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Ag_2S deposited on oxidized polypropylene as composite material for solar light absorption

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ABSTRACT

Thin film metal chalcogenides are superior solar light absorbers and can be combined into a functional material when deposited on polymeric substrates. Ag_2S composite materials were synthesized on oxidized polypropylene using chemical bath deposition method and their properties were explored using XRD, XPS, AFM and UV–Vis. Polypropylene surfaces were modified using solution methods to introduce hydrophilicity via carboxylic group formation which resulted in Ag_2S film deposition and adhesion. These films showed slightly sulfur enriched composition from XPS analysis with the sulfate-like species forming, presumably at the oxidized polymer surface sites. Ag_2S particle growth mechanism included nucleation and rather large (few μm) aggregate formation eventually covering the complete polymer surface, as inferred from AFM analysis. Absorption edge of the composite material shifted toward the higher wavelength in UV–Vis spectrum with the number of Ag_2S exposure times showing a decreasing bandgap and the possibility of obtaining tunable optical property Ag_2S–polymer composites using CBD methods.

Introduction

The rapid growth of the world economy as well as the Earth's population puts a strict requirement toward the new way and methods for inexpensive energy generation. Renewable energy sources, such as solar, wind, hydro and biomass recently have attracted significant amount of attention. Among these alternatives, conversion of solar light into electrical energy has become the most popular due to the large surplus of solar radiation available. Each year, 120.000 TW of solar radiation strikes the Earth's surface. For comparison, the global annual energy consumption is 13.5 TW, and is expected to increase to about 30 TW by the 2050 [1,2], which means that an immense potential lies in harvesting solar energy. However, using our current technologies, providing 30% of global energy needs in 2050 would require to cover an area of 250.000 km^2 with semiconductors even assuming an optimistic 10% solar-to-hydrogen conversion efficiency [3]. This surface area implies tremendous amounts of solar absorber material, while also invoking their corresponding efficiency, cost and availability criteria. In the latest considerations, non-metal oxide based materials, such as sulfides are proposed to convey the highest electricity potential vs. materials cost ratio [4,5].

To minimize the amount of the solar absorber material, thin films of high absorptivity need to be considered. Silver sulfide (Ag_2S) is an important metal chalcogenide semiconductor compound with the band gap of ~1.5 eV [6] and a high absorption coefficient of approximately 10^4 cm^{-1} [7], able to ensure most of the solar light absorption in a thin layer. Ag_2S belongs to I–VI compound semiconductor materials with monoclinic crystal structure. It possesses a unique combination of properties, such as high dark ionic or electronic conductivity, photoconductivity, as well as related photovoltaic and photochromic effects [6,8–10]. Silver sulfide thin films have been produced as functional materials with applications in the contemporary advanced technologies ranging from photoconductive and photovoltaic cells, solar selective coatings, ion selective electrodes and membranes to IR detectors and laser recording media [11–18].

Composite materials consisting of polymers covered by thin layers of inorganic compounds possess tunable characteristic optical and semiconducting properties. In the recent years, metal

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chalcogenide semiconducting thin films on polymeric surfaces have been extensively studied due to their technological importance. Polypropylene is one of the fastest growing classes of thermoplastics and can serve as a model metal chalcogenide–polymer composite. It is low cost, low density, and has high heat distortion temperature (HDT). However, in its intrinsic state, hydrophobic polypropylene does not possess the surface properties required for preparation of thin solar absorber film composites. Polypropylene is resistant toward many solvents and chemicals. It is known due to its apolar characteristics, which has direct influence on its adhesion properties [19–22]. One of the polypropylene surface modification methods is its oxidation. The oxidation of isotactic polypropylene (iPP) in solid phase has been done via reactions with ozone, γ-initiated corona method and UV ray or with chemical oxidizing mixture [19,23–30]. The oxidation of iPP leads to the formation of oxygen-containing surface functional groups, which greatly affect the surface polarity and the adhesion properties of the polymer toward the metal chalcogenide deposition.

Thin film solar light absorbers are of particular interest for fabrication of large area arrays, solar selective coatings and solar cells. As such, tuneable and controllable thickness thin film deposition is of crucial importance in attaining their desired absorbing. Previously, Ag_2S thin films with different morphologies have been prepared via various methods, such as solid–vapor reactions [31], radio frequency sputtering [32], thermal evaporation [33], electro deposition [34], successive ionic layer absorption and reaction (SILAR) [35] and chemical bath depositions (CBD) [6]. As in most of metal sulfide materials, a crucial property for solar energy harvesting is the resulting conductivity. It has already been shown that elemental stoichiometry affects the conductivity of sulfide thin films. Pyrite, FeS_2, for example, has been proposed as the next potentially efficient, abundant and inexpensive solar absorber [5]. However, tiny differences in elemental composition via sulfur defect states have been shown to affect the semiconducting properties of pyrite tremendously [36]. Consequentially, methods of solar absorber Ag_2S thin films need to be obtained for a reproducible thin films with the desired stoichiometry. Compared with other deposition methods, previously proposed modification of the chemical bath deposition technique is very convenient, facile, low cost and environmentally friendly [30,37]. This is due to the fact that Ag_2S sediments can be re-used after the reaction since they redissolve in nitric acid [37].

In this study, Ag_2S thin films were synthesized on the partially oxidized hydrophilic polymeric material – isotactic polypropylene (iPP) – using chemical bath deposition. This method is based on a controlled precipitation of the desired compound from its corresponding ions in the reaction bath solution. While Ag_2S has previously been deposited on hydrophilic or partially hydrophilic polymers, such as polyamide [37], here we employ hydrophobic polymer – polypropylene – as a substrate. Oxidized polypropylene – which possesses a hydrophilic character – was also prepared and structurally characterized to provide maximum adhesion for the Ag_2S material. Structural, chemical and optical properties of the resulting composite materials were determined using XRD, XPS, UV–Vis and AFM.

Experimental methods

Materials

All solutions were prepared using distilled water and analytical grade reagents. Only freshly prepared solutions were used for measurements and were not de-aerated during the experiments. H_2SO_4 (96%, Barta a Cihlar, Czech Republic), H_3PO_4, (60%, Lach-Ner, Czech Republic), CrO_3 (>99%, Reachim, Russia), sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$) (>99%, Sigma-Aldrich, Germany), and HNO_3 (65%, Penta, Czech Republic) were used as received.

Polypropylene oxidation

Isotactic polypropylene (iPP) used in this study was supplied by KWH Plast (Finland). 15 × 70 mm samples of non-oriented isotactic polypropylene film of 150 μm thickness were used for these experiments. First, polypropylene surface was oxidized to obtain hydrophilic properties for silver sulfide adhesion to proceed. Surface of the commercial iPP samples was treated for 25 min at 90 °C with oxidizing solution consisting of H_2SO_4/H_3PO_4 (1:1, saturated with CrO_3) and finally rinsed with distilled water.

Ag_2S deposition on oxidized polypropylene

Ag_2S deposition on oxidized polypropylene was performed using procedures described previously for polyamide substrate [37]. Briefly, samples of the oxidized iPP were treated with aqueous $Na_2S_2O_3$ (0.2 mol/dm^3) and $AgNO_3$ (0.06 mol/dm^3) solution at 20 °C with pH 2.3 (by adding nitric acid). All reactions of iPP treatment were carried out in the glass reactor. iPP films were immersed for 40 min up to six times in the precursor solution. Samples were withdrawn at certain time intervals, rinsed with the distilled water, dried with filter paper, left over anhydrous $CaCl_2$ for 24 h and then used in analysis. Throughout the text, index added to the iPP-Ag_2S represent the number of immersions with iPP-Ag_2S-1, iPP-Ag_2S-2, iPP-Ag_2S-3, iPP-Ag_2S-4, iPP-Ag_2S-5 and iPP-Ag_2S-6 corresponding to 1, 2, 3, 4, 5 and 6 immersions, respectively.

XPS and AFM analysis

XPS surface elemental analysis of the iPP-Ag_2S composites was performed using a custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system [38]. The surface analysis chamber is equipped with aluminum K_α X-ray gun and 500 mm Rowland circle silicon single crystal monochromator. The X-ray gun was operated using a 15 mA emission current at an accelerating voltage of 15 kV. Low-energy electrons were used for charge compensation to neutralize the sample. High-resolution spectra were acquired in the region of interest using the following experimental parameters: 20–40 eV energy window; pass energy of 20 eV; step size of 0.1 eV, and dwell time of 1000 ms. One sweep was used to acquire a survey spectrum of all binding regions. The absolute energy scale was calibrated to the Cu $2p_{2/3}$ peak binding energy of 932.6 eV using an etched copper plate. All spectra were calibrated using the adventitious C 1s peak at 285.0 eV. A Shirley-type background was subtracted from each spectrum to account for inelastically scattered electrons that contribute to the broad background. CasaXPS software was used to process the XPS data [39]. Transmission corrected relative sensitivity factor (RSF) values from the Kratos library were used for elemental quantification. An error of ±0.2 eV is reported for all peak binding energies.

Atomic force microscopy height images were obtained using a Bruker Multimode 8 (NanoScope V controller) in tapping mode and Peakforce QNM mode. A Bruker TAP150 (MPP-12100) rectangular beam cantilever was used with a nominal spring constant of 5 N/m for the iPP-Ag_2S-1 and iPP-Ag_2S-3 samples (Peakforce QNM mode). A Bruker TAP525 (MPP-13100) rectangular beam cantilever was used with a nominal spring constant of 200 N/m for the iPP-Ag_2S-6 samples (tapping mode). Image analysis was performed using Bruker Nanoscope Analysis 1.40. For the particle analysis a threshold was used which allowed for particle recognition on the image. A bin size of 50 bins was chosen in each case.