



## Sonochemistry Synthesis of Lanthanum Ions-Doped Polyaniline/Montmorillonite Nanocomposites and Their Conductivity and Thermostability Characterization

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A new network structure nanocomposites consisting of polyaniline (PANI), montmorillonite (MMT) and  $\text{La}^{3+}$  have been successfully synthesized sonochemically at normal pressure, the as-prepared products have been characterized by transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and four-probe method. The test results show that the composites have a unique conductivity and flame resistance. The factors affecting the reaction process were discussed. Furthermore, the mechanisms of phase formation and morphology control of lanthanum ions-doped polyaniline/MMT nanocomposites during the ultrasonic synthesizing process are proposed and discussed.

**Keywords:** Sonochemistry, Polyaniline, Montmorillonite, Lanthanum.

### INTRODUCTION

In recent years, nanocomposite hybrid compounds have been the subject of considerable investigation. The inorganic lattices provide confined spaces which can force the polymer molecules into organized arrays, thereby modifying their bulk properties. Sonication can generate high-frequency oscillation signal, which is transformed into a kind of high-frequency mechanical vibration wave by a converting transducer. Whereas, the mechanical vibration wave transmitted forward in the solvents, it can constantly change the density of the liquid, produce tens of thousands of tiny bubbles called "cavitation", the mathematical models has been reported<sup>1</sup>.

The interest in clay polymer nanocomposites materials, initially developed by researchers at Toyota, has grown dramatically over the last decade. They have attracted great interest both in industry and in academia, because they often exhibit remarkable improvement in materials' properties when compared with virgin polymer or conventional micro- and macro-composites<sup>2</sup>. Polyaniline is one of the most extensively studied conducting polymers, not only due to its easy chemical synthesis and high stability towards environmental exposition, but also to its inherently excellent versatility including novel electronic, optical and electrochemical properties, thus it can be used for a variety of industry applications<sup>3</sup>. However, it is known that pure polyaniline is brittle, infusible and insoluble in most of the solvents and hence not processable<sup>4</sup>. Therefore, the poor processability should be

overcome for the application of this electrically conducting polymer, which led to intensive research on the preparation and new property studies of novel nanocomposites consisting of polyaniline with various layered materials.

Among the layered materials, montmorillonite has been extensively investigated because they are abundant, inexpensive and has attractive properties such as large surface area, ion exchange. Montmorillonite is composed of silicate layers with 1 nm thickness and 200-300 nm in the lateral dimensions. Its layer structure consists of two silica tetrahedral sheets and one aluminum octahedral sheet (about 100 nm wide and long) that stack 1 nm thick layers by weak dipolar forces, giving rise to interlayer galleries<sup>5</sup>. The galleries are generally occupied by hydrated cations to balance the charge deficiency, which is generated by the isomorphous substitution in the tetrahedral sheets. Therefore, monomer (aniline) can be easily introduced into the galleries by ion exchange and are hardly separated from the galleries anymore<sup>6,7</sup>. Thus, substitution of hydrated cations in the galleries of montmorillonite for  $\text{La}^{3+}$  enhances the ion exchange process and promote montmorillonite layer stripping. In general, polymer molecules are intercalated into the montmorillonite, which intend to form exfoliated clay structure<sup>8</sup>. Soundararajah *et al.*<sup>2</sup> investigated the mechanical property enhancement of polyaniline intercalated with montmorillonite and found that the montmorillonite/polyaniline (MMT-PANI) nanocomposites displayed improved mechanical properties compared to the neat polymer or clay.

In this paper, we show that by introducing a sonochemical method in the preparation of lanthanum ions-doped PANI/MMT nanocomposites. The composite could be transformed into a novel network structure, the montmorillonite platelets separated from clay particles could be dispersed in the polyaniline matrix during the ultrasonic assistant polymerization process. With the doping of  $\text{La}^{3+}$  in the composites, the conductivity increased obviously.

## EXPERIMENTAL

Montmorillonite was purchased from Gansu Jinchang Company (China), Aniline monomer was purified by distillation under reduced pressure and kept at  $0\text{ }^{\circ}\text{C}$  prior to use. Ammonium peroxydisulphate (APS) was used as an oxidant without other purification. Concentrated hydrochloric acid, ethanol and  $\text{La}_2\text{O}_3$  were of analytical grade and used as received.

