

## CONTROLLED POLYMERIZATION OF METANILIC ANION WITHIN THE INTERLAYER OF NiAl LAYERED DOUBLE HYDROXIDE

XIAOFEI TIAN, MIN WEI\*, DAVID G. EVANS, GUOYING RAO AND HELI YANG

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

**Abstract**—The controlled chemical oxidative polymerization of metanilic anion ( $m\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$ ) within the interlayer of NiAl layered double hydroxide was performed using, for the first time, ammonium persulfate as the oxidizing agent. The quantity of oxidizing agent required for control of the interlayer polymerization was investigated systematically and it was found that interleaved polyaniline sulfonic (PANIS) was present in different oxidation states and protonation levels when different quantities of external oxidizing agents were added. A mechanism for the oxidative polymerization of metanilic anion in NiAl layered double hydroxide is proposed, based on the intercalation of the oxidizing agent and the interlayer polymerization of monomer. The resulting PANIS/NiAl LDH composites were characterized by powder X-ray diffraction, ultraviolet-visible absorption spectra, Fourier transform infrared and X-ray photoelectron spectroscopy.

**Key Words**—*In Situ* Polymerization, Layered Double Hydroxide, Polyaniline.

### INTRODUCTION

Recently, organic/inorganic nanocomposite materials have attracted extensive attention due to their unusual physicochemical properties which cannot be achieved by conventional solid-state reactions (Leroux and Besse, 2001). One focus of this investigation is the intercalation of conducting polyconjugated polymers, such as polyaniline, polythiophene and polypyrrole etc., into the ‘galleries’ within layered double hydroxides (LDHs) which are excellent anion-exchange materials and can be represented by the general formula  $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}(A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$  (where  $M^{II}$  and  $M^{III}$  are metallic cations,  $A$  is an anion) (Moujahid *et al.*, 2002; Vieille *et al.*, 2004). In the conjugated polymer/LDH nanocomposites, the polymers act as guests or functional materials which can be obtained by *in situ* polymerization of the interlayer monomer or by direct intercalation; the constrained interlamellar region of LDHs serves as a templating agent, positioning and orienting the polymer molecules within the interlayer. The interaction between hosts and guests at the nanometer scale integrates the merits of each component into the novel nanocomposites which will potentially possess electrochemical, optical or magnetic applications. Several conjugated polymer/LDH composites have been synthesized and studied, such as polyaniline/CuCr LDH, polyaniline/CuAl LDH (Challier and Slade, 1994), polyaniline/LiAl LDH (Isupov *et al.*, 2001), thiophene dimers/ZnAl LDH, thiophene dimers/ZnCr LDH (Tronto *et al.*, 2004).

It is well known that the oxidative polymerization of aniline gives rise to polyaniline existing in a variety of oxidation states (from A to C) and doping levels (D) as

depicted in Figure 1, differing greatly in color (from colorless to violet) and electrochemical properties (from insulator to metal) (Wei *et al.*, 1999). As a result, controlling the polymerization of the aniline intercalated in the restricted region of LDHs under given conditions and keeping the polymer interlayered at electroactive states are necessary for applications of the novel polyaniline/LDH nanocomposite materials.

In this study, the controlled chemical oxidative polymerization of metanilic anion ( $m\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$ ) within the interlayer region of NiAl LDH has been performed, by the use of ammonium persulfate as the oxidizing agent, for the first time. The restricted region of NiAl LDH has been used as novel nano-reaction vessels for the *in situ* polymerization of interlayer monomers (Moujahid *et al.*, 2003). The effect of the quantity of oxidizing agent on the oxidation states and the protonation levels of the PANIS formed in the interlayer has been investigated, and the mechanism of the interlayer oxidative polymerization has been proposed. The characteristics of the resulting PANIS/NiAl LDH composites were identified through X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Therefore, the polymerization of metanilic anion in the restricted environment between LDH sheets creates new opportunities for further research into chemical reactions in inorganic hybrids at the nanoscale and for their use in catalytic applications.

