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Modification of Polyaniline/Polystyrene and Polyaniline/Metal Oxide Structure by Surfactant

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A B S T R A C T

Polyaniline/polystyrene (PAni/PS) composites were prepared in aqueous solution by polymerization of styrene and aniline in two-stages. Firstly, styrene polymerize using Ammonium persulfate (APS) as an oxidant in the presence of various surfactants such as poly(vinyl pyrrolidone) (PVP), hydroxypropylcellulose (HPC), poly(vinyl alcohol) (PVA) and surfactive dopant sodium dodecylbenzenesulfonate (DBSNa). In next stage, aniline polymerize using potassium iodate (KIO_3) as an oxidant in the presence of PS latex. In addition, nanocomposites of polyaniline containing nanometer-size CuO (Copper oxide) and Ag_2O (Silver oxide) were synthesized by a chemical method using DBSNa as a surfactant. Products were characterized in terms of particle size, conversion of monomer to polymer, morphology, chemical structure and glass transition temperature that were dependent on the type of surfactant and metal oxide. The chemical structure, morphology and glass transition temperature of product were studied by fourier transform infrared (FTIR) spectroscopy, X_ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetery (DSC).The results show that the type and concentration of surfactant, type of metal oxide and concentration of oxidant play a major role on the surface morphology and particle size of products. The size range of the PAni/PS and PAni/metal oxide composites was about 80–240 nm and 70-140 nm, respectively.

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1. INTRODUCTION

polymers such as polyacetylene, polyaniline, polypyrrole, and polythiophene, have attracted so much research interest in wide range applications such as rechargeable batteries [1], electromagnetic interference (EMI) shielding [2], antistatic coatings [3], gas sensors [4], optical devices [5] and removal of heavy metals [6-8], and so forth. The process of doping of conductive polymers is the addition of a substance or impurity, which drastically change electrical, optical and magnetic properties. PAni is doped by protonation reaction, in which the number of electrons remains unchanged. In this process the emeraldine base reacts with protons from the acid becoming a conductor, whose conductivity can be increased up to 10 orders of magnitude. However, the doping process is reversible, as the polymer returns to its initial state without undergoing great changes in its structure. The

protonation occurs preferentially at imine nitrogen with the formation of semiquinone segments (radical cation) through an internal redox reaction [9]. The insolubility in common solvents and infusibility of conducting polymers, in general, make them poorly processable, either by a solution technique or by melt processing methods [10, 11]. Improvement of these material properties can be achieved by forming copolymers, composites, or blends with commercially available polymers or with inorganic materials which offer better mechanical and optical properties, stability, and processability [12–17]. Composite of PAni with various materials have been reported. For instance, Vaezi et al. [18], synthesized $PAni/CoFe_2O_4$ nanocomposite. Magnetic measurement shows that resulting nanocomposite exhibit ferromagnetic behavior. The metal nanoparticles, such as silver and gold, have attracted much attention in recent years due to their interesting properties and potential applications in technological fields [19]. Silver particles have applications in catalysis, conductive inks, thick film

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pastes and adhesives for various electronic components, in photonics and in photography [20–23].

As one of the important metal oxides, copper oxide (CuO) is frequently used as anode materials for LIBs owing to its high capacity, environmental benignity, safety and low-cost [24–26]. Therefore, the preparation of composite of polyaniline and metal oxide becomes a novel challenge for people.

Conducting polyaniline (emeraldine base salt) has been commonly mixed with thermoplastic polymers to overcome processability limitations of polyaniline (PAni) derived of its infusibility and poor solubility in common solvents. PAni/thermoplastic composites are quite popular because depending on the thermoplastic matrix conducting composites with different attributes can be obtained [27–31]. Colloidal PAni/thermoplastic core–shell composites are a particular form to produce conducting composites. This kind of arrangement allows controlling composite morphology and composition [32].

Polystyrene (PS) is an insulating polymer, transparent, rigid and fragile, which can be easily prepared through four main routes: anionic, cationic, coordination or via free radical reaction. However, the most used technique is the free radical polymerization [33]. The styrene monomer discovered in 1786 by Newman and the polystyrene was later discovered by Simon. With the knowledge of the formation process and its applications greater commercial importance was given for polystyrene, being commercially available in 1938, produced by Dow Chemical Company [34]. Due to the poor mechanical and thermal properties of PAni, the casting films obtained are fragile and delicate with limited resistance to external action. In the last three decades, polymer blends of PAni with conventional materials such as PS, Polystyrene sulfonate (PSS), poly(vinyl alcohol) (PVA) and others have been developed in order to correlate the spectroscopic properties of PAni with the excellent thermo-mechanical properties of plastics [35–37].

Nanostructured films of the conducting polymer polyaniline were prepared by its potentiostatic polymerization in the presence of thin polystyrene (PS) nanoparticle templates [38].

The preparation and characterization of PAni/Fe$_3$O$_4$ and PAni/Fe$_2$O$_3$ nanocomposite using hydroxypropylcellulose as a steric stabilizer were reported [39]. Core–shell polyaniline–polystyrene Sulfonate/Fe$_3$O$_4$ nanoparticles with both conductive and magnetic properties was also demonstrated [40]. Suspension polymerization of aniline in the presence of dodecylbenzenesulfonic acid (DBSA) with and without styrene–butadiene–styrene (SBS) was carried out. The result indicates that DBSA acts simultaneously as a surfactant (emulsifier) and as a dopant [41, 42]. In addition, surfactant affects on the morphology (degree of crystalline order and orientation) [42].

In this study, Polyaniline/polystyrene (PAni/PS) composite was prepared in the aqueous solution by polymerization of styrene and aniline using potassium iodate (KIO$_3$) and ammonium peroxy disulfate ((NH$_4$)$_2$S$_2$O$_8$) as oxidants in the presence of various surfactants. In addition, Polyaniline/Ag$_2$O and Polyaniline/CuO nanocomposites were prepared in aqueous media using DBSNa as surfactant.

2. EXPERIMENTAL

2. 1. Instrumentation   A magnetic stirrer (model MK20, Iran), digital balance (Helmer model FR 200, Germany), scanning electron microscope (SEM) (Philips model XL30, Netherland), fourier transform infrared (FT-IR) spectrometer (Shimadzu model 4100, Japan), X-ray diffraction (XRD) (Philips model PW3040/60, Netherland), differential scanning calorimeter (DSC) (model PL-DSC, England) and centrifuge (Hermle Labrotechnik model Z36HK, Germany) have been used in these experiments.

2. 2. Reagents and Standard Solutions   Materials used in this work were aniline (extra pure > 99%, d =1.02 g/cm^3), styrene (d = 0.906 g/cm^3), potassium iodate (Merck,Germany), ammonium peroxy disulfate (Merck,Germany), sulfuric acid (Pars chemie, Iran), sodium dodecylbenzensulfonate (DBSNa) (Loba chemie, India), hydroxypropylcellulose (HPC, Mw = 10^6) (Aldrich, England), poly (vinyl pyrrolidone) (PVP, M$_W$ = 25000, Merck, Germany), poly(vinyl alcohol) (PVA, M$_w$= 72000, Merck, Germany), nanometer size silver oxide (Aldrich, England) and nanometer size copper oxide (Merck,Germany).