Transmission electron microscopy (TEM) was performed with a JEOL100CX model transmission electron microscope at 100 kV accelerated voltage and the observations were carried out after retrieving the slices onto Cu grids. Fourier transforms infrared (FT-IR) spectra of the composites in KBr pellets were recorded on an EQUINOX55 FT-IR spectrometer (Bruker). X-ray diffraction studies were performed by using D/max-2400 diffraction X-ray diffractometer (Rigaku) with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ) operated at 40 kV and 30 mA. The weight loss temperature of the nanocomposites was determined with a Perkin-Elmer thermogravimetric analyzer (TG-DTA; model SSC-5200) from 20 to  $800\text{ }^{\circ}\text{C}$  under nitrogen atmosphere ( $10\text{ }^{\circ}\text{C}/\text{min}$ ). The conductivity of the composite nanospheres was measured by the conventional four-probe method.

**Synthesis of lanthanum ions-doped PANI/MMT nanocomposites:** The clay mineral bentonite was cation exchanged with a saturated lanthanum chloride solution to get lanthanum montmorillonite ( $\text{La}^{3+}$ -montmorillonite), the typical process is as follows: A total of 0.5 g of montmorillonite was dispersed in 20 mL of saturated lanthanum chloride solution [ $\text{LaCl}_3(\text{S})$ ], purged with nitrogen for few minutes, the container was irradiated by strong sonication (performed by using FS-600T sonifier cell disrupter, 20 KHz, 600 W, purchased from Shanghai Shengxi ultrasonic instrument Co., Ltd.) with the ultrasound power output kept 400 for 2 h at room temperature. Then 2 g aniline monomer were added to the suspension, sonication for another 2 h to promote the intercalation of aniline into the silicate layers and the exfoliation of montmorillonite.

After that, 3 g ammonium peroxydisulphate [ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] dissolved in minimum quantity of 1 M HCl (20 mL) was added dropwise to initiate the polymerization under stirring in an ice water bath. The process was carried out very slowly and carefully to prevent the warming of the solution. After the addition, ultrasonic stirring was continued for 1 h to ensure the completion of the reaction. The precipitate was then filtered and washed with excess of deionized water to remove free anilinium ions and lanthanum ions and dried under vacuum at  $60\text{ }^{\circ}\text{C}$  for 24 h.

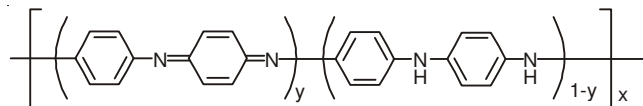
To prepare composites of different ratios of polyaniline and montmorillonite, the following steps were followed: 0.35 g or 0.65 g of montmorillonite were mixed with 2 g aniline monomer in 20 mL solution of lanthanum chloride or deionized water in a set of reaction vessels. Then 2 g ammonium

peroxydisulphate was added to initiate the polymerization under stirring in an ice water bath. The work-up procedure was the same as described above.

## RESULTS AND DISCUSSION

Chemical polymerization of anilinium-montmorillonite takes place easily when a moderately strong oxidizing agent such as ammonium persulfate was used. The color changed from milk white through blue to dark green was observed during the polymerization process. For free aniline, the color of mixture turns progressively to blue and finally to dark green. These color changes have been explained in the literature<sup>9</sup>, on the basis of the formation of pernigraniline salt as intermediate, which is the protonated fully oxidized form of polyaniline with blue color. For lanthanum ions-doped PANI/MMT nanocomposite, the appearance of intermediate brown color proves that the mechanism of polymerization is different from that free aniline<sup>10</sup>.

The base forms of polyaniline can be schematically represented by the following general formula:



where the  $y$  value ranges from 1 for the fully oxidized polymer (so-called pernigraniline) to 0.5 for the half-oxidized polymer (emeraldine) and to 0 for the fully reduced polymer (leucoemeraldine)<sup>11</sup>. From TEM micrograph of the resulting nanocomposites (Fig. 1), it clearly can be observed that the nanocomposites have formed nanowires with diameter about 20-50 nm. The formation of this structure indicates that under the action of ion exchange of  $\text{La}^{3+}$  and ultrasonic force, polyaniline molecules have been inserted into the interlayer of montmorillonite and then the silicate layers as a template, promote the growth of the polymer towards certain direction and what is more, the growth of the polymer and ultrasonic force forced the silicate layers stripping into small pieces (Fig. 1b).

