Characteristics of zinc sulphide nanostructures grown on silica modified-polyaniline with polymerization time-dependent

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Abstract. Growth of zinc sulphide (ZnS) nanostructures on silica modified-polyaniline (SM-PAni) with polymerization time-dependent was prepared using chemical bath deposition (CBD) technique. The grown samples were characterized by scanning electron microscopy (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) and fourier transform infrared spectroscopy (FTIR). SEM images revealed that polyaniline rod-like nanostructures and ZnS nanospheres were successfully grown. The average diameter of the grown ZnS nanospheres did not significantly change by changing the growth time of the polyaniline. However, ZnS nanospheres grown with longer polymerization time of PAni is less dense and loosely bound as compared to shorter polymerization time of PAni. The less density of ZnS nanostructures with longer polymerization time of PAni may be due to the presence of PAni agglomerates that hinders the growth of ZnS nanospheres. Furthermore, FTIR spectra confirmed that the grown polyaniline is of emeraldine salt oxidation state which is the most conductive state of PAni.

1. Introduction
Polyaniline (PAni) is one of the most studied forms of conducting polymers [1-5]. PAni has three distinct oxidation states, namely; the leucoemeraldine, emeraldine base, and pernigraniline [6]. However, emeraldine salt oxidation state of PAni which is derived from the emeraldine base is the most investigated form due its conductivity, environmental stability, and simple fabrication method [7-8]. The synthesis of this polymer can produce a variety of “one-dimensional” morphologies, like rectangular structures [9], nanotubes [10], nanofibers [1, 11], micromats [11], or even nanodisks [11], which made them unique materials for specific device application. One way to tune and improve the morphology of PAni nanostructures is by the introduction of a suitable steric stabilizer [12]. Smoother and more uniform surface will be achieved due to the non-formation of PAni agglomerates upon the introduction of steric stabilizer [13]. It is also believed that aside from the influence of steric stabilizer, polymerization time of PAni may also affect the growth of the grown nanostructures [14].

Another promising material that has been widely studied in the field of optoelectronics application is zinc sulphide (ZnS) [15-17]. ZnS belongs to II-VI group compound semiconductors and has a wide energy band gap [18, 19]. Several studies present different techniques in its fabrication which leads to its different morphologies [19-21]. One noble way in preparing ZnS nanostructures is by chemical
bath deposition (CBD). In this method, nanostructures are deposited on substrate immersed in a solution containing metal ions source, hydroxides, and sulphide ions [22]. The morphology of the ZnS nanostructures is also affected by the chemical precursors used in CBD [23, 24].

In this work, we report on the growth of zinc sulphide nanostructures on the surface of the time-dependent silica modified-polyaniline films on glass substrate. Elucidation on the surface morphology, elemental composition, and the vibrational modes of the functional groups of the grown SM-PAni/ZnS nanostructures were thoroughly investigated.

2. Experimental details

2.1. Preparation of substrate
Rectangular glass substrates with a dimension of 26mm x 76mm x 1mm are cleaned with acetone, ethanol, and hydrochloric acid, and distilled water. This method is necessary to remove the impurities and unnecessary compounds present on the glass slides which may affect the growth of the nanostructures. The purpose of acetone in substrate cleaning is to remove oils and organic substances while ethanol and HCl were employed to remove the residue of acetone and oxides in the substrate respectively. The cleaned substrates were then air dried at room temperature.

2.2. Synthesis of silica modified-polyaniline and zinc sulphide
Silica modified-polyaniline (SM-PAni) nanostructures were produced on glass surfaces immersed in the reaction mixture during the oxidative polymerization of aniline. Liquid aniline was dissolved in hydrochloric acid to form 50mL aniline hydrochloride solution. Steric stabilizer in the form of silica (SiO₂) extracted from rice husk ash was introduced forming the silica-aniline hydrochloride (SiO₂ – AHCl) solution and oxidized with ammonium peroxydisulfate (APS) solution for the synthesis of SM-PAni. The progress of polymerization was monitored by the change in temperature of the solution recorded by a thermometer. Two SM-PAni nanostructures, with 16 minutes and 25 hours polymerization time were produced. These nanostructures grown on the glass substrates were washed with HCl to remove the residual monomer, oxidants and its decomposition products; and ethanol to remove low-molecular-weight organic intermediates and oligomers; and then air dried at room temperature.

The air dried samples were then subjected to chemical bath deposition (CBD) for the synthesis of zinc sulphide. ZnS nanostructures were deposited from the stirred aqueous solution containing zinc (II) chloride (ZnCl₂), urea ((NH₂)₂CO), and thiocetamide (CH₃CSNH₂). The total volume of the solution is increased to 200mL by the addition of distilled water. The pH of the solution was monitored by OAKTON Acorn pH meter and adjusted to the desired value which is 2.0 to 4.5 by dropwise addition of HCl. The solution was stirred using a magnetic stirrer and heated on the hot plate while monitoring its temperature with a maintained pH. The SM-PAni thin films were then dipped into the solution for 90 minutes. After the deposition time, samples were removed and washed with distilled water then air dried at room temperature.