All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

2.3. Preparation of Polystyrene Latex   Polymerization of polysterene was carried out in an aqueous media at 75 °C for 4 hours under stirring rate of 500 rpm. For the preparation of polystyrene 0.6-2.5 g of ammonium peroxy disulfate was added to 100 mL water containing 0.2-1.0 g surfactant. Then, 6 mL styrene monomer was added to solution. The obtained PS latex was highly stable and precipitation was not observed even after centrifugation at 1500 rpm for 30 min.

2.4. Preparation of Polyaniline/Polystyrene Composite   A 100 mL sulfuric acid 1.0 M containing 1 g potassium iodate added to polystyrene latex solution at room temperature. Then, 1 mL aniline monomer was injected to the solution. Polymerization

was carried out at room temperature for 5 hours under stirring rate of 500 rpm.

2.5. Preparation of Polyaniline/CuO and Polyaniline/Ag₂O Nanocomposite

1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid 1.0 M containing 2.5 g of ammonium peroxy disulfate. After 2 hours, 0.2 g of metal oxide was added to stirred aqueous solution. The reaction was carried out in aqueous media at room temperature. After 3 hours, the polymer was filtered.

2.6. Preparation of Polyaniline/CuO and Polyaniline/Ag₂O Nanocomposite using DBSNa

0.2 g of metal oxide was added to stirred aqueous solution (100 mL) of sulfuric acid 1.0 M containing 0.4 g of surfactant (DBSNa). After 1 hours, 2.5 g of ammonium peroxy disulfate was added to stirred aqueous solution. The reaction was carried out in aqueous media at room temperature for 3 hours. After 3 hours, the polymer was filtered.

In all experiments, in order to remove the unreacted monomers and oxidants, the final product was washed properly with deionized water followed by centrifugating at 1500 rpm for 30 min. This washing process was repeated three times. Finally, the product dried in 40°C for 24 hours.

3. RESULTS AND DISCUSSION

3. 1. Surface Morphology   The morphology of composite was studied using scanning electron microscopy (SEM). SEM images of pure polyaniline and PAni/PS composites synthesized without surfactant are shown in Figures 1 and 2. As shown in Figures 1 and 2, the bulk polymer and composite tends to aggregate in large particles in the form of large globules. This is probably due to an increased inter-chain interaction as compared to stabilized particles in which the polymeric surfactant chains act as a limiting factor for such an interaction. The particles have a wide polydispersity, presumably due to increased rate of polymerization. As shown in Figures 3a, b, c and d, by addition of surfactant into the reaction media, particle size decreased and homogeneity increased, because surfactant influence the physical and chemical properties of the solution, by chemically adsorption to the polymer, and prevented from Preventing undesirable grass particles. As shown in the figures, the composite obtained using various surfactants (PVP, DBSNa, HPC and PVA) exhibits spherical particles. For instance, as shown in Figure 3a, the composite obtained using PVP is composed of small spherical particles, because the surfactant was prevented from gross aggregation of the particles. Moreover, by

comparison between Figures 3a, b, c and d, the size and homogeneity of the particles were dependent on the type of surfactant because the surfactant are known to influence the size and hemogeneity of particles. Furthermore, as can be seen in Figures 3a and 4a, particle size decreased and homogeneity increased by increasing the concentration of surfactant, because surfactant affects the viscosity of solution and also the rate of polymerization. The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology, and homogeneity of particles [43–47]. As can be seen, particle size and conversion of monomer to polymer are dependent on the type of surfactant, because the surfactants are adsorbed physically or bonded chemically (graft copolymer) to growing polymer [48]. As shown in Figures 4a, b and Table 1, by increasing the concentration of PVP as surfactant from 6 g/L to 10 g/L, significant changes didn't observe in particle size. So, the optimum concentration of surfactant is 6 g/L.

It was found that in the preparation of PAni/PS composite, concentration of oxidant $((NH_4)_2S_2O_8)$ affect on the particle size and conversion of monomer to polymer (see Figures 5a, b and 6). The particle size decreased and conversion of monomer to polymer increased by increasing the amount of oxidant. It is probably due to the rate of polymerization increased by increasing concentration of oxidant. However, by increasing the amount of oxidant, weak spherical particles were obtained. The effect of type and concentration of surfactant and oxidant on the particle size and conversion of PAni/PS composite are listed in Table 1. Furthermore, SEM images of Polyaniline/metal oxide (with and without surfactant) are shown in Figures 7 and 8. As can be seen, the type of additive has a considerable effect on the size and homogeneity of particles. As shown in Figures 7a and 8a (compare with Figure 1), By adding metal oxide, particle size decreases. It can be also deduced that (Figures 7b and 8b), the composites obtained using Ag₂O and CuO as additives in the presence of DBSNa as a surfactant are composed of homogenate particles. Particle size of products is shown in Table 2.
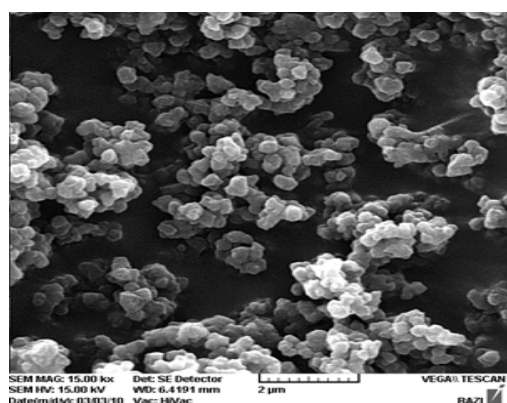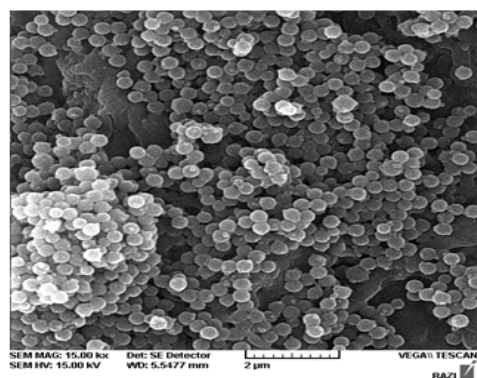

Figure 1. Scanning electron micrograph of PAni Prepared in aqueous media

TABLE 1. Preparation conditions and effect of type of surfactant on particle size and yield of monomer to polymer

Type of surfactant	Type and concentration of oxidant (g/L)	Conversion of monomer to polymer (% w/w)	Concentration of surfactant (g/L)	Average particle size (nm)
Surfactant free	----	78	--	240
PVP	KIO_3=10 , $(NH_4)_2S_2O_8$=6	72	2.0	180
PVP	KIO_3=10, $(NH_4)_2S_2O_8$=6	78	6.0	150
PVP	KIO_3=10, $(NH_4)_2S_2O_8$=6	84	1.0	142
PVP	KIO_3=10,$(NH_4)_2S_2O_8$=15	82	2.0	107
PVP	KIO_3=10, $(NH_4)_2S_2O_8$=25	88	2.0	80
HPC	KIO_3=10, $(NH_4)_2S_2O_8$=6	71	2.0	130
HPC	KIO_3=10, $(NH_4)_2S_2O_8$=25	82	2.0	90
DBSNa	KIO_3=10, $(NH_4)_2S_2O_8$=6	75	2.0	140
PVA	KIO_3=10, $(NH_4)_2S_2O_8$=6	70	2.0	130

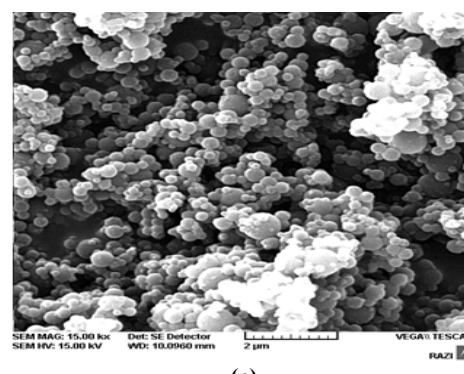**TABLE 2.** Effect of surfactant and metal oxide on the polyaniline nanocomposite size.