Conventional chemical oxidative polymerization approaches to nanostructured electronic polymers include the use of insoluble solid templates such as zeolites or soluble templates such as polymers and surfactants. A "nontemplate" approach has also been described in which the use of large organic anions results in polyaniline nanofibers<sup>12</sup>. Recently, an interfacial polymerization method has been reported where 50 nm diameter fibers of polyaniline are produced at the interface of two immiscible liquids<sup>13</sup>. Despite the diversity in these synthetic approaches, we believe that the dramatic change in polymer morphology points to an underlying mechanistic rationale is, polymeric nanostructures formed (or present) during the very early stages of the reaction can orchestrate bulk formation of similar nanostructures.

The exfoliating property of montmorillonite offers the possibility to synthesize nanocomposites with insoluble polymers, by *in situ* polymerization-encapsulative precipitation<sup>14</sup>. In this method, a solution of a suitable monomer (anilinium) is mixed with an exfoliated suspension of the inorganic host. When an initiator is added, the polymerization causes the

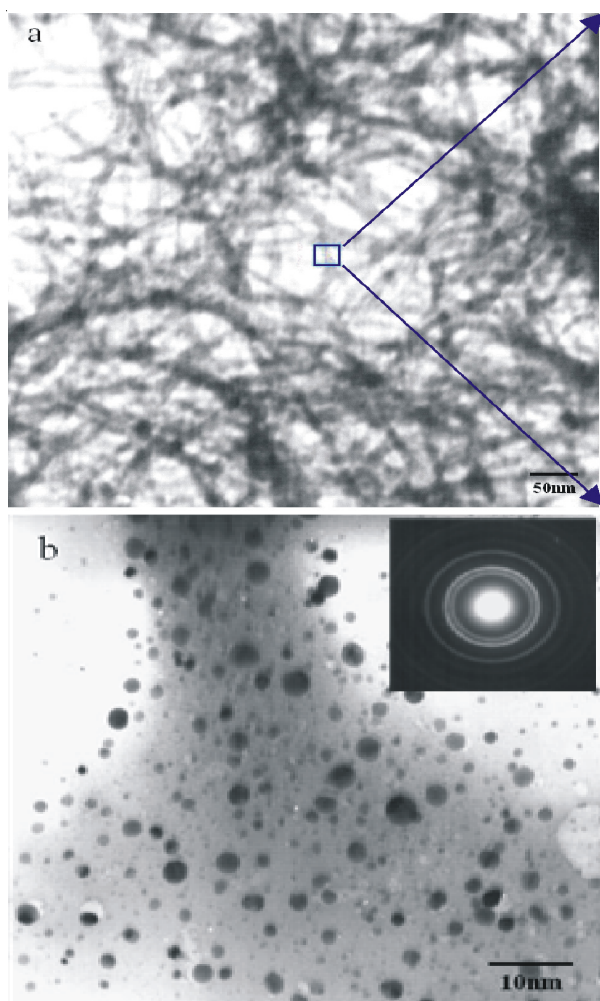


Fig. 1. (a) TEM of network structure of lanthanum ions-doped PANI/MMT composites; (b) A high resolution TEM image taken from the rectangular area in (a) The inset shows the SAD of the composites

coprecipitation of the polymer and host monolayers, forming a nanocomposite. This happens because the growing polymer is a positively charged species and adheres to the negatively charged inorganic layers mainly due to electrostatic forces. The initiator in this case is the  $\text{La}^{3+}$  ions.