2.3. Characterization of the nanostructures
The fabricated SM-PAni/ZnS nanostructures were characterized with JEOL Model JSM-6510LA scanning electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDS) for its surface morphology and elemental analysis respectively. Samples were scanned at a working distance of 12mm and accelerating voltage of 20kV to generate its SEM micrographs. Furthermore, Fourier Transform Infrared Spectroscopy (FTIR) with Perkin Elmer Spectrum 100 Spectrometer was also used for the determination of the vibrational modes and to find other functional groups present on the surface of the grown nanostructures. The spectrum has been recorded using the technique of Universal Attenuated Total Reflection (UATR) at 20 scans per sample in the region of 650 cm⁻¹ to 4000 cm⁻¹. Data were carbon dioxide corrected and were fitted using Gaussian fitting for the determination of the peaks.
3. Results and discussion

3.1. Morphology and elemental analysis of the grown nanostructures

Zinc sulphide nanostructures in the form of nanospheres are successfully grown on polymerization time-dependent silica modified-polyaniline as shown in Figure 1. Figure 1(a) shows the SEM micrograph of SM-PAni/ZnS nanostructures with 16 minutes polymerization time of SM-PAni. It is observed that the rod-like nanostructures polyaniline (white arrow) and ZnS nanospheres which are uniform in size were formed on the surface of the film. The diameters of the ZnS nanospheres are about 100nm and the PAni rod-like nanostructures are about 800nm. The length of the PAni rod-like nanostructures extends from 20μm to 30μm. On the other hand, Figure 1(b) shows the SEM image of the 25 hours polymerization time of SM-PAni/ZnS nanostructures. It is observed that more PAni agglomerates on the surface are present compared with the 16-minute polymerization time. The PAni rod-like (white arrow) nanostructures of the 25hrs polymerization time have larger diameter when compared with the 16 min polymerization time. Furthermore, the length of the PAni rod-like nanostructures present on the 25hrs polymerization time is longer when compared to 16min polymerization time. This result suggests that the formations of bigger and longer PAni rod-like structures might be due to the longer submersion of the substrate on the reaction mixture. Formation of the rod-like nanostructures might be attributed to the low acidity (pH > 4) of the reaction mixture at the start of the polymerization. Low-molecular weight aniline oligomers are produced during the first phase of oxidation. These aniline oligomers serve as a soft template for the growth of the PAni rod-like nanostructures [25, 26]. On the other hand, both samples shown in Figures 1(a) and 1(b) have agglomerates. These agglomerates are believed to be PAni precipitates which are produced during bulk polymerization [27, 28]. It can be observed that 25-hour polymerization time of SM-PAni/ZnS has more PAni agglomerates. These may be due to the neutral aniline molecules that continually oxidize after the exothermic reaction during oxidative polymerization. The oxidized neutral aniline molecules lead to the formation of short aniline oligomers at the trimer level which serve as soft templates for the formation of PAni agglomerates [29].

Figure 1. SEM micrograph images of the grown ZnS nanostructure on SM-PAni with different polymerization time (a) 16 minutes and (b) 25 hours.

ZnS nanospheres are present on the film and on the top of PAni precipitates as observed from the SEM images. These nanospheres have the same average diameter for both samples. However, ZnS nanospheres on 16min polymerization time SM-PAni is denser and more compact compared with the 25hrs SM-PAni. This result can be attributed to the agglomeration of PAni nanostructures that may hinder the attachment of ZnS nanospheres onto the SM-PAni film. Wei et al. [30] proposed that...
formation of ZnS nanostructures during CBD is dominated by cluster-by-cluster process instead of ion-by-ion process. In cluster-by-cluster process, ZnS nanoparticles preformed in the solution and then adsorbed onto the surface. Grown ZnS nanostructures by this process possess poor adherence on the film. For the two samples, 16 min polymerization time SM-PAni has minimal agglomeration and more uniform compared with the 25 hours polymerization time.

The morphology of SM-PAni and ZnS nanostructures grown on glass substrate are shown in Figures 2 (a) and 2 (b) respectively. SEM micrograph of SM-PAni reveals the formation of PAni rod-like nanostructures (block arrow) and PAni agglomerates (line arrow). It is also observed that PAni agglomerates also grow on top of the PAni rod-like nanostructures. Furthermore, Figure 2 (b) shows that the grown ZnS nanostructures are nanospheres. The morphology of ZnS nanospheres grown on glass substrate agrees with the nanospheres structure from Figures 1(a) and 1(b).