Type of Composite	Concentration of Metal Oxide (g/L)	Average Particle Size (nm)
Pure polyaniline	----	140
PAni+CuO	2	101
PAni+CuO+DBSNa	2	82
PAni+Ag_2O	2	92
PAni+Ag_2O+DBSNa	2	70

(b)

(c)

(d)

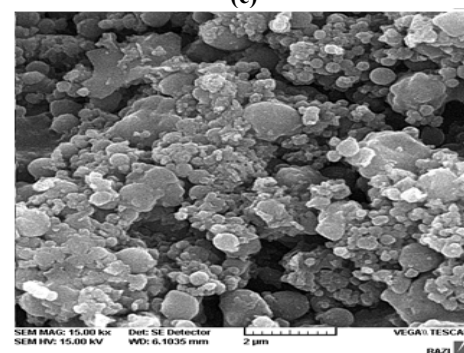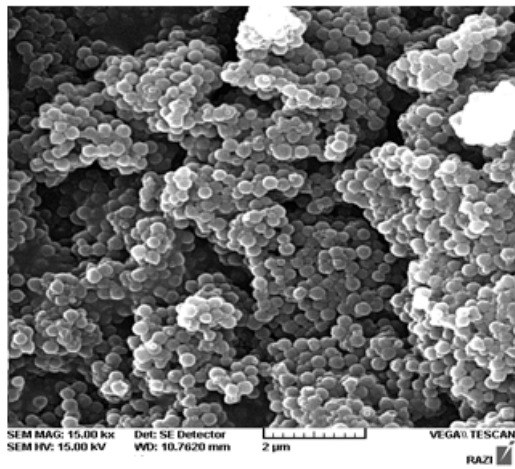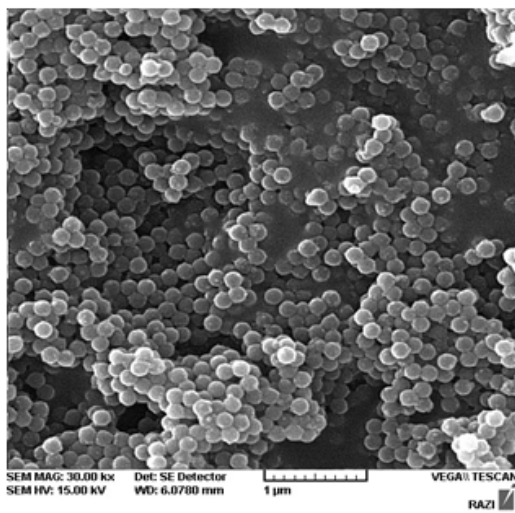**Figure 2.** Scanning electron micrograph of PAni/PS Prepared in aqueous media

(a)
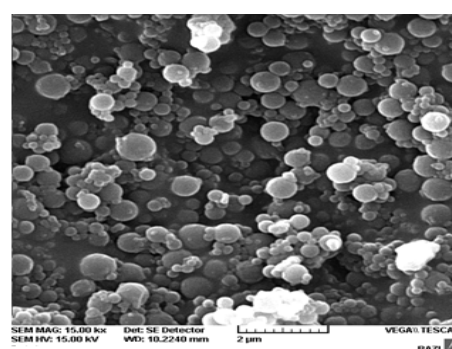
Figure 3. Scanning electron micrograph of PAni/PS Prepared with (a) PVP (b) PVA (c) DBSNa (d) HPC as surfactant in aqueous media, Reaction conditions: ($(NH_4)_2S_2O_8$ = 6 g/L, KIO_3=10 g/L, surfactant = 2 g/L).

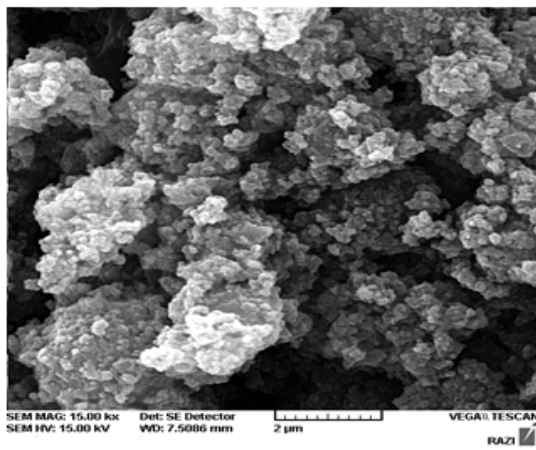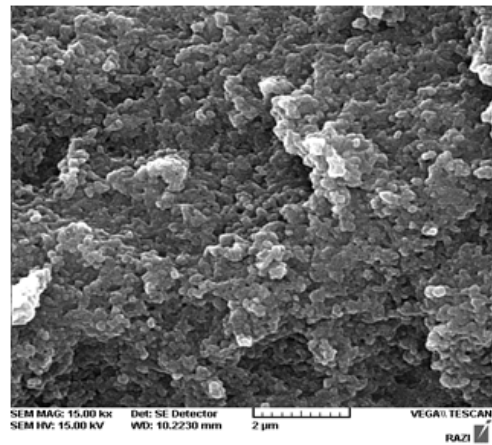(a)

(b)

Figure 4. Scanning electron micrograph of PAni/PS Prepared with (a) PVP=6 g/L (b) PVP=10 g/L in aqueous media, Reaction conditions: $((NH_4)_2S_2O_8 = 6$ g/L, $KIO_3=10$ g/L)
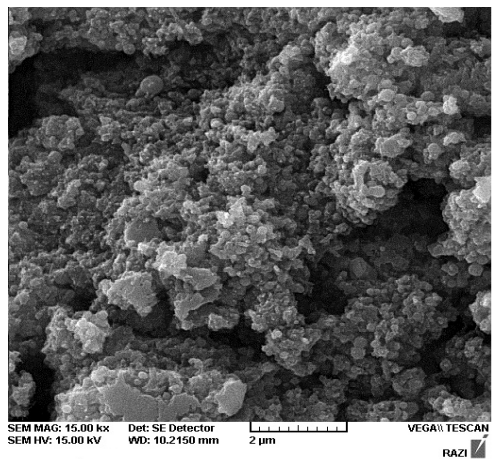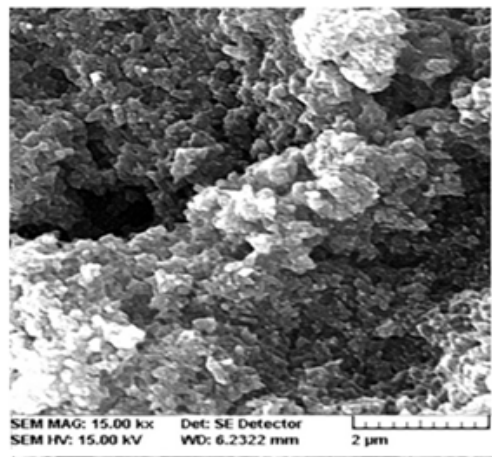