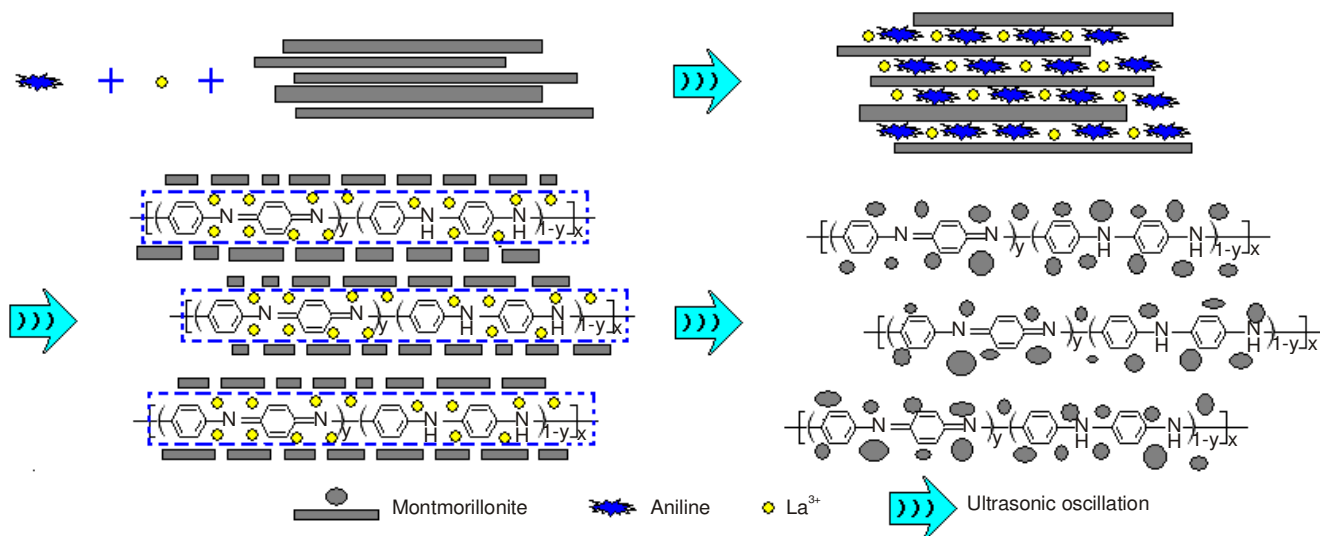


Fig. 2. Schematic illustration of possible network hybrid structures

In the process of intercalation, the  $\text{La}^{3+}$  centers are very stable due to their low spin character<sup>29</sup>, the electron configuration maximizes the ligand field stabilization energy (LFSE) and probably acts as a powerful driving force for the oxidation of aniline, as has been demonstrated in the intercalative polymerization of aniline in  $\text{FeOCl}$ <sup>15</sup> and  $\text{V}_2\text{O}_5$ <sup>16</sup>. Since the doped ions can act as separators of the electron-hole pairs, the doped  $\text{La}^{3+}$  mainly acts as a charge-carrier recombination center, the delicate balance between the increase in trap sites lead to efficient trapping and the decrease in trapped carriers, which leads to longer lifetimes for interfacial charge transfers<sup>7</sup>. The selected area diffraction (SAD) of the nanocomposites indicate that  $\text{La}^{3+}$  stably exist in the nano-composites. When polyaniline molecules are intercalated into the galleries of montmorillonite, there is a strong self-assembly effect between polyaniline molecules and montmorillonite, the interaction of  $\text{La}^{3+}$  and polyaniline during polymerization also makes  $\text{La}^{3+}$  immobility.

Pioneering work by researchers at Toyota has led to the discovery of nanoscale polymer-clay hybrid composites as promising candidates for lightweight materials applications<sup>17</sup>. There are two end-members which define the realm of structures possible in such nanocomposites<sup>18</sup>. At one end are the well-ordered and stacked multi-layers that result from intercalated polymer chains within host silicate clay layers. At the other end of the spectrum are delaminated materials, in which the host layers have lost all their registry and are well-dispersed in a continuous polymer matrix (Fig. 2). This latter case could be refer to as a "house-of-cards" structure to indicate the random and highly disordered nature of the individual chains<sup>28</sup>.

FTIR spectra of lanthanum ions-doped PANI/MMT composites are shown in Fig. 3. The formation of polyaniline between the montmorillonite layers and  $\text{La}^{3+}$  is supported by IR spectroscopy. The characteristic absorption bands of polyaniline appear at 1301 ( $\nu\text{C-N}$ ), 1482 and 1575  $\text{cm}^{-1}$  ( $\nu\text{C=C}$ ) of benzenoid and quinoid rings, respectively<sup>19</sup>. The band at 1296  $\text{cm}^{-1}$  in the spectrum of a mechanical mixture of polyaniline and montmorillonite is shifted to 1301  $\text{cm}^{-1}$  in the spectra of the intercalated nanocomposites<sup>20</sup>. This shift is due to the physico-chemical interaction (hydrogen bonding between the  $-\text{NH}$  group of polyaniline and  $-\text{OH}$  of silicate) in the intercalated