### EXPERIMENTAL

#### Reagents

All the chemicals used in this synthesis, including  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , NaOH, metanilic acid

\* E-mail address of corresponding author:

weimin@mail.buct.edu.cn

DOI: 10.1346/CCMN.2006.0540402

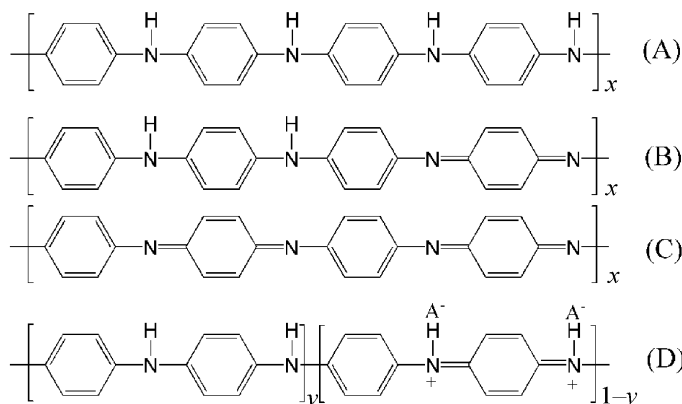


Figure 1. Variable redox states and doping levels of polyaniline.

(*m*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H), and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were of analytical grade, purchased from Aldrich, and used without further purification. All solutions were prepared using distilled and decarbonated water.

#### Synthesis

The precursor LDH [Ni<sub>2</sub>Al(OH)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>·*n*H<sub>2</sub>O was prepared following a standard aqueous co-precipitation and thermal crystallization method (Wilson *et al.*, 1999). A solution of NaOH (8.0 g, 0.20 mol) in water (100 cm<sup>3</sup>) was added dropwise over 2 h to 100 cm<sup>3</sup> of a solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (19.4 g, 0.066 mol) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (12.5 g, 0.033 mol) with vigorous stirring under a nitrogen atmosphere. The value of the solution pH at the end of the addition was 6.0. The resulting gelatinous precipitate was maintained at 100°C for 72 h, centrifuged and then washed thoroughly until the pH of the supernatant solution was 7.0. The powder was dried at 70°C for 24 h under vacuum.

The metanilic intercalated NiAl LDH was prepared following the ion-exchange method. A 100 cm<sup>3</sup> solution of metanilic acid (5.2 g, 3.0 mmol) with pH adjusted to 6.5 was added to a suspension of NiAl-NO<sub>3</sub> LDH (5.0 g, ~1.5 mmol) in water (100 cm<sup>3</sup>). The mixture was held at 30°C under a nitrogen atmosphere for 72 h. The product was washed extensively with water, centrifuged and dried under vacuum for 24 h.

The PANIS/LDH was synthesized by oxidizing the metanilic LDH through an external oxidizing agent [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]. Three samples were prepared with different quantities of the oxidizing agent in order to investigate its effect on the reaction products. Powders of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> weighing 0.002 g, 0.02 g and 0.2 g were added to a suspension of 2.0 g metanilic LDH in 100 cm<sup>3</sup> water under a nitrogen atmosphere. The pH of the slurries was adjusted to 6.5 using NaOH (2.0 M) and maintained at room temperature for 72 h. The products were washed extensively, centrifuged and dried under vacuum for 24 h.

#### Characterization

Powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using CuK $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV, 30 mA. Data were collected over the angular range from 3 to 70°2 $\theta$  at a scanning rate of 0.02° s<sup>-1</sup> at room temperature.

The UV-vis spectra were collected in reflectance mode using a Shimadzu UV-2401 spectrophotometer, in the ~240–800 nm region with the samples dissolved in 0.1 M hydrochloric acid solution.

Fourier transform infrared spectra were recorded using a Vector22 (Bruker) spectrophotometer in the range 4000 to 400 cm<sup>-1</sup> with 2 cm<sup>-1</sup> resolution. A standard KBr disk (1 mg of sample in 100 mg of KBr) was used.

The chemical compositions, the local environmental changes of the atoms and the quantitative evaluation of the various oxidation states of PANIS were determined by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCALab220i-XL (VG Scientific Ltd., UK) spectrometer. Before scanning, the sample was sputtered using Ar gas to remove absorbed impurities on the surface. In recording the spectra, AlK $\alpha$  irradiation was employed as the photon source with a primary tension of 12 kV and an emission current of 20 mA. The pressure of the analysis chamber during the scans was  $\sim 3 \times 10^{-9}$  mbar. In the data analysis, the binding energy (BE) of the core level C 1s peak was set at 284.5 eV to compensate for surface-charging effects. The satellite peaks were removed for all element peaks before curve fitting. The iteration curve fit program (Levenberg-Marquardt method) was customized in order to meet the specific needs of resolving N 1s peaks in the spectrum. The experimental spectra were fit with Gaussian profiles. The surface elemental compositions were determined by the ratios of peak areas corrected with empirical sensitivity factors.