(b)
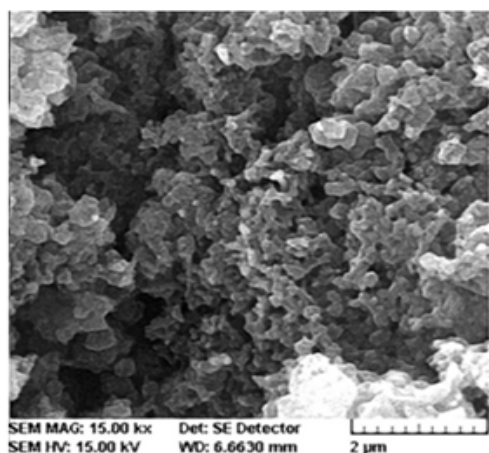
Figure 5. Scanning electron micrograph of PAni/PS Prepared with (a) PVP (b) HPC as surfactant in aqueous media, Reaction conditions: $((NH_4)_2S_2O_8 = 25$ g/L, $KIO_3=10$ g/L, surfactant = 2 g/L)

Figure 6. Scanning electron micrograph of PAni/PS Prepared with PVP in aqueous media, Reaction conditions: $((NH_4)_2S_2O_8 = 15$ g/L, $KIO_3=10$ g/L, PVP = 2 g/L).
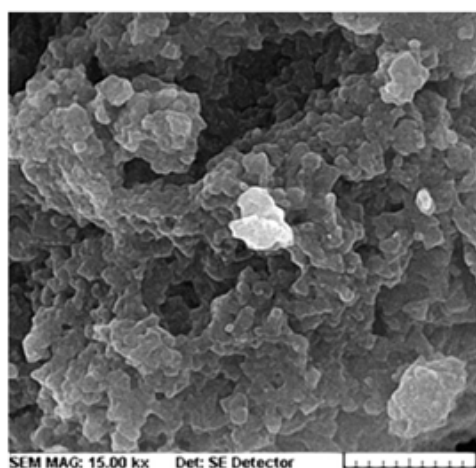

(a)

(a)

(b)

Figure 7. Scanning electron micrograph of PAni/Ag$_2$O nanocomposie Prepared in aqueous media (a) without surfactant (b) with DBSNa as surfactant.

(a)
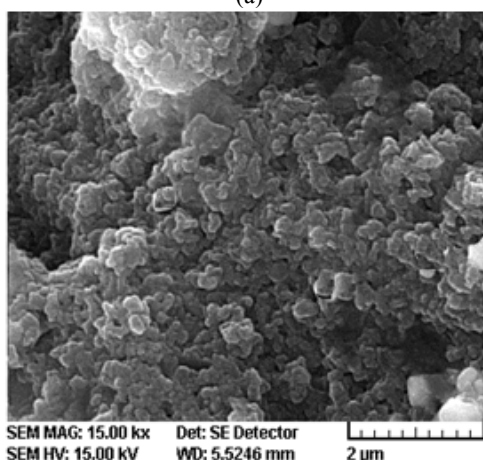

(b)

Figure 8. Scanning electron micrograph of PAni/CuO nanocomposie Prepared in aqueous media (a) without surfactant (b) with DBSNa as surfactant.

3. 2. Structural characterization The chemical structure of obtained product was determined by FTIR spectrum. The FTIR spectroscopy has provided valuable information regarding the formation of polyaniline/polystyrene composite. FTIR analysis has been done to identify the characteristic functional groups of product.

FTIR spectrum of pure surfactant was shown in Figure 9 and   FTIR spectra in the 4000-400 cm^{-1} region, for PAni/PS composites were shown in Figure 10. For example, as can be seen in Figure 10a, the characteristic peaks of the PAni/PS composite were shown at 1601 cm^{-1} (C=C stretching vibration of the quinoid ring), 1493 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1305 cm^{-1} (C-N stretching vibration), 1178 cm^{-1} (C-H in-plane deformation), 850 cm^{-1} (C-H out-of-plane deformation) selected to polyaniline. In addition, characteristic absorbtion bands at 3435 cm^{-1} (aromatic C-H stretching) and 2923 cm^{-1} (methylene C-H stretching) are asigned to polystyrene.

Figure 11 also shows the FTIR spectra of pure polyaniline, polyaniline/silver oxide, polyaniline/copper oxide, polyaniline/silver oxide with DBSNa and polyaniline/copper oxide with DBSNa. FTIR spectra in the 4000-450 cm^{-1} region, for PAni is shown in Figure 11a. PAni polymer shows the presence of characteristic absorption bands at 1562 cm^{-1} (C=C stretching vibration of the quinoid ring), 1475 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1302 cm^{-1} (C-N stretching vibration), 1137 cm^{-1} (C-H in-plane deformation) and 804 cm^{-1} (C-H out-of-plane deformation).
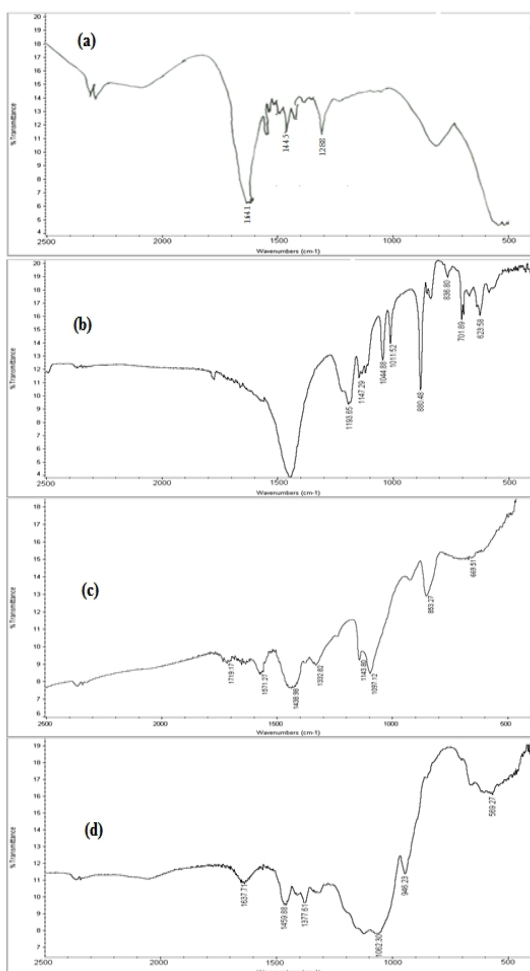
3. 3. Differential Scanning Calorimetry   The thermal properties of the chemically prepared pure polyaniline, pure polystyrene and PAni/PS composites have been studied using differential scanning calorimetry (DSC). Figures 12-15 show the DSC heating curves of polystyrene, polyaniline and PAni/PS composites at a heating rate of 10°C/min under nitrogen atmosphere.