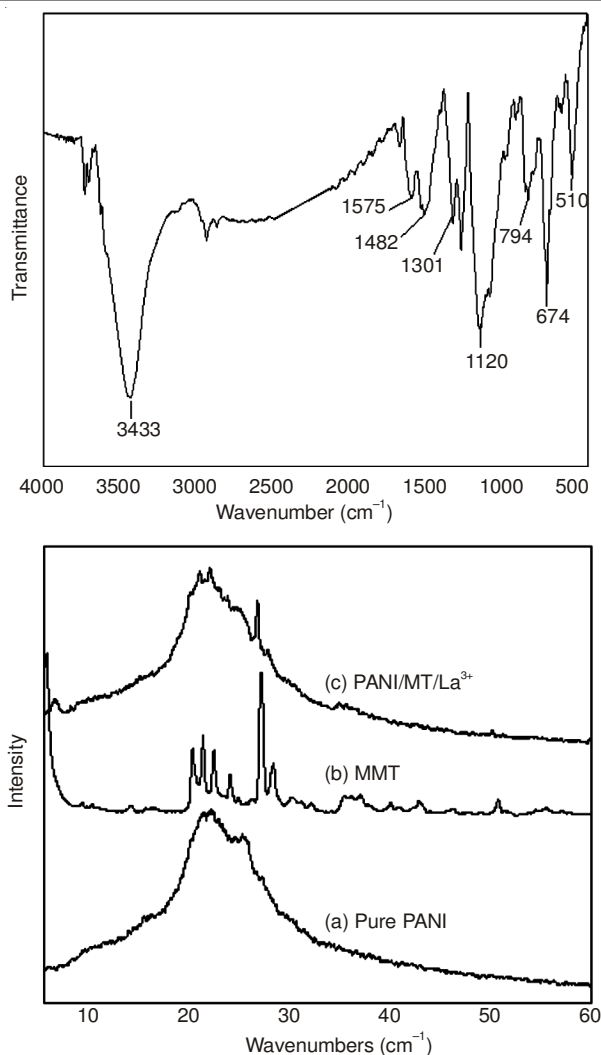


Fig. 3. FT-IR spectra of lanthanum ions-doped PANI/MMT nanocomposites (above); XRD patterns of all samples (below)

PANI-MMT<sup>21</sup> whereas mechanical mixtures of polyaniline and montmorillonite lack such an interaction. A similar trend was observed by Stutzmann and Siffert for the acetamide-montmorillonite system, the C-N stretching vibration of acetamide observed at 1380 cm<sup>-1</sup> shifted to higher wavenumbers (1400 cm<sup>-1</sup>) after adsorption onto a clay surface, they attributed this shift to the hydrogen bonding between -NH<sub>2</sub> groups of acetamide and oxygen atoms of the basal surface of the clay<sup>22</sup>. The region 900-700 cm<sup>-1</sup> corresponds to the aromatic rings and out-of-plane deformation vibrations, the band observed at position at 1120 cm<sup>-1</sup> (vibration mode of the -NH<sup>+</sup> structure), 794 cm<sup>-1</sup> (C-H out-of-plane bending vibrations)<sup>23</sup> and 510 cm<sup>-1</sup> (silicon bonds Si-O-Al)<sup>24,28</sup> further certificated the linkage of the lanthanum ions-doped PANI/MMT composites, the peak at 3435 cm<sup>-1</sup> attributes to the stretching vibration of O-H bond resulting from the presence of adsorbed molecular water<sup>8</sup>.

During the ultrasonic intercalation, anilinium ions and lanthanum ions can also be absorbed on the surface of the montmorillonite tactoid as it is structurally the same as the interlayer-oxygen basal plane with exchangeable cations. However, any such absorbed ions were most likely removed during elution with an excess of deionized water. During a sonochemical *in situ* polymerization process of the aniline

monomer in La<sup>3+</sup> and montmorillonite, the lanthanum ions-doped PANI/MMT nanocomposites have successfully synthesized. Moreover, there is a strong interaction between polyaniline, La<sup>3+</sup> and montmorillonite.

X-ray diffractions of the montmorillonite, polyaniline and lanthanum ions-doped PANI/MMT nanocomposites are presented in Fig. 3 (below). From Fig. 3a, it can be seen that the pattern of montmorillonite presents a series of peaks, which illustrates that the composites have high degree of crystallinity. In Fig. 3b, we observe two broad peaks around from 2θ = 20-25° which are characteristic peaks of polyaniline<sup>8</sup>. And the two peaks of polyaniline can be ascribed to the periodicity and perpendicular to the polymer chains<sup>25</sup>. It is evident that the XRD pattern of the nanocomposites contains contributions from both the polyaniline and the montmorillonite. However, the maximum peak centered at 2θ = 26.72° in the montmorillonite has shifted to 2θ = 26.5° and some peaks of the montmorillonite have disappeared in the nanocomposites. Moreover, it is observed that the peaks in the nanocomposites are sharper than in the pure polyaniline. These indicate that polyaniline molecules are intercalated into the galleries of the montmorillonite and the arrangement of polyaniline is more ordered in the lanthanum ions-doped PANI/MMT nanocomposites than that of pure polyaniline<sup>26,30</sup>.

The electrical conductivities of composite have been measured using a four-point probe technique. The conductivities of these composites with different montmorillonite and polyaniline molar ratio in the system are shown in Fig. 4. The conductivity of composites obtained using saturated LaCl<sub>3</sub> as doping solution in micro-emulsion is about 3.82 S cm<sup>-1</sup>, while the conductivity of composites obtained using deionized water is about 1.73 S cm<sup>-1</sup>. This may be because the La<sup>3+</sup> ions could enhance electric conductivity of the composites. Apparently the conductivities of the composites decrease with the increase of montmorillonite content used for polymerization, the conductivities of the composite prepared at the same MMT/PANI ratio decreased by about one order of magnitude (Table-1).

TABLE-1  
SYNTHESIS CONDITION OF THE NANOCOMPOSITES

Samples	Aniline (g)	Montmorillonite (g)	Solution (20 mL)	Conductivity (S cm <sup>-1</sup> )	Montmorillonite % in product <sup>*</sup>
1	2	0	LaCl <sub>3</sub> (S)	3.82	0
2	2	0.35	LaCl <sub>3</sub> (S)	2.66	0.175
3	2	0.50	LaCl <sub>3</sub> (S)	1.71	0.25
4	2	0.65	LaCl <sub>3</sub> (S)	1.15	0.325
1'	2	0	DI water	1.73	0
2'	2	0.35	DI water	0.91	0.175
3'	2	0.50	DI water	0.08	0.25
4'	2	0.65	DI water	0.03	0.325

\* (g montmorillonite/g aniline) × 100

Fig. 5 shows the TGA curves of polyaniline and lanthanum ions-doped PANI/MMT nanocomposite. In Fig. 5a-c, all the initial mass loss starting from 20 to 100 °C is attributed to the loss of water and lower molecular-weight oligomers<sup>27</sup>. Further mass loss of polyaniline that takes place at a slower rate up to 300 °C mainly due to the elimination of acid dopant (HCl) in the polyaniline system and the sharp mass loss occurring at

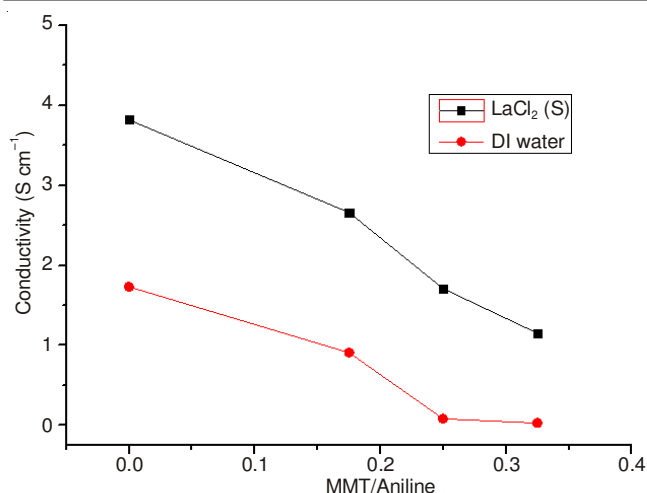


Fig. 4. Conductivities of the nanocomposites prepared at different MMT/PANI ratio and solution (with saturated  $\text{LaCl}_3$  and deionized water, respectively)

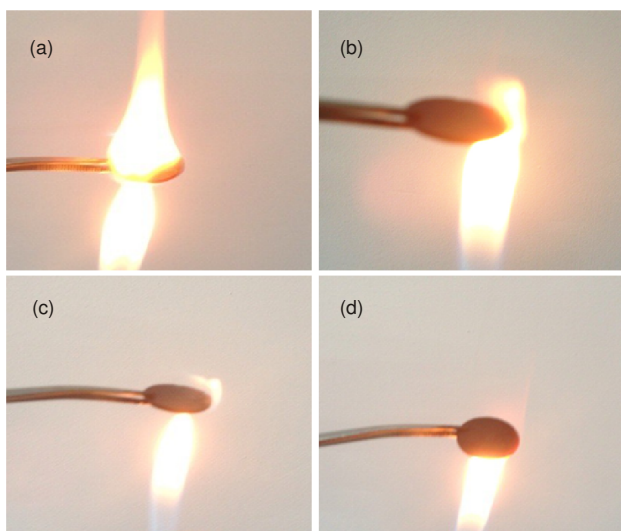
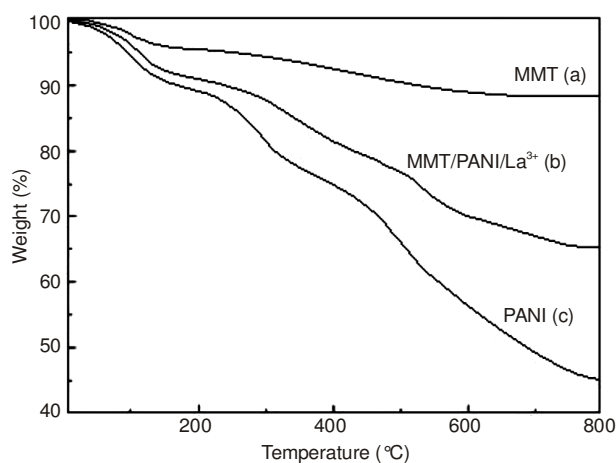


Fig. 5. TGA curves (above) of (a) MMT and (b) lanthanum ions-doped PANI/MMT nanocomposite (c) PANI; below: (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4

300 °C is possibly due to dopant anions from the polyaniline and a large of thermal decomposition of the polyaniline backbone chains. Compared Fig. 5b with 5c, it obviously shows that the weight loss curve of lanthanum ions-doped PANI/MMT nanocomposite appears above of pure polyaniline and

the weight loss curve is not sharper than pure polyaniline, indicating the enhanced thermal stability for the nanocomposite. In order to test the heat resistance of the products, a series of combustion experiments were carried out. The power of composites were firstly compressed into tablets, then the tablets were roasted on the flames of alcohol lamp. The results show that, with the montmorillonite content increasing, fire retardancy of the composites improved obviously, as shown in Fig. 5.

This markedly enhanced thermal stability of the nanocomposites can be ascribed to the montmorillonite nanolayers acting as barriers for the degradation of polyaniline in the interlayer spacings and the inorganic nanoparticles trammelled the movement of the polyaniline molecule chains. Therefore the needed energy of the thermal decomposition increased, namely the thermal stability of nanocomposite increased. The unique properties of the composites make it potentially be used as heat-resistant conductive materials.

## Conclusion

Lanthanum ions-doped PANI/MMT nanocomposites with a novel network structure and conductivity/retardant property were successfully prepared by an sonochemistry *in situ* polymerization. The nanocomposites have formed nanowires with diameter about 20-50 nm. XRD and FT-IR analysis indicate that polyaniline molecules have been successfully intercalated into the galleries of montmorillonite clay. The markedly enhanced thermal stability of the nanocomposite is believed to be ascribed to the detached montmorillonite platelets acting as barriers for the degradation of polyaniline and the inorganic nanoparticles trammelled the movement of the polyaniline molecule chains. Even more importantly, the sonochemistry *in-situ* polymerize method has the potential of promoting the high dispersions of silicate layers in a one-step process, it also demonstrates that this process can be used for fast reactions<sup>30</sup> and in the synthesis of polymer products.

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