![Figure 2. SEM micrograph images of the grown SM-PAni and zinc sulphide nanostructures on glass substrate.](image)

The elements present on the samples that correspond to Figures 1(a) and 1(b) are shown in Table 1 including the bare glass substrate. The presence of other elements such as oxygen (O), Sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), and calcium (Ca) is attributed to the components of the glass substrate being used. One way to determine the quality of the grown ZnS nanostructures for both samples is to calculate the ratio between the zinc atoms and sulfur atoms (i.e. [Zn]/[S]) from the results of EDS. The ideal ratio for zinc versus sulfur atoms is 1. Film sample with 16min polymerization time of SM-PAni/ZnS obtains a ratio of 0.97 compared with 25hrs polymerization time of SM-PAni/ZnS which obtains 0.91 for zinc atoms versus sulfur atoms. From this result, it is believed that more ZnS nanostructures have grown for 16min polymerization time of SM-PAni compared with the other sample as supported also by the SEM images shown in Figure 1(a) and 1(b). Excess atoms of sulfur can be attributed to the presence of sulfuric acid as the by-product during oxidative polymerization of polyaniline. Large percentage of carbon (C) atoms is detected on the sample which attributes to the quinone and benzene ring forming the polymer chains [31]. Nitrogen (N) atoms are also present in the samples which constitute the imine and amine nitrogen groups in the polymer chains [26]. Traces of Chlorine (Cl) are detected for both samples. The presence chlorine elements can be traced from the HCl that was being used in oxidative polymerization of SM-PAni.

| Table 1. Elemental analysis of ZnS nanospheres grown on polymerization time dependent SM-PAni. |  |  |
Table 2 shows the elemental analysis corresponding to Figure 2 (a) and 2 (b). Traces of chlorine and sulphur atoms are detected for SM-PAni sample which are by-products during oxidative polymerization. Furthermore, elemental analysis for ZnS nanostructures shows that the ratio of zinc atoms to sulfur atoms is 0.96 which is very close to the theoretical value. Chlorine atoms are not detected in the spectrum which is probably removed during the rinsing of distilled water.

Table 2 Elemental analysis of the grown SM-PAni and zinc sulphide nanostructures corresponding to the SEM images in Figure 2.

3.2. FTIR spectra of the grown nanostructures

FTIR spectra of SM-PAni, as-grown ZnS, and ZnS nanostructures on polymerization dependent SM-PAni are shown on Figure 3. Since the FTIR spectrum has been taken in the specified range, the presence of the chemical constituents of zinc sulphide cannot be determined because the metal sulphides bond occurs within 200 cm⁻¹ to 400 cm⁻¹[32].

Absorption peaks of all the functional groups of polyaniline are present for both samples. The peak at around 1651 cm⁻¹ corresponds to the O-H bending vibration which indicates the presence of water moisture in the sample [32]. This peak is not observed for SM-PAni on glass substrate (Figure 3 (c)) which confirms that water moisture are produced during the CBD of ZnS nanospheres since the reaction between hydronium ions and hydroxides are favorable in the acidic reaction bath. The main peaks at around 1585 cm⁻¹ and 1497 cm⁻¹ corresponds to quinine and benzene stretching ring-deformation of polyaniline [33]. Strong absorption band at around 1306 cm⁻¹ is attributed to the C–N stretching of secondary aromatic amine strengthened during the protonation of SM-PAni [34]. The signature peak at around 1245 cm⁻¹ confirms that the PAni films being produced are of the emeraldine salt oxidation state. This peak is interpreted as C–N+• stretching vibration in the polaron structure [33, 34]. Absorption band at around 1380 cm⁻¹ is due to Zn-O (HCO₂) which indicates the possible formation of ZnO during CBD [32]. Another absorption peak is observed at around 1144 cm⁻¹ which is assigned to the vibration mode of –NH⁺= structure produced during protonation [35]. Strong absorption band at around 896 cm⁻¹ is assigned Si-H bending from the glass substrate used [36].

4. Conclusion

ZnS nanospheres were successfully grown on polymerization time-dependent polyaniline. SEM images show that the ZnS nanospheres are denser and more compact for 16 minutes polymerization time of SM-PAni compared to 25 hours polymerization time. Tailoring the size of PAni nanostructures and density of ZnS nanostructure can be done by changing the polymerization time. These results proved that polymerization time of SM-PAni nanostructures would influence the growth of ZnS nanostructures. The absorption peak at around 1245 cm⁻¹ from FTIR spectra confirmed that the grown polyaniline nanostructures in the glass substrate are of the emeraldine salt oxidation state.
Figure 3. FTIR Spectra of the grown nanostructures on glass substrate: (a) bare glass (b) SM-PAni (c) 16min SM-PAni/ZnS (d) 25 hours SM-PAni/ZnS and (e) ZnS.

5. References
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