There appeared to be three endotherms in the region. The first endotherm in Figures 13-15 is most likely attributed to the removal of water /moisture that is around 3.5°C in Figure 13a and the other around 84.22°C in Figure 15b, which also contributes to the endotherm in this temperature region in the DSC measurement. In Figure 13a, both first peak and second peak attributed removal of water/moisture and third peak is glass transition temperatures (Tg) of PAni. The glass transition temperatures (Tg) of pure PAni is 209°C.
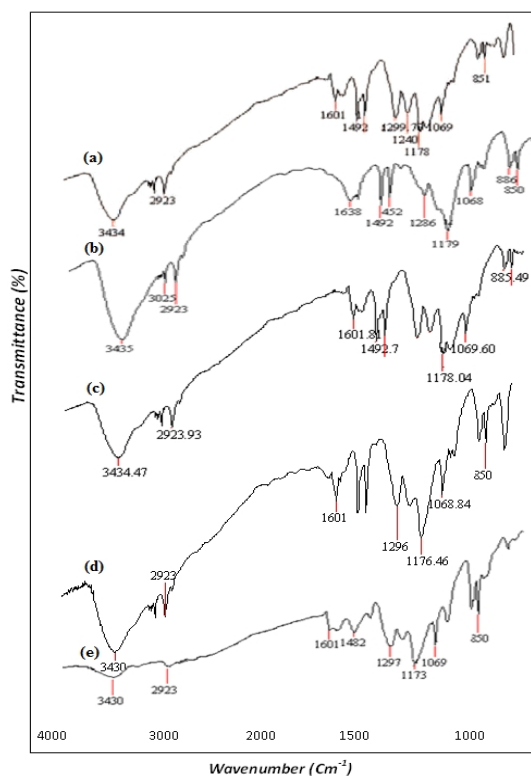
From the DSC result, the glass transition temperatures (Tg) of PS is 67.8°C in Figure 12, also cannot be assigned to the pure PS melting point, bacause PS is amorphous.

The second endotherms observed in thermograms (Figures 13b, 14a, 14b, 15a and 15b) are attributed to the glass transition temperature of PAni/PS composites (175.35°C , 187.26 °C, 193.74°C, 219.2°C, 210.15°C, respectively). These figures show that PAni/PS composites with surfactant are more stable than pure PAni/PS composite. The glass transition temperature are dependent on the surfactants (PVP, PVA, DBSNa and HPC), which were used in the preparation of composites. As shown in the thermograms (Figures 14 and 15), the presence of surfactant can be shifted the glass transition temperature to upper temperatures in the PAni/PS composites.

As shown in Figures 13b, 14a, 14b, 15a and 15b, the third endotherms (277.17°C, 265.84°C, 257.59°C, 230.79°C, 259.23°C, respectively) are melting point of PAni/PS composites and dependent on the surfactant. The melting point of PAni/PS composites decreases with adding surfactant.

Figure 10. FTIR spectra of PAni/PS composite (a) without surfactant (b) with PVP (c) DBSNa (d) PVA and (e) HPC used as surfactant in aqueous media.

Figure 9. FTIR spectra of (a) pure PVP (b) pure DBSNa (c) pure PVA and (d) pure HPC
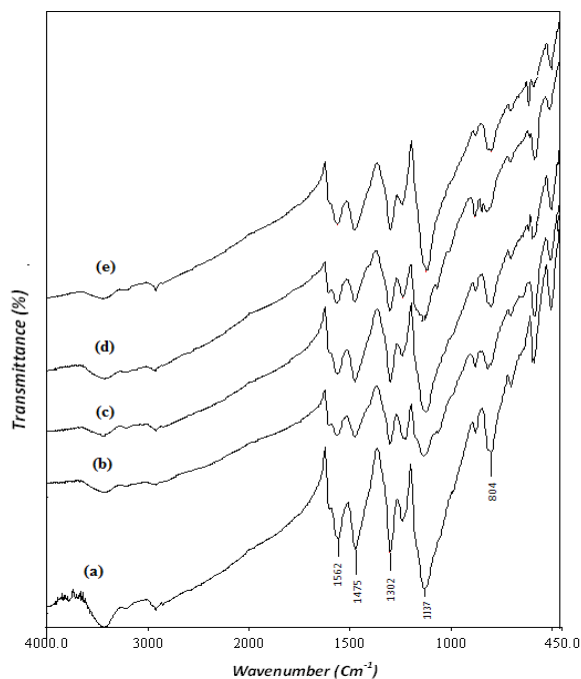
Figure 11. FTIR spectra of (a) purePAni (b) PAni/Ag$_2$O nanocomposite (c) PAni/Ag$_2$O nanocomposite with DBSNa(d) PAni/CuO nanocomposite (e) PAni/CuO nanocomposite with DBSNa.

Figure 12. DSC thermograms of PS

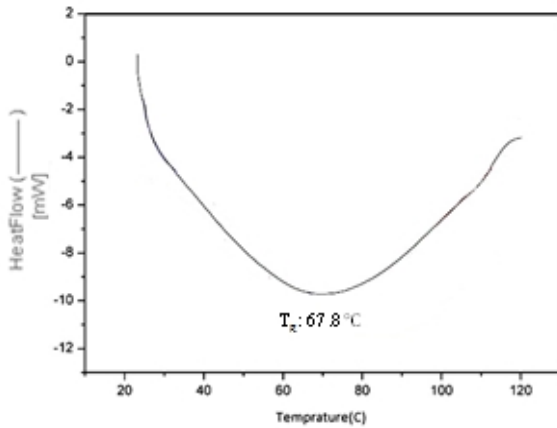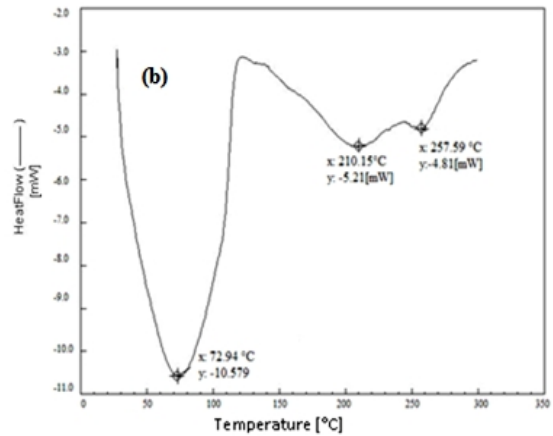**Figure 14.** DSC thermograms of PAni/PS composite (a) PVP, and (b) PVA, used as surfactant.
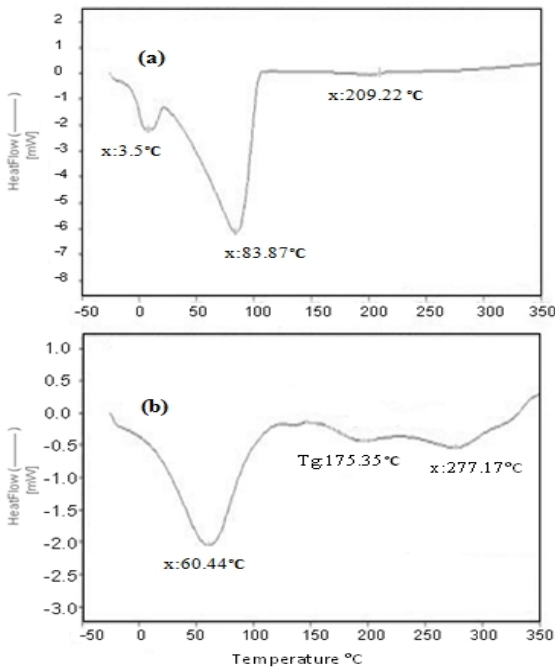
Figure 13. DSC thermograms of (a) pure PAni and (b) PAni/PS composite.
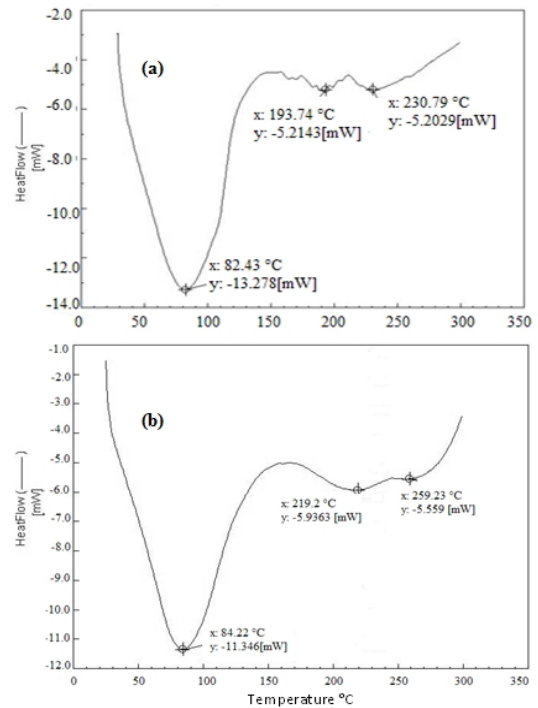
Figure 15. DSC thermograms of PAni/PS composite (a) DBSNa, and (b) HPC, used as surfactant.
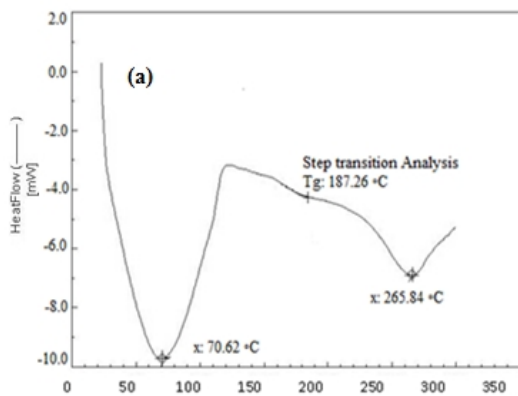
3. 4. X-ray Diffraction Polyaniline is inherently amorphous and hence there are no sharp peaks for polyaniline. The crystalline nature of nanocomposites is determined from XRD analysis. The XRD patterns of CuO nanoparticle, pure polyaniline and PAni/CuO nanocomposite are shown in Figures 16a, b and c, respectively. The main peaks of CuO nanoparticles are at $2\theta = 24.8, 31.75, 37.6, 56.65, 68.8$. In addition, The main peaks in the XRD pattern of pure PAni are observed at $2\theta = 19.8$ and 25.2. The characteristic peaks ascertained from the XRD pattern of PAni/CuO nanocomposite are at $2\theta = 25.2, 31.75, 37.6, 56.6$ and

68.8. These peaks in the XRD pattern of nanocomposites verify the presence of copper nanoparticles in the polyaniline matrix.

Furthermore, the XRD patterns of pure polyaniline, Ag_2O nanoparticle and PAni/Ag_2O nanocomposite are shown in Figures 17a, b and c, respectively. The main peaks of Ag_2O nanoparticles are at 2θ =18.65, 20.6, 32.9, 38.15, 55, 65.55. The characteristic peaks ascertained from the XRD pattern of PAni/Ag_2O nanocomposite are at 2θ = 19.5, 25.2, 33, 38.2, 55 and 65.5. These peaks in the XRD pattern of nanocomposites verify the presence of silver nanoparticles in the polyaniline matrix.
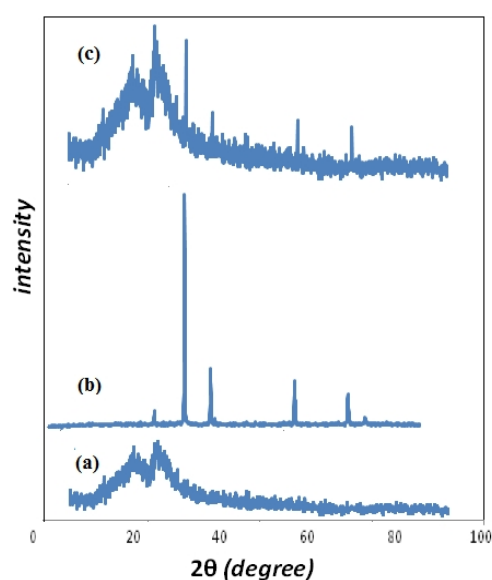
Figure 16. XRD pattern of (a) PAni, (b) CuO and (c) PAni/CuO nanocomposite

Figure 17. XRD pattern of (a) PAni, (b) Ag_2O and (c) PAni/Ag_2O nanocomposite.

The average crystallite size was estimated using the Scherrer's Equation (1) [49]:

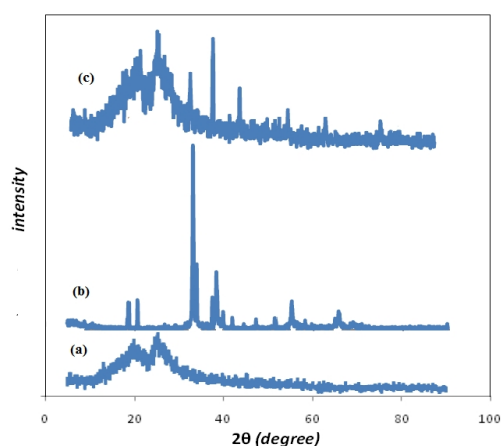$$\beta = k\lambda / D\cos\theta \qquad (1)$$

where, λ is the X-ray wavelength, k, the shape factor, D, the average diameter of the crystals in angstroms, θ, the Bragg angle in degree, and β is the line broadening measured by half-height in radian. The value of k depends on several factors, including the miller index of the reflection plane and the shape of crystal. If the shape is unknown, k is often considered to be 0.89.

The crystallite size of copper and silver in the nanocomposite, calculated by Equation (1), is about 40 and 15 nm, respectively. When the reflecting peak at $2\theta = 31.75$ (for PAni/CuO) and $2\theta = 33$ (for PAni/Ag_2O) is chosen for calculating the average diameter, the average size of the PAni/CuO and PAni/Ag_2O particles is achieved 101 and 82 nm respectively, which is consistent with the result of the SEM.

4. CONCLUSIONS

In this work, the characteristics of the polyaniline/polystyrene composite, such as morphology, glass transition temperature and molecular structure, were investigated in aqueous media using various surfactants. The SEM micrographs show that the type and concentration of surfactant play a major role on the surface morphology of products, because by increasing the concentration of surfactant, particle size decreases and homogeneity increases. The particle size and conversion of monomer to polymer are dependent on the type of surfactant, because the surfactants are adsorbed physically or bonded chemically (graft copolymer) to growing polymer. Moreover, by increasing the amount of oxidant, particle size decreases and conversion of monomer to polymer increases. However, by increasing the amount of oxidant, weak spherical particles were obtained. As could be seen, homogeneity of products increased when PVP used as surfactant. By increasing the concentration of PVP as surfactant from 6 g/L to 10 g/L, significant changes didn't observe in particle size. Thus, the optimum concentration of surfactant is 6 g/L. The nano-meter size of particles obtained when PVP and HPC were used as surfactant in the presence of 25g/L of APS.