Elemental analysis was performed with a Shimadzu ICPS-7500 instrument. The C, H and N contents were determined using an Elementarvario elemental analysis

Table 1. Chemical compositions of NiAl-NO<sub>3</sub> LDH and the organic intercalated LDHs.

Samples	Chemical composition
NiAl-NO <sub>3</sub> LDH	Ni <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>0.33</sub> ·0.74H <sub>2</sub> O
Metanilic-LDH	Ni <sub>0.66</sub> Al <sub>0.34</sub> (OH) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> SO <sub>3</sub> ) <sub>0.23</sub> (NO <sub>3</sub> ) <sub>0.11</sub> ·0.78H <sub>2</sub> O
Sample 1	Ni <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> SO <sub>3</sub> ) <sub>0.23</sub> (NO <sub>3</sub> ) <sub>0.08</sub> (SO <sub>4</sub> ) <sub>0.01</sub> ·0.78H <sub>2</sub> O
Sample 2	Ni <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> SO <sub>3</sub> ) <sub>0.23</sub> (NO <sub>3</sub> ) <sub>0.02</sub> (SO <sub>4</sub> ) <sub>0.04</sub> ·0.77H <sub>2</sub> O
Sample 3	Ni <sub>0.66</sub> Al <sub>0.34</sub> (OH) <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> SO <sub>3</sub> ) <sub>0.22</sub> (SO <sub>4</sub> ) <sub>0.06</sub> ·0.74H <sub>2</sub> O

Samples 1, 2 and 3 refer to NiAl-metanilic LDH treated with 0.002 g, 0.02 g and 0.2 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, respectively.

instrument. The chemical compositions of NiAl-NO<sub>3</sub> LDH and the organic intercalated LDHs are reported in Table 1.

## RESULTS AND DISCUSSION

### Powder X-ray diffraction

The powder XRD patterns of the NiAl-NO<sub>3</sub> LDH, NiAl-metanilic LDH and the oxidative products are shown in Figure 2. Table 2 lists the corresponding basal spacing and lattice parameters. The reflections of all the materials can be indexed to a hexagonal lattice with  $\bar{R}3m$  rhombohedral symmetry, commonly used for the description of the LDH structures (Whilton *et al.*, 1997). The XRD pattern for NiAl-metanilic LDH exhibits the characteristic reflections for inorganic LDH materials. The layer thickness for the new compound is ~1.63 nm, which is 0.74 nm greater than that of the NiAl-NO<sub>3</sub> LDH. The expansion of the basal spacing resulted from the intercalation of metanilic anion into the LDH interlayer. Thus, the interaction of NiAl-NO<sub>3</sub> LDH with an aqueous solution of metanilic acid at pH 6.50 led to the anion exchange of NO<sub>3</sub><sup>-</sup> for the anions of metanilic acid with the conservation of the layered structure.

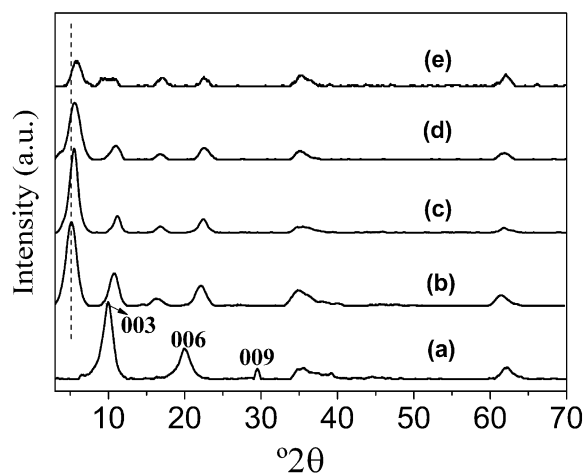


Figure 2. XRD patterns for NiAl-NO<sub>3</sub> LDH (a), NiAl-metanilic LDH (b), and NiAl-metanilic LDH treated with 0.002 g (c), 0.02 g (d) and 0.2 g (e) of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

