissolved in 100 ml distilled water. From each these solutions, we have used 20 ml in the first reaction step. Initially, 20 ml $AgNO_3$ salt solution was added into the reaction flask and vigorously stirred with polymer mixture half an hour and a film was prepared on a glass substrate by taking from the reaction conditions. Afterward, 20 ml thiourea was poured into a solution by dropwise with strongly stirring. While the color of the solution changed from transparent to the darkest brown some drops of solution have been taken for preparing a film on a glass substrate. In 5 min, we have added 2 ml hydrazine in the reaction condition for precipitation of Ag_2S/PVA nanocomposite material. The last stage of the reaction was carried out one an half hour. The powder was completely separated from the solution and washed up 5 times with excess DI water for purification. The obtained nanocomposite powder firstly dried at ambient condition and then in a vacuum furnace at 60 °C for the complete removal of water.

The formation reaction of silver sulfide nanoparticles in the polymer matrix can be written as following:

$$AgNO_3 + CS(NH_2)_2 \rightarrow Ag_2S\downarrow + \ldots.$$
$$AgNO_3 \leftrightarrow Ag^+ + NO_3^-.$$
$$(NH_2)_2CS + OH^- \leftrightarrow CH_2N_2 + H_2O + HS^-.$$
$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}.$$