Facile Single-step Technique for Simultaneous In Situ Fabrication of Ag/Ag_2S–Polymer Nanocomposites via PPS Cyclization Route

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We herein propose a facile single-step approach involving solid-state reaction between silver salt and engineering thermoplastic polyphenylene sulfide for simultaneous in situ generation of nanoscale metallic silver as well as semiconducting silver sulfide.

Inorganic–polymer nanocomposite systems have received immense attention in recent years owing to the amalgamation of their intrinsic inorganic and polymeric properties leading to unique and equally versatile nanoregime applications in the fields of optics, electronics, mechanics, photoconduction, etc.[1] Metal chalcogenide–polymer nanocomposites is one such family of widely studied[1] materials because of their distinctive properties. Amongst the assorted metal chalcogenides, semiconducting silver sulfide with direct band gap of 1 eV and relatively high absorption coefficient (about $10^4\,cm^{-1}$) is potentially superior candidate for various semiconductor opto-electronic devices.[2] It is also noted that nanoscale composites of metallic silver with polymer are being explored for wide range of applications relating to electronics, nonlinear optics,[3] and also as membranes for separation of organic materials like olefin and paraffin.[4] Curiously, in situ generation of nanoparticles of metallic silver along with semiconducting silver sulphide could be viewed as an interesting development towards realizing futuristic nanoscale electronic devices. However, there exist only occasional reports in the literature which deal with in situ simultaneous generation of Ag and Ag_2S nanoparticles.[5–7] In their most promising efforts, Tang et al.[5] reported in situ (separate and simultaneous) generation of Ag and Ag_2S nanoparticles from a single source precursor molecule by using a two-step instant thermal activation technique. We herein propose an extremely simple and single-step protocol involving solid-state reaction between silver salt (viz. silver acetate, $AgC_2H_3O_2$) and polymer, i.e., polyphenylene sulfide (PPS) for simultaneous in situ fabrication of silver/silver sulfide nanoparticles embedded in cyclized PPS matrix. For this solid-state reaction, we deliberately selected an engineering thermoplastic, PPS, which plays a twofold role of stabilizing polymer matrix as well as chalcogen precursor for the fabrication of Ag/Ag_2S–polymer nanocomposite. Besides, PPS with its excellent mechanical and chemical resistance properties (in addition to the polymer being inherently self-extinguishing[8]) can be extruded/processed in any desired shape/form, which could be an important aspect from the perspective of nanocomposite-based device fabrication. The most preliminary account of this novel and facile approach is furnished in this letter.

To explore the feasibility of the in situ generation of Ag_2S/Ag in polymer matrix via proposed solid-state route, we have performed the pilot reactions involving equimolar quantities of PPS & $AgC_2H_3O_2$. The reactions were typically carried out by admixing equimolar quantities of the two reactants in an agate pestle–mortar using doubly distilled acetone (for ensuring homogeneous admixing of the reactants). The resultant admixture, after drying at room temperature, was subjected to heating at 285 °C (melting temperature of PPS) in a quartz crucible for 6 and 48 h, respectively, in an ambient atmosphere. The product was allowed to cool to room temperature. The resultant samples were characterized by physicochemical techniques like X-ray diffraction (Rigaku Miniflex X-ray diffractometer with Cu Kα radiation), transmission electron microscopy (Jeol-2100X), scanning electron microscopy (Philips XL-30 equipped with EDAX facility). UV–vis spectra of the methanol-mediated dispersions of the samples were recorded using a JASCO, V-570, UV–vis–NIR spectrophotometer. Figure 1 shows X-ray diffractograms corresponding to equimolar admixtures of PPS and $AgC_2H_3O_2$ heated at 285 °C for 6 h (diffractrogram "a") and 48 h (diffractrogram "b"). These diffractograms disclose occurrence of predominantly metallic cubic silver (JCPDS # 30-0931) for both the samples (i.e., corresponding to reaction time of 6 and 48 h). Additionally, the sample corresponding to reaction time of 48 h also reveals formation of monoclinic acanthite Ag_2S (JCPDS # 14-0072) as a minor phase. Simultaneous formation of semiconducting Ag_2S along with metallic silver for the samples subjected to prolonged heating (48 h) is the most salient aspect of our work which can be linked with favorable reaction kinetics and partial thermal degradation of PPS. Such a situation presumably facilitates release of more sulfide species from heated PPS matrix in order to react with silver ions over a time scale which, in turn, leads to formation of Ag_2S in cyclized PPS matrix. It may be noted that the minor diffraction peak at $2\theta = 20°$ is the main diffraction peak of PPS. FWHM values of the strongest diffraction peaks associated with cubic Ag and monoclinic Ag_2S were used to calculate the primary particle size using

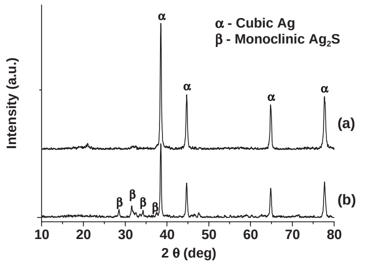

Figure 1. Typical X-ray diffractograms of heated admixtures of PPS with silver acetate corresponding to reaction time of (a) 6 h, (b) 48 h.

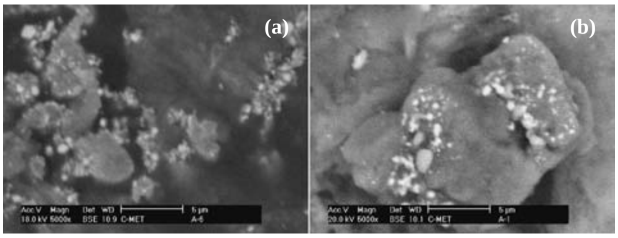

Figure 2. SEM (BSE mode) images of heated admixtures of PPS with silver acetate corresponding to reaction time of (a) 6 h, (b) 48 h.

Scherer equation. Such an exercise provided the particle size values in the range of 20–27 nm for cubic silver (depending upon the reaction time) and around 31 nm for monoclinic silver sulfide. Considering the high atomic weight of silver, SEM images were acquired in BSE mode (Figure 2) in order to ascertain the dispersion of silver nanoparticles in polymer matrix. The bright spots in SEM images suggest the presence of silver in polymer network.

We have further noticed relatively more uniform distribution of silver particles in PPS matrix for samples corresponding to reaction time of 6 h (Figure 2a) than that of sample corresponding to reaction time of 48 h which rather exhibits tendency of agglomeration of particles (Figure 2b).

Closer examination of the resultant nanoproducts has been accomplished by TEM-SAED. TEM image of sample corresponding to heating period of 6 h (Figure 3a) elucidates the formation of nanoparticles (dark spots in the image) having size in the range of 5–10 nm which are more or less uniformly dispersed in polymer matrix (grey background). The apparent variation in particle size by TEM and Scherer formula can be ascribed to inherent limitations of Scherer formula. Besides, an interesting nanocage like morphology is detected for this sample.

In case of sample corresponding to reaction time of 48 h, the TEM image (Figure 3b) clearly discloses the formation of mainly spherical nanoparticles, although irregular and hexagonal (faceted growth) nanoparticles could be located at few places. The particle size of the obtained nanoparticles is in the range of 25–50 nm. The presence of spots in SAED pattern implies single crystalline nature of nanoparticles formed as a result of 6 h reaction (inset of Figure 3a) while the presence of spots with rings signifies random positioning of single crystalline nanoparticles in polycrystalline pattern in case of samples heated for 48 h (inset of Figure 3b).

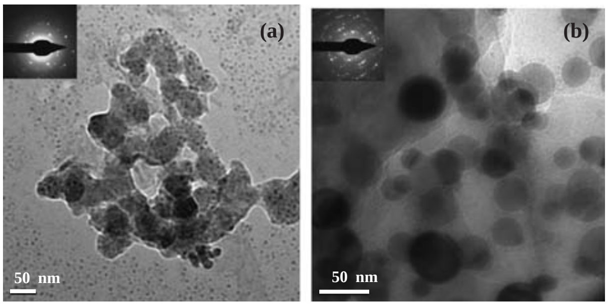

Figure 3. TEM images of heated admixtures of PPS with silver acetate corresponding to reaction time of (a) 6 h, (b) 48 h. Inset: SAED patterns.

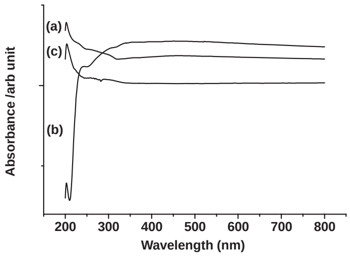

Figure 4. UV–vis spectra of heated admixtures of PPS with silver acetate corresponding to reaction time of (a) 6 h, and (b) 48 h. (c) represents only PPS heated at 285 °C.

UV–vis spectra (recorded in the range 200–800 nm) corresponding to heated PPS/admixtures of silver acetate with PPS are displayed in Figure 4. All the spectra appeared to be rather featureless in close resemblance with earlier reports.[9] The Surface plasmon resonance (SPR) peak around 425 nm ascribable to silver nanoparticles has not been observed. Perhaps, the near-bulk/bulk entrapment of Ag nanoparticles in polymer matrix might preclude such a phenomenon to occur. Nonetheless, we could observe relatively sharp absorption peak around 202 nm for the resultant nanocomposites (curves a and b in Figure 4). This peak can be attributed to heated/cyclized PPS in the resultant nanocomposites as the absorption peak of similar nature around 202 nm has also been observed for PPS heated at 285 °C for six hours (curve c in Figure 4).

In conclusion, we have exemplified a facile single-step solid-state approach for simultaneous fabrication of nanoparticles of metallic Ag and semiconducting Ag_2S in thermally stable state, mechanically sturdy and tractable polymer matrix which serves a dual role of chalcogen source as well as stabilizing agent.

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