An interlayer thickness of 1.15 nm for NiAl-metanilic LDH was obtained by subtracting the thickness of the Al hydroxide sheet (0.48 nm) from the layer thickness (1.63 nm). This thickness is greater than the length of a single metanilic anion chain oriented normal to the hydroxide sheets (0.64 nm, calculated using Chemwin 6.0), but it is less than twice that value. This may indicate that the monomer anions adopted an interpenetrating arrangement leaving interstices between the monomer anions and the hydroxide sheet. Water molecules and nitrate anions may occupy these interstices. The structure of LDHs is based on brucite-like sheets, where octahedrally coordinated metal ions share edges to form infinite sheets (Brindley and Kikkawa, 1979). The area within the 00 $l$  plane occupied by each [Ni<sub>1-x</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup> octahedral unit is related to the unit-cell parameter  $a$  by the formula:  $S = \sqrt{3}(a^2/2)$  (Yun and Pinnavaia, 1995). The value of  $a$  can be calculated from  $d_{110}$  as determined using the XRD pattern in Figure 2b ( $a = 2d_{110} = 0.30$  nm). The area of each octahedral unit is therefore 0.78 nm<sup>2</sup>, giving one positive charge per 2.30 nm<sup>2</sup> in the case of  $x = 0.34$ . The maximum dimension of the anion was calculated as 0.60–0.70 nm, and thus the corresponding cross-sectional area of the complex anions can be estimated to be in the range 2.80–3.80 nm<sup>2</sup>. Consequently, it is impossible for the metanilic anion alone to balance the positive charge of the hydroxide sheet, suggesting the co-intercalation of NO<sub>3</sub><sup>-</sup>. The presence of nitrate and water was also supported by the results of elemental analysis (Table 1). Based on the discussion above, the structure of NiAl-metanilic LDH can be represented as alternating NiAl hydroxide sheets and interlayers containing metanilic anions, nitrate anions and water molecules. The schematic model of NiAl-metanilic LDH is illustrated in Figure 3.

The XRD patterns of the samples to which 0.002 g, 0.02 g and 0.2 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were added, are shown in Figure 2c–e, respectively. Apparently, the values of lattice parameter  $a$  for the three products are the same. However, the  $d_{003}$  values of the three products decreased slightly from 1.61 nm (0.002 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) to 1.51 nm (0.2 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), indicating that a reorientation of the interlamellar species occurred. This phenomenon is usually observed in the case of an *in situ* polymerization,

Table 2. Lattice parameters (nm) of NiAl-NO<sub>3</sub> LDH and the intercalated materials.

LDHs	NiAl-NO <sub>3</sub> LDH	Metanilic-LDH	Sample 1	Sample 2	Sample 3
$d_{003}$	0.89	1.63	1.61	1.58	1.51
$d_{110}$	0.15	0.15	0.15	0.15	0.15
interlayer spacing	0.41	1.15	1.13	1.10	1.03
lattice parameter $a$	0.30	0.30	0.30	0.30	0.30
lattice parameter $c$	2.67	4.89	4.83	4.74	4.53

Samples 1, 2 and 3 refer to NiAl-metanilic LDH treated with 0.002 g, 0.02 g and 0.2 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, respectively.

as is illustrated by the *in situ* polymerization of  $\alpha,\beta$ -aspartate into hydrotaalcite-type compounds (Whilton *et al.*, 1997), vinyl and amino-benzene sulfonates (VBS and ABS) into the sheets of Zn<sub>2</sub>Al LDHs (Moujahid *et al.*, 2003), and Cu<sub>2</sub>Cr LDHs (Moujahid *et al.*, 2005) after a soft thermal treatment ( $T = 473$  K). Therefore, the occurrence of *in situ* polymerization of the intercalated metanilic anion monomer in the restricted region of NiAl LDH can be deduced from the decrease in the  $c$  parameter. This was further confirmed by UV-vis, FTIR and XPS.

#### UV-vis spectroscopy

Results obtained by UV-vis spectroscopy yield strong evidence for the polymerization of the metanilic anion intercalated with NiAl LDH and provide information regarding the oxidation states of the interