Regular Article

In Situ Polymerization of Polyaniline in Silane Modified Calcium Based Layered Double Hydroxide Intercalated Tartrate

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(Received 25 September 2020, Accepted 3 October 2020)

In the present study, the goal was the synthesis, characterization, surface morphology and thermal properties of organic-inorganic hybrid material of polyaniline/Ca-Fe layered double hydroxide nanocomposites (Ca/Fe-LDH/PANI NCs). At first, Ca/Fe-LDH with intercalate bio-safe tartrate anion (TA-Ca/Fe-LDH) was prepared *via* the co-precipitation and hydrothermal method. The surface of as-synthesized TA-Ca/Fe/LDH was successfully modified by 3-aminopropyltriethoxysilane coupling agents. Then, polymer matrix nanocomposites (PMNCs) were fabricated by in situ polymerization of aniline in the presence of different amounts of modified LDH. The as-prepared PMNCs were characterized by X-ray diffraction, Fourier transform infrared, transmission electron microscopy, field emission scanning electron microscopy, and thermogravimetric analysis (TGA) techniques. The results of morphological studies showed the morphological structure similar to the lamellar structure and plate-like shape particles. According to the TEM results, the sizes of the particle were reduced less than 33 nm. According to TGA results, the thermal stability of polyaninline wad improved by adding modified LDH. Also by increasing silane modified LDH contents in the final NCs, the char yields at 700 °C were improved.

Keywords: Calcium based layered double hydroxide, Anionic clays, Polyaniline, Nanocomposites

INTRODUCTION

Nanocomposites (NCs), obviously contains definite matrix containing one or more nanofiller where at least one of these nanofillers has critical dimension scale below 100 nm [1]. For production of NCs, the generally used host materials include carbonaceous materials, cellulose, silica, sands, and polymers. Among them, polymers have emerged as a type of attractive host materials due to their controllable porous space and surface chemistry and also their excellent mechanical strength for long-term use [2]. The resultant polymer-based NC, incorporate the excellent features of both polymers and nanoparticles (NPs), while the polymer support materials provide higher stability, compatibility, processability, unique physical and chemical properties, high interfacial reactivity of nanofillers, and some interesting enhancements caused by the NP-matrix interaction [2-4].

The π-conjugated polymer composites with nanoscale dimensions are in great demand over the years, due to their wide applications in batteries, sensors, solar cells and anticorrosion coatings [5]. Polyaniline (PANI) is one of the most unique nitrogen-containing conjugated polymers with high surface area that it has unique advantages [6], like multi-redox state [7], good environmental stability [8], low prices, ease to prepare, tunable electrical conductivity, high capacitive characteristics [9-11]. This capabilities of PANI makes it an ideal candidate in many applications such as, flexible electronic devices [12], solid-state supercapacitors, flexible supercapacitors [13,14], suitable adsorbent [6], photocatalytic activities, electronic displays, electromagnetic, electro-luminescence, biological sensors, membrane, and batteries [15,16]. PANI has a strong affinity for grafting inorganic and organic molecules due to exist of imine and amine functional groups on its backbone [16]. Polyaniline powder was chemically prepared by oxidative

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polymerization of aniline using definite amount of ammonium peroxydisulfate (APS) in the solutions of strong acids [11]. The PANI can mainly occur in three forms, fully reduced state known as leucoemeraldine, half oxidized emeraldine base and fully oxidized pernigraniline [7,15].

Anionic clays or layered double hydroxides (LDHs) are laminar materials, can be found in nature and are easily synthesized with a large range of chemical composition by modifying the nature of the intercalated anions or metal cations [17-19]. LDH is accumulate by a non-covalent bond, an interaction between the positively charged main lamellar and non-framework interlayer anions [20]. The general formula of LDHs is $[M^{2+}_{1-x}M^{3+}x(OH)_2][A^{n-}_{x/n}.\ mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations in the positively charged sheets and A^{n-} represents an inorganic or organic interlayer anions in an octa-hedral arrangement [21-23]. The tunable and distinctive properties of LDHs are high surface area and fast ion transfer rates [24], significant variation in functional performance [25], low cost [26], high and tunable charge density, surface basicity, adsorptive navigate, anion exchangeability, enormous compositional and dimensional diversity and biological and environmental compatibilities, Which makes them an ideal candidates in many applications [27,28]. LDH have received great potential for application in many fields such as electrocatalysts for the oxygen evolution reaction [29], biological applications [30], excellent antimicrobial activities [31], photocatalysts [32,33], cosmetic [34], gene therapy [35], superb adsorbents [36,37], delivery of drug [38]. Owing to the versatility in chemical composition and unique physical structure of LDH, This could greatly studied and intensively used in different areas and materials in recent years. For example, LDH has been incorporated into polymers to improve mechanical properties, flame-retardant properties, thermal stability, and anti-ultraviolet aging performance [39]. So, it is expected to modify the PANI by inorganic LDHs to prepare the organic-inorganic PANI/LDHs NCs through in-situ oxidative polymerization. Tartaric acid derivatives are a class of chiral acid compounds, which widely available and an inexpensive relatively inexpensive natural resource from a large variety of fruits [40-42], However, these reagents due to their poor solubility and dispersity in aqueous solutions, usually play the major roles in organic system [41]. Tartrate salts are non-toxic and recyclable, and they are commonly supposed to show potential and promising applications in the field of industry, electronics, medicine, and use as a suitable green alternative for traditional inorganic salts [43]. Tartrate intercalated layered double hydroxides are commonly applied in the field of heterogeneous asymmetric catalysis [44,45]. The release of tartrate into the biological waste water and biosphere is safe for the environment and ecosystem, as well as good for the plants [43].

The uniform distribution of NPs in polymer matrices is one of major challenge for producing highly performing NCs. Poor dispersion of NPs might result in low improvements in physical, morphological, and mechanical property of NCs [46]. The consistency problem between the hydrophobic polymer and hydrophilic LDHs will be encountered when LDHs are dispersed into polymer matrix. Also, surface modification of LDH with an organic surfactant is a general route to change the hydrophilic surfaces of LDHs to hydrophobic ones. Silylation has been extensively applied in the modification of the LDH surface when organosilanes are with nucleophilic groups. In this case, organosilane not only leads to increase the hydrophobicity of substrates by the surface grafting, but also help to bond with the polymer matrix by amino groups [1,47].

In the work leading to this study, the organic-inorganic hybrid materials of PANI/LDH NCs were fabricated by in situ polymerization of aniline in the presence of modified LDH. For this purpose, at first, TA-LDH based on calcium and iron with good accessible chemically active sites have been synthesized *via* one-step co-precipitation and hydrothermal technique, which potassium tartrate as a bio-safe, and non-toxic agent was used as a negative ion source to intercalate the Ca/Fe-LDH for functional enhancement. The surface of TA-LDH was modified with 3-aminopropyltriethoxysilane (APTES) to stronger interaction between polymer matrix and LDH. Then, silane modified LDH were then inscribed in 5 and 10 wt.% into PANI matrix to formed different polymer NCs. The structure, morphology and thermal stability behavior of as-prepared NCs were investigated by different techniques such as XRD, FT-IR, FE-SEM, TEM and TGA analyses.

EXPRIMENTAL

Material and Methods

Aniline, APTES, APS, potassium tartrate, Iron(III) nitrate nona-hydrate, Calcium(II) nitrate tetra-hydrate, ethanol, and sodium hydroxide (NaOH), were obtained from Merck chemical Co.

Synthesis of Tartrate Intercalated Ca/Fe LDH

The Ca/Fe LDH with interlayer anions of tartrate was fabricated by the co-precipitation technique followed by hydrothermal method with mole ratio of Ca/Fe 2:1 [16]. An aqueous solution (30 ml) containing 2.964 mmol of $Ca(NO_3)_2.4H_2O$ and 1.482 mmol of $Fe(NO_3)_3.9H_2O$ was added in a solution (10 mL) containing 1.976 mmol of potassium tartrate in a three neck flask. The pH of the solution was adjusted to constant value of 10-10.5 with 2 M NaOH solution. The solution was stirred for 120 min (25 °C) under N_2 atmosphere, and the orange solution was sealed in a Teflon-lined stainless-steel autoclave for 24 h at 140 °C. After cooling, the tartrate intercalated LDH (TA-LDH) was isolated by filtration and the product was thoroughly washed five times with distilled water until the pH value of the washings reached 7.0, and dried in an oven at 60 °C for 24 h.

Surface Modification of LDH by APTES

After drying TA-LDH powder at 120 °C, to produce a particle surface with high coating of hydroxyl groups, it was added in a solution containing 2 mL of APTES in 15 mL of ethanol, and solution was refluxed for 6 h. Then the product was washed with ethanol in ultrasonic bath to remove unreacted APTES. Finally, the resulting silane modified LDH (m-TA-LDH) precipitate was collected by filtration and dried for 24 h.

Preparation of Polyaniline/LDH NCs

The PANI/LDHs NCs were synthesis by in-situ oxidative polymerization. First, m-TA-LDH (5, 10%) was dispersed in 30 ml of methanol. After the ultrasonication at room temperature for approximately 30 min, the suspension was kept for stirring for about 2 h under a nitrogen atmosphere. Then a desired amount of distilled aniline was added drop by drop to m-TA-LDH suspension at R.T. under

constant stirring for 2 h. In order to initiate the process of the oxidative polymerization, the solution containing definite amount of APS in 14 mL of 1 M HCl was added into the reaction vessel, then the reaction mixture was retained in the range of 0-5 °C with ice bath for 8 h. Finally, the dark greenish tint PANI/LDHs product was obtained and washed with methanol and then dried at 65 °C for 24 h.

Characterization Techniques

FT-IR spectra using KBr pellets were recorded by a Jasco-680 spectrophotometer (Tokyo, Japan). Thermogravimetric analysis (TGA) of the samples under an N_2 atmosphere was measured with STA 503 TA instrument (USA) at the heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns of samples were collected using a Philips X'PERT-MPD diffractometer under the conditions of $\lambda = 1.54$ Å (Cu Kα), at a tube voltage of 45 kV and 100 mA. The surface morphology of modified LDH and PANI NCs was study by TEM obtained from a Philips CM120 using an accelerator voltage of 100 kV and FE-SEM (HITACHI; S-4160, Tokyo).

RESULTS AND DISCUSSION

The NCs of PANI and silane modified TA-LDH was prepared by *in situ* polymerization process as shown in Scheme 1. First the surface of LDH was modified by APTES and the PANI/LDHs NCs were prepared by polymerization of aniline monomer in the presence of silane modified TA-LDH.

FT-IR Study

Figure 1 shows the FTIR spectra of modified LDH and PANI based NCs. For TA-LDH, the broad signal around 3427 cm^{-1} corresponds to the –OH stretching vibration of interlayer water molecules and hydroxyl groups of the host layers of the pristine LDH. Two characteristic bands at 1384 and 1594 cm^{-1} were observed indicating a symmetric and asymmetric stretching vibrations corresponds to the carboxylate group, which confirmed the existence of the tartrate anions (Fig. 1a). Characteristic bands observed at 1027, 1112 cm^{-1} was corresponding to the stretching vibrations of the C-O in alcoholic groups in tartrate [19]. Stretching modes of CH_2 in tartrate was appeared at
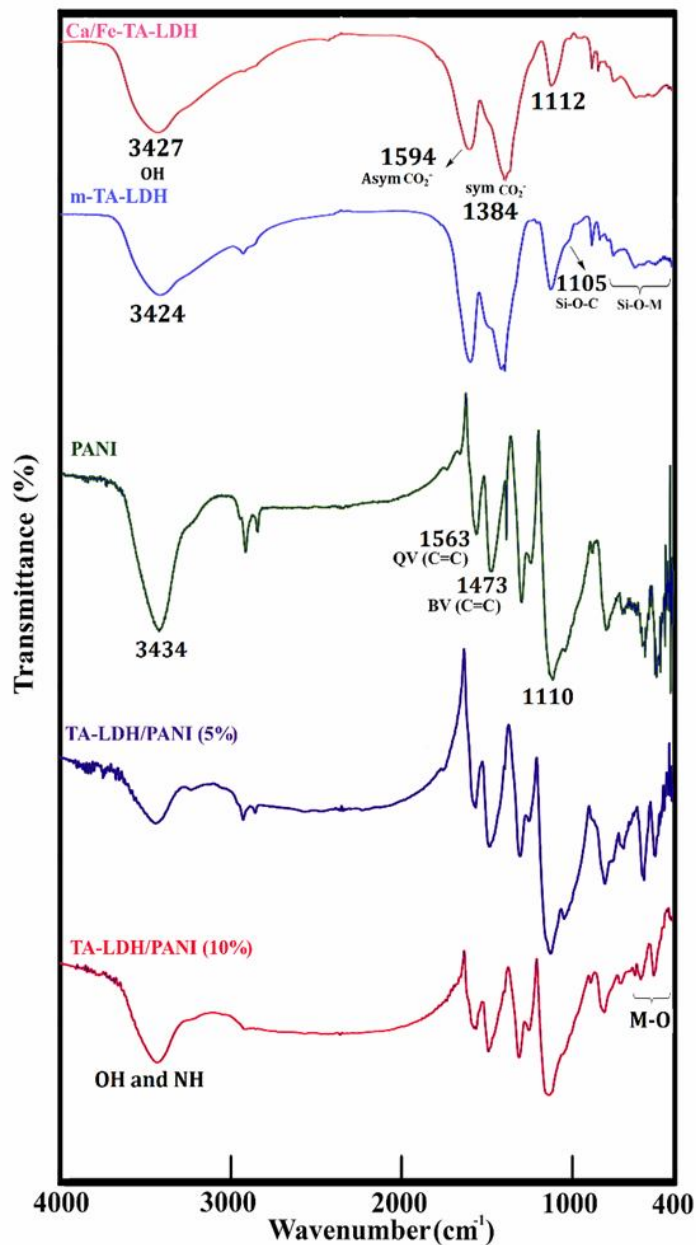
Fig. 1. The FT-IR spectra of TA-LDH, m-TA-LDH, pure PANI, PANI/LDH NC5% and NC10%.

2920 cm^{-1}. For silane modified TA-LDH (m-TA-LDH), the presence of new bands attributing to the organic moiety of the silane coupling agent was observed. The absorption band at 1105 cm^{-1} is characteristic band of Si-O-C asymmetric stretching vibration and the bands at around 400-800 cm^{-1} characterize the Si-O-M vibration, as well as

new absorption band at 2925 may be assigned to the CH_2 stretching of APTES groups. In the FTIR spectra of bare PANI, the absorption peaks located at 1110 cm^{-1} can be ascribed to the N=Q=N stretching band, and the bands appeared at 1563 and 1473 cm^{-1} attributed to the characteristic peaks of quinoid imine groups and benzenoid
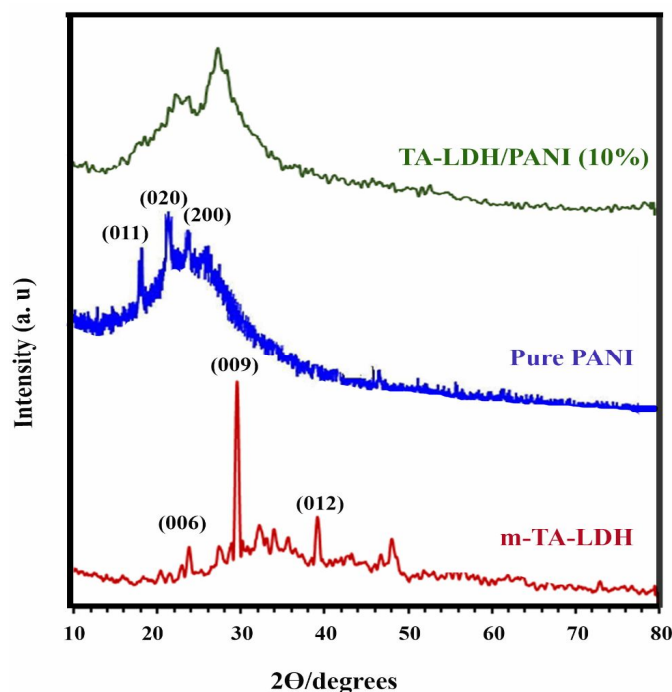
Fig. 2. XRD pattern of m-TA-LDH, pure PANI and the PANI/LDH NC10%.

rings, respectively. The relative absorption peaks appeared at 1294 and 1240 cm^{-1} can be ascribed to C=N and C-N stretching vibrations, respectively. Appearance of the absorption peak at 793 cm^{-1} can be ascribed to the out-of-plane bending vibrations of C-H band within the aromatic ring. For the PANI/TA-LDH NCs, the absorption peaks located at 3448 cm^{-1} associated to the N-H and O-H groups. Characteristic bands observed at 1473 and 1558 cm^{-1} are assigned to the amine groups and quinoid imine groups, respectively. The presences of the characteristic bands at 400-800 cm^{-1} corresponding to the Si-O-M and M-O vibrational modes in PANI/TA-LDH NCs confirming the existence of PANI and LDH in the hybrid materials.

X-ray Diffraction

The XRD patterns for silane modified TA-LDH nanoparticle, pure PANI and as synthesized PANI/TA-LDH NCs are presented in Fig. 2. The XRD pattern of TA-LDH clearly exhibits three characteristic diffraction signals at (006), (009), (012), which are corresponding to the typical hydrotalcite-like characteristics and established the construction of the crystalline structure for LDH. For m-TA-LDH the (003) was disappeared, suggesting an exfoliation of LDH nanoparticles. Pure PANI, displays two broad diffraction peaks at $2\theta = 20°$ and $26°$ recognized to the periodicity parallel and the periodicity perpendicular to the polymer chain, respectively. In the XRD pattern of PANI/LDH NC10%, the reflection at around $2\theta = 20°$ and $26°$ are related to PANI in PANI/LDH NC, and failure to appear the reflection peaks of LDH in the PANI/LDH NC10 %, which perchance illustrates that the LDH has been partially exfoliated in the polymer matrix.

These results confirm that the PANI and LDH structure of the material are maintained in the NCs.

FE-SEM and TEM Study

The surface morphology and topography of the TA-LDH, pure PANI and PANI/TA-LDH NCs were Investigated by means of FE-SEM technique. Agreeing to the Fig. 3, TA-LDH have spherical form-like, and TEM
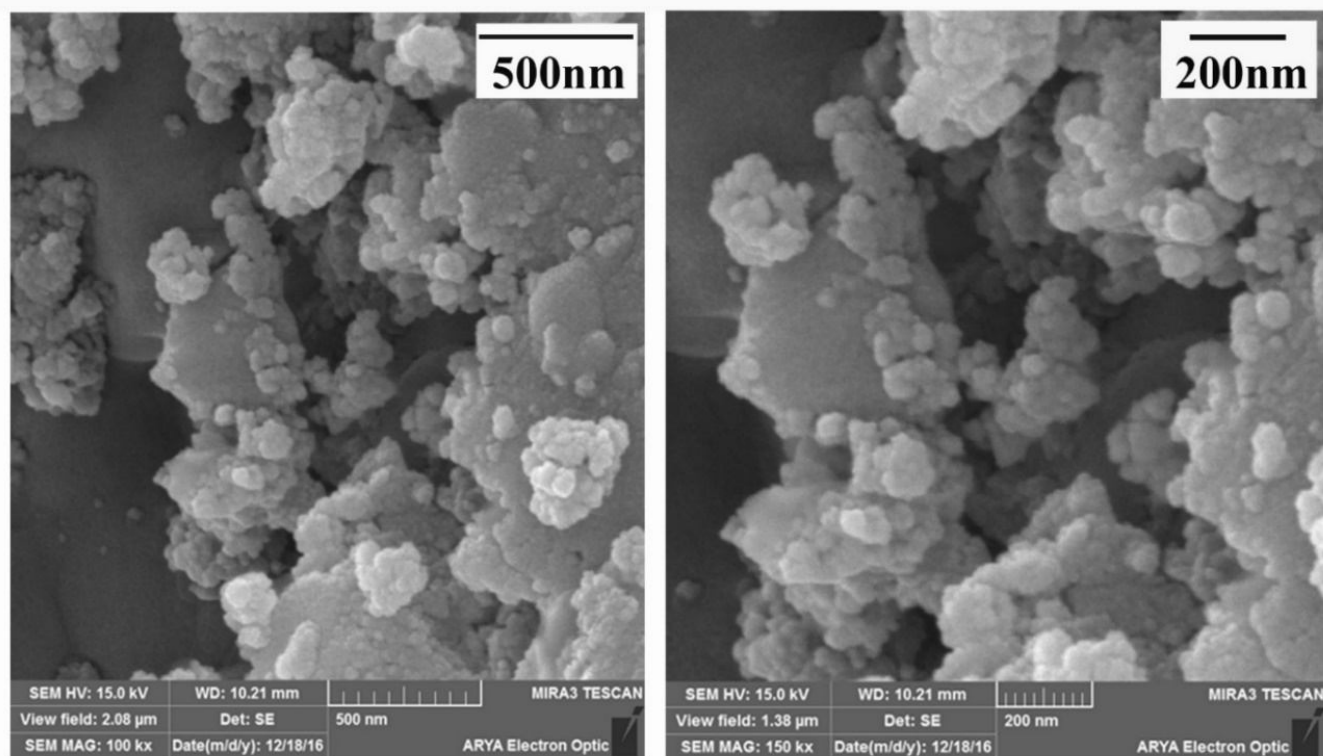
Fig. 3. FE-SEM of m-TA-LDH.

image of m-TA-LDH show an overlapping of crystals with smooth surfaces and polyhedra order arrays, as well as the sizes of modified LDH were about 26 nm. The FE-SEM image of the synthesized polyaniline shows that the morphology of the polyaniline is very short nanorods (Fig. 4). For PANI/LDH NC5% and NC10% a uniform dispersion of TA-LDH nanoparticles in the polymer matrix was observed (Fig. 5). Also, The presence of m-LDH on the polymer matrix was confirmed by the appearance of the silane modified TA-LDH vibrational modes in the FT-IR spectra of the relevant NCs, which is also confirms the results of FE-SEM images. TEM images of the PANI/LDH NC10% are shown in Fig. 6. According to the TEM results, the sizes of the particle were reduced less than 33 nm. For LDH/PANI NCs, owing to applied processing conditions, such as, the effect of ultrasonication technique method [48], surface modification of the nanoparticle by tartrate anions, and hydrogen bonding interaction between PANI and m-TA-LDH, as well as the using of silane coupling agents

in dispersion and particle size. The use of these reagents and conditions caused good dispersion of m-TA-LDH in the PANI matrix by creating a gap between NPs.

Thermal Properties

The thermal decomposition of the m-TA-LDH, pure PANI and PANI/m-TA-LDH NCs was examined by TGA under an N_2 atmosphere and the results provided in Fig. 7. In all samples three different weight loss steps are observed. The first weight-loss step occurs below 150 °C for the m-TA-LDH, which is owing to the elimination of physisorbed the interlayer water, The second decomposition happened in the interval 250-400 °C, which could be related to the thermal dehydroxylation of the brucite-like layers. The final weight loss stage in the range of 600-700 °C is attributed to the removal of hydroxyl groups of the brucite-like layers and decomposition of intercalated tartrate anions. The weight loss region observed below 200 °C for pure PANI probably corresponded to the loss of water, alcohol
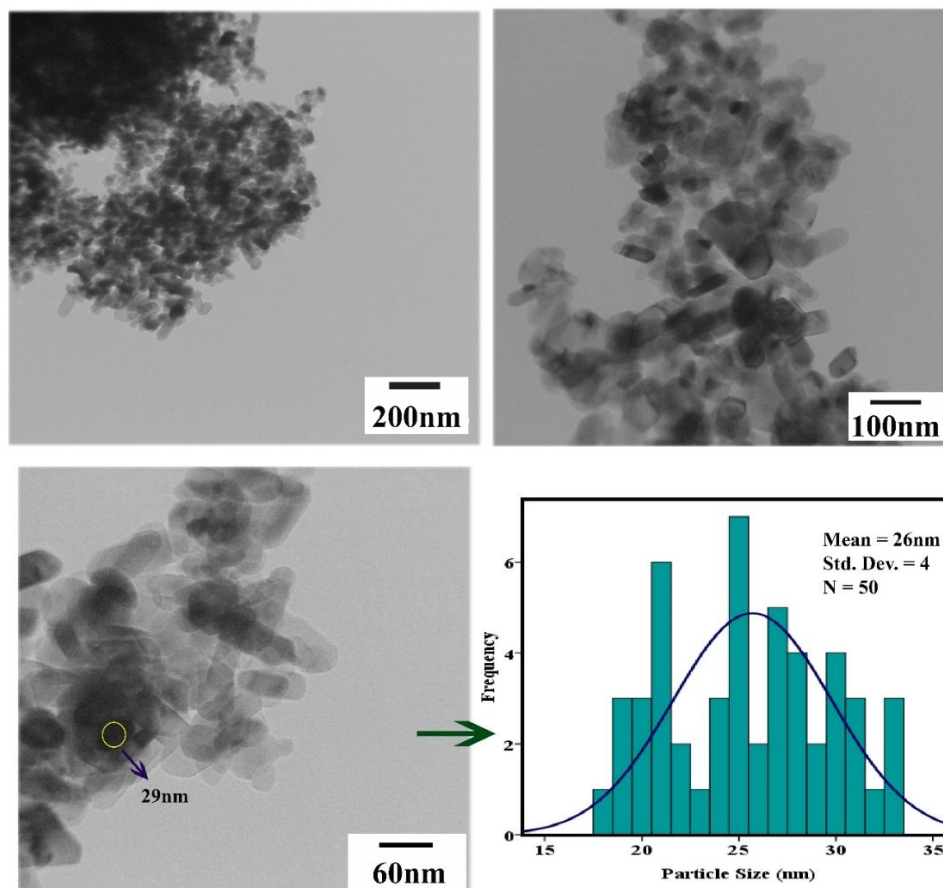
Fig. 4. TEM of m-TA-LDH.

moieties, solvent and acid dopant. The mass loss occurred in the range of 300-400 °C, might be ascribed to the thermal decomposition of PANI backbone. The mass loss regions below 150 °C for the PANI/m-TA-LDH NCs corresponding to the removal of physically adsorbed and intercalated water, the weight loss above 150 °C attributed to the concomitant dehydroxylation of LDH layer as well as the elimination of tartrate anions and the loss of the doped acid bound to PANI chains and thermal decomposition of pure PANI backbone. The thermal properties of the PANI/m-TA-LDH NCs were improved in comparison with pure polymer. Also by increasing silane modified LDH-TA contents in the final NCs, the char yields at 700 °C were improved. Therefore, an improvement in the thermal stability of the PANI/m-TA-LDH NCs can be due to the good compatibility of modified LDH with polymer matrix.

CONCLUSIONS

In this paper, bio-safe Ca-Fe/LDH-TA was fabricated through the co-precipitation technique. Surface modification by silane coupling agent and ultrasonic technique was employed to increase the organic nature of LDH layers for develop the effective interactions of LDH nanoparticles with organic polymer matrix, and moreover for decrease the aggregation and accomplish promote distribution of LDH layers in the PANI matrix. Then, it has been demonstrated that m-LDHs can be uniformly dispersed onto the PANI matrix by in situ oxidative polymerization. Furthermore, the results of FE-SEM and TEM analyses showed the
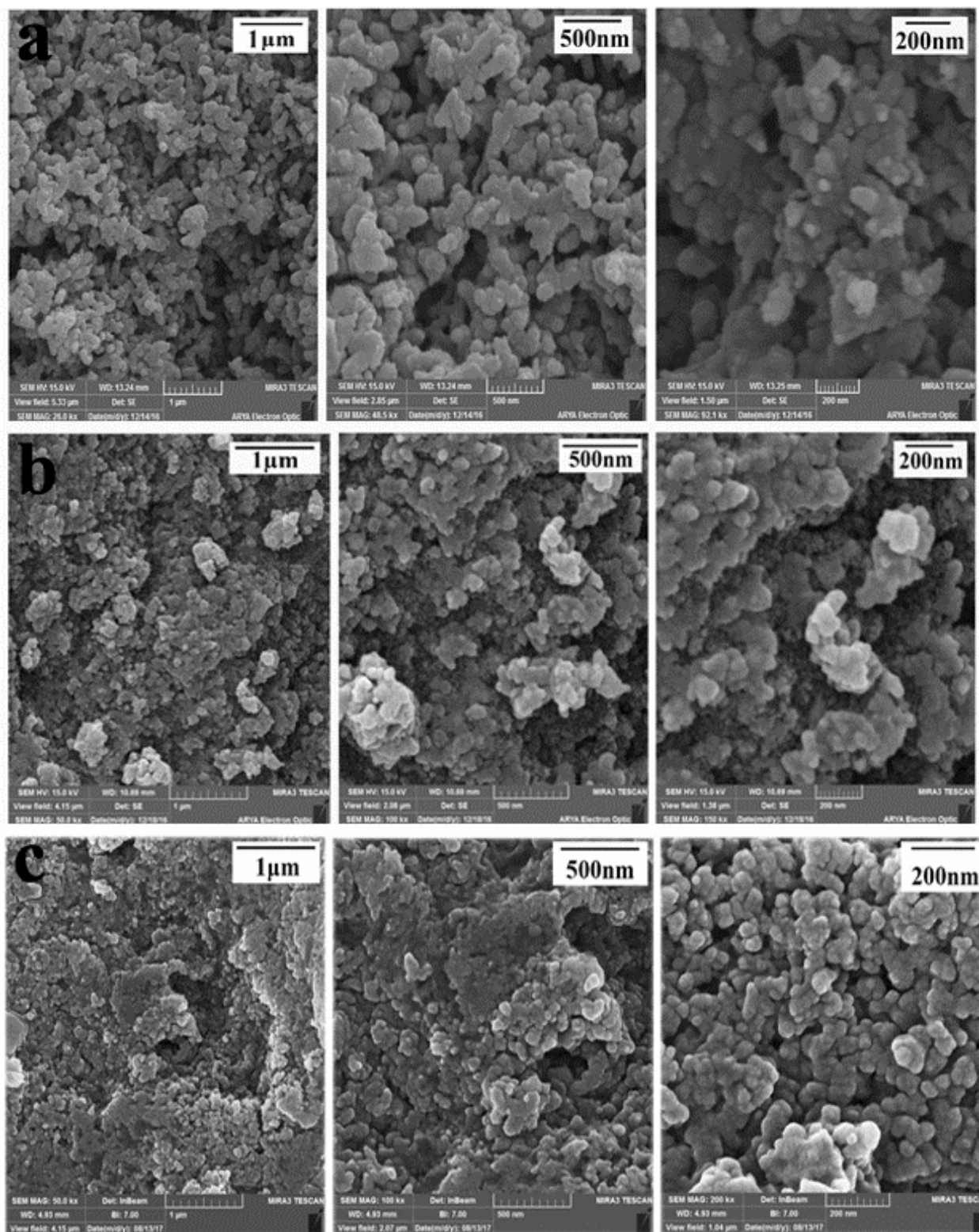
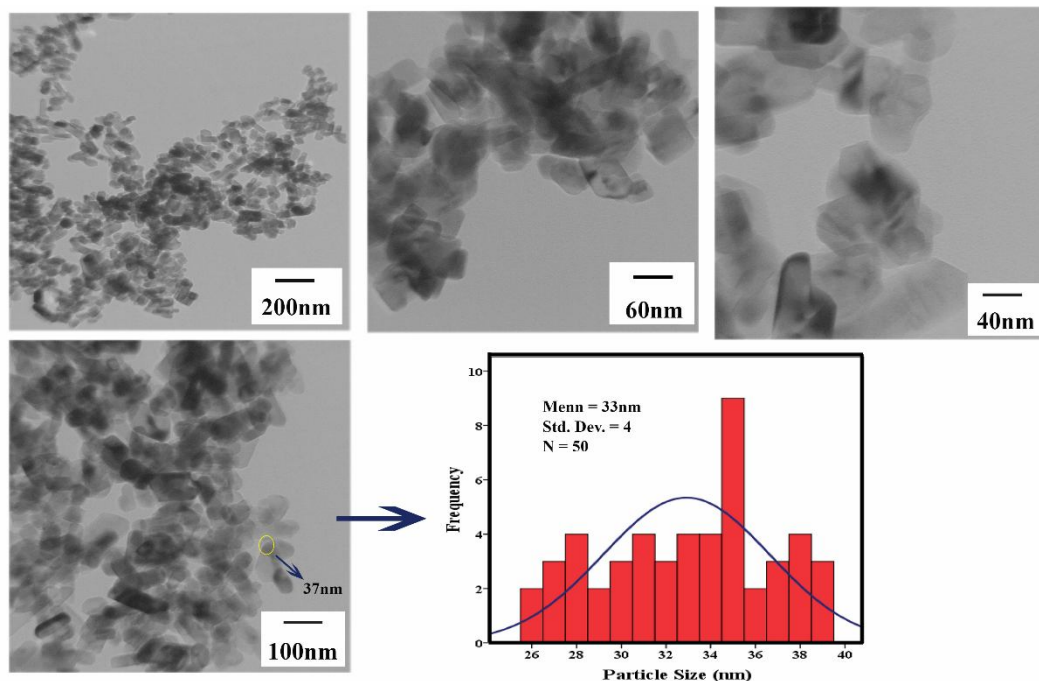**Fig. 5.** FE-SEM of (a) pure PANI, (b) m-TA-LDH/PANI NCs (5%) and (c) m-TA-LDH/PANI NCs (10%).

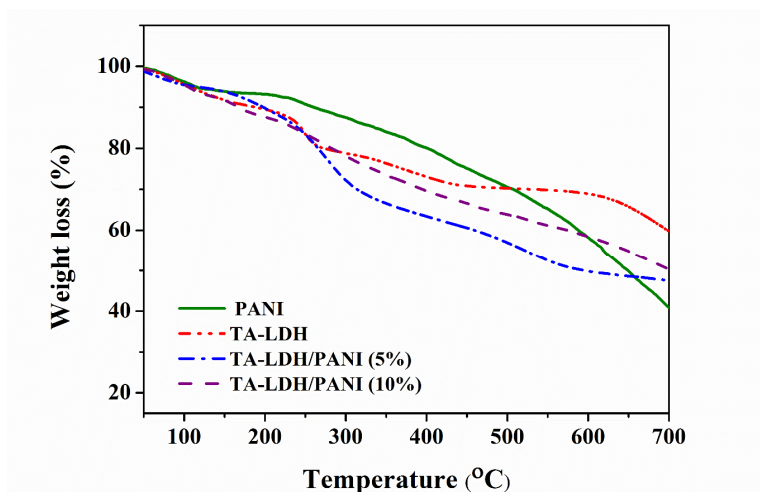**Fig. 6.** TEM of m-TA-LDH/PANI NC (10%).

Fig. 7. TGA thermogram of pure PANI, TA-LDH, PANI/LDH NC5% and NC.10.

homogenous dispersion of m-LDH into polymer matrix without any aggregation. The results of XRD analysis illustrates that the LDH has been partially exfoliated in the polymer matrix. As a result, thermal stability of the PANI/LDH NCs dramatically improved due to the good compatibility of modified LDH with polymer matrix.

ACKNOWLEDGMENTS

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