The chemical structure of the product was determined by FTIR spectrum. The results indicate that the intensity of peaks is dependent on the type of surfactant, presumably due to the interaction of surfactant and polyaniline. The DSC thermograms clearly demonstrate the relationship between type of surfactant and Tg of the PAni/PS composite. In all thermograms, the first peak is observed due to loss of

water/moisture while the second peak is the glass transition temperature of composite and the third peak is melting point of composite.

In addition, PAni/CuO and PAni/Ag$_2$O nanocomposite can be successfully prepared by chemical polymerization of aniline and metal oxide in the presence of sulfuric acid using ammonium peroxy disulfate as an oxidant and DBSNa as surfactant.

The SEM studies have shown that by addition of metal oxide to the solution, particles size decrease. The type of metal oxide had considerable effects on the morphology and particle size of the resulting products. Morever, by addition DBSNa as surfactant particles size decrease and hemogeneity increases. The size range of the particles was about 70–140 nm. The FTIR analysis was done in order to identify the characteristic peaks of the products. The x-ray pattern of PAni/CuO and PAni/Ag$_2$O nanocomposite verify the presence of copper and silver nanoparticles in the polyaniline matrix.

5. REFERENCES

1.   Li, N., Lee, J. and Ong, L., "A polyaniline and nafion® composite film as a rechargeable battery", *Journal of Applied Electrochemistry*, Vol. 22, No. 6, (1992), 512-516.

2.   Epstein, A. and MacDiarmid, A., "Polyanilines: From solitons to polymer metal, from chemical currosity to technology", *Synthetic Metals*, Vol. 69, No. 1, (1995), 179-182.

3.   Ohtani, A., Abe, M., Ezoe, M., Doi, T., Miyata, T., and Miyake, A., "Synthesis and properties of high-molecular-weight soluble polyaniline and its application to the 4mb-capacity barium ferrite floppy disk's antistatic coating", *Synthetic Metals*, Vol. 57, No. 1, (1993), 3696-3701.

4.   Matsuguchi, M., Io, J., Sugiyama, G. and Sakai, Y., "Effect of NH$_3$ gas on the electrical conductivity of polyaniline blend films", *Synthetic Metals*, Vol. 128, No. 1, (2002), 15-19.

5.   Falcão, E. H. and de Azevêdo, W. M., "Polyaniline-poly (vinyl alcohol) composite as an optical recording material", *Synthetic Metals*, Vol. 128, No. 2, (2002), 149-154.

6.   Eisazadeh, H., "Removal of mercury from water using polypyrrole and its composites", *Chinese Journal of Polymer Science*, Vol. 25, No. 04, (2007), 393-397.

7.   Eisazadeh, H., "Removal of chromium from waste water using polyaniline", *Journal of Applied Polymer Science*, Vol. 104, No. 3, (2007), 1964-1967.

8.   Eisazadeh, H., "Removal of arsenic in water using polypyrrole and its composites", *World Applied Sciences Journal*, Vol. 3, No., (2008), 10-13.

9.   Izumi, C. M., Ferreira, A. M. D., Constantino, V. R. and Temperini, M. L., "Studies on the interaction of emeraldine base polyaniline with Cu (II), Fe (III), and Zn (II) ions in solutions and films", *Macromolecules*, Vol. 40, No. 9, (2007), 3204-3212.

10.   Yin, W., Li, J., Li, Y., Wu, J. and Gu, T., "Conducting composite film based on polypyrrole and crosslinked cellulose", *Journal of Applied Polymer Science*, Vol. 80, No. 9, (2001), 1368-1373.

11.   Machado, J., Karasz, F. E. and Lenz, R., "Electrically conducting polymer blends", *Polymer*, Vol. 29, No. 8, (1988), 1412-1417.

12.   De Paoli, M.-A., Waltman, R. J., Diaz, A. F. and Bargon, J., "Conductive compostes form poly (vinyl chloride) and polypyrrole", *Journal of the Chemical Society, Chemical Communications*, Vol., No. 15, (1984), 1015-1016.

13.   Eisazadeh, H., "Copolymerization of aniline and vinyl acetate by using various surfactants in aqueous media", *Journal of Vinyl and Additive Technology*, Vol. 13, No. 4, (2007), 229-233.

14.   Eisazadeh, H. and Kavian, A., "Copolymerization of aniline and styrene using various surfactants in aqueous media", *Polymer Composites*, Vol. 30, No. 1, (2009), 43-48.

15.   Lindsey, S. and Street, G., "Conductive composites from polyvinyl alcohol and polypyrrole", *Synthetic Metals*, Vol. 10, No. 1, (1984), 67-69.

16.   Cassignol, C., Cavarero, M., Boudet, A. and Ricard, A., "Microstructure–conductivity relationship in conducting polypyrrole/epoxy composites", *Polymer*, Vol. 40, No. 5, (1999), 1139-1151.

17.   Bhat, N., Gadre, A. and Bambole, V., "Structural, mechanical, and electrical properties of electropolymerized polypyrrole composite films", *Journal of Applied Polymer Science*, Vol. 80, No. 13, (2001), 2511-2517.

18.   Vaezi, M. R., Nikzad, L. and Yazdani, B., "Synthesis of cofe2o4-polyaniline nanocomposite and valuation of its magnetic properties", *International Journal of Engineering*, Vol. 22, No., (2009), 381-386.

19.   Sun, Y. and Xia, Y., "Large-scale synthesis of uniform silver nanowires through a soft, self-seeding, polyol process", *Nature*, Vol. 353, No., (1991), 737.

20.   Wang, Y. and Toshima, N., "Preparation of pd-pt bimetallic colloids with controllable core/shell structures", *The Journal of Physical Chemistry B*, Vol. 101, No. 27, (1997), 5301-5306.

21.   Lin, J. and Wang, C., "Effects of surfactant treatment of silver powder on the rheology of its thick-film paste", *Materials Chemistry and Physics*, Vol. 45, No. 2, (1996), 136-144.

22.   Jin, R., Cao, Y., Mirkin, C. A., Kelly, K., Schatz, G. C., and Zheng, J., "Photoinduced conversion of silver nanospheres to nanoprisms", *Science*, Vol. 294, No. 5548, (2001), 1901-1903.

23.   Gould, I. R., Lenhard, J. R., Muenter, A. A., Godleski, S. A. and Farid, S., "Two-electron sensitization: A new concept for silver halide photography", *Journal of the American Chemical Society*, Vol. 122, No. 48, (2000), 11934-11943.

24.   Morales, J., Sanchez, L., Martin, F., Ramos-Barrado, J. R. and Sánchez, M., "Nanostructured cuo thin film electrodes prepared by spray pyrolysis: A simple method for enhancing the electrochemical performance of CuO in lithium cells", *Electrochimica ACTA*, Vol. 49, No. 26, (2004), 4589-4597.

25.   Debart, A., Dupont, L., Poizot, P., Leriche, J. and Tarascon, J., "A transmission electron microscopy study of the reactivity mechanism of tailor-made CuO particles toward lithium", *Journal of The Electrochemical Society*, Vol. 148, No. 11, (2001), A1266-A1274.

26.   Zhou, J., Ma, L., Song, H., Wu, B. and Chen, X., "Durable high-rate performance of cuo hollow nanoparticles/graphene-nanosheet composite anode material for lithium-ion batteries", *Electrochemistry Communications*, Vol. 13, No. 12, (2011), 1357-1360.

27.   Khan, M. A. and Armes, S. P., "Conducting polymer-coated latex particles", *Advanced Materials*, Vol. 12, No. 9, (2000), 671-674.

28. Castillo-Ortega, M., Castillo-Castro, T. D., Encinas, J., Perez-Tello, M., De Paoli, M. A., and Olayo, R., "Electrically conducting polyaniline-pbma composite films obtained by extrusion", *Journal of Applied Polymer Science*, Vol. 89, No. 1, (2003), 179-183.

29. Ho, C.-H., Liu, C.-D., Hsieh, C.-H., Hsieh, K.-H. and Lee, S.-N., "High dielectric constant polyaniline/poly (acrylic acid) composites prepared by in situ polymerization", *Synthetic Metals*, Vol. 158, No. 15, (2008), 630-637.

30. Janaki, V., Oh, B.-T., Shanthi, K., Lee, K.-J., Ramasamy, A., and Kamala-Kannan, S., "Polyaniline/chitosan composite: An eco-friendly polymer for enhanced removal of dyes from aqueous solution", *Synthetic Metals*, Vol. 162, No. 11, (2012), 974-980.

31. Wu, C., "Preparation and characterization of an aromatic polyester/polyaniline composite and its improved counterpart", *Express Polymer Letters*, Vol. 6, No. 6, (2012), 465-475.

32. Barthet, C., Armes, S. P., Chehimi, M. M., Bilem, C. and Omastova, M., "Surface characterization of polyaniline-coated polystyrene latexes", *Langmuir*, Vol. 14, No. 18, (1998), 5032-5038.

33. Craver, C. and Carraher, C., "Applied polymer science: 21st century: 21st century", Elsevier, (2000).

34. Carraher, C. E., "Giant molecules: Essential materials for everyday living and problem solving", Wiley. com, (2003).

35. Bae, W. J., Jo, W. H. and Park, Y. H., "Preparation of polystyrene/polyaniline blends by in situ polymerization technique and their morphology and electrical property", *Synthetic Metals*, Vol. 132, No. 3, (2003), 239-244.

36. Rubinger, C., Costa, L., Faez, R., Martins, C. and Rubinger, R., "Hopping conduction on pani/pss blends", *Synthetic Metals*, Vol. 159, No. 5, (2009), 523-527.

37. Adhikari, S. and Banerji, P., "Polyaniline composite by in situ polymerization on a swollen PVA gel", *Synthetic Metals*, Vol. 159, No. 23, (2009), 2519-2524.

38. Kazimierska, E., Smyth, M. R. and Killard, A. J., "Size-dependent electrocatalytic reduction of nitrite at nanostructured films of hollow polyaniline spheres and polyaniline–polystyrene core–shells", *Electrochimica ACTA*, Vol. 54, No. 28, (2009), 7260-7267.

39. Eisazadeh, H. and Khorshidi, H. R., "Preparation and characterization of pan-HPC/Fe_3O_4 and pan- HPC/Fe_2O_3 nanocomposite using hydroxypropylcellulose as a steric stabilizer", *Polymer-Plastics Technology and Engineering*, Vol. 49, No. 15, (2010), 1591-1596.

40. Lee, H.-Y., Rwei, S.-P., Wang, L. and Chen, P.-H., "Preparation and characterization of core–shell polyaniline–polystyrene sulfonate HPC/Fe_3O_4 nanoparticles", *Materials Chemistry and Physics*, Vol. 112, No. 3, (2008), 805-809.

41. Xie, H.-Q., Ma, Y.-M. and Guo, J.-S., "Conductive polyaniline-SBS composites from in situ emulsion polymerization", *Polymer*, Vol. 40, No. 1, (1999), 261-265.

42. Österholm, J.-E., Cao, Y., Klavetter, F. and Smith, P., "Emulsion polymerization of aniline", *Polymer*, Vol. 35, No. 13, (1994), 2902-2906.

43. Armes, S. and Aldissi, M., "Preparation and characterization of colloidal dispersions of polypyrrole using poly (2-vinyl pyridine)-based steric stabilizers", *Polymer*, Vol. 31, No. 3, (1990), 569-574.

44. Aldissi, M., "Is there a colloid in every solution-processable conducting polymer?", *Advanced Materials*, Vol. 5, No. 1, (1993), 60-62.

45. Eisazadeh, H., Wallace, G. and Spinks, G., "Influence of steric stabilizers on the electropolymerization and properties of polypyrroles", *Polymer*, Vol. 35, No. 8, (1994), 1754-1758.

46. Eisazadeh, H., Spinks, G. and Wallace, G., "Electrodeposition of polyaniline and polyaniline composites from colloidal dispersions", *Polymer International*, Vol. 37, No. 2, (1995), 87-91.

47. Chattopadhyay, D., Chakraborty, M. and Mandal, B. M., "Dispersion polymerization of aniline using hydroxypropylcellulose as stabilizer: Role of rate of polymerization", *Polymer International*, Vol. 50, No. 5, (2001), 538-544.

48. Aldissi, M. and Armes, S., "Colloidal dispersions of conducting polymers", *Progress in Organic Coatings*, Vol. 19, No. 1, (1991), 21-58.

49. Klug, H. P. and Alexander, L. E., "X-ray diffraction procedures: For polycrystalline and amorphous materials", *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd Edition, by Harold P. Klug, Leroy E. Alexander, pp. 992. ISBN 0-471-49369-4. Wiley-VCH, May 1974.*, Vol. 1, No., (1974).

Modification of Polyaniline/Polystyrene and Polyaniline/Metal Oxide Structure by Surfactant

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چکیده

کامپوزیت های پلی آنیلین/پلی استایرن در محلول آبی بوسیله پلیمریزاسیون استایرن و آنیلین در دو مرحله تهیه شد. ابتدا استایرن با استفاده از آمونیوم پروکسی دی سولفات به عنوان اکسیدان در حضور پایدارکننده های مختلف نظیر پلی وینیل پیرولیدون، هیدروکسی پروپیل سلولز، پلی وینیل الکل و دودسیل بنزن سولفونات سدیم به پلیمر تبدیل شد. در مرحله بعد، آنیلین توسط پریدات پتاسیم به عنوان اکسیدان در حضور لاتکس پلی استایرن به پلیمر تبدیل شد. همچنین نانوکامپوزیت پلی آنیلین شامل نانوذرات اکسید مس و اکسید نقره بوسیله یک روش شیمیایی با استفاده از دودسیل بنزن سولفونات سدیم به عنوان پایدار کننده، سنتز شد. خواص محصولات از قبیل سایز ذرات، درصد تبدیل مونومر به پلیمر، مورفولوژی، ساختار شیمیایی و دمای شیشه ای شدن مورد بررسی قرار گرفت. نتایج نشان داد که این خواص به نوع پایدارکننده و اکسید فلزی بستگی دارد. ساختار شیمیایی، مورفولوژی و دمای شیشه ای شدن به ترتیب بوسیله طیف سنجی FTIR، پراش اشعه ایکس، میکروسکوپ الکترونی پویشی و گرما سنجی پویشی تفاضلی مورد بررسی قرار گرفت. نتایج نشان داد نوع و غلظت پایدار کننده، نوع اکسید فلزی و غلظت اکسیدان نقش مهمی در مورفولوژی سطح و سایز ذرات دارد. محدوده سایز ذرات برای کامپوزیت های پلی آنیلین/پلی استایرن و پلی آنیلین/اکسید فلزی به ترتیب در حدود ۲۴۰-۸۰ نانومتر و ۱۴۰-۷۰ نانومتر بدست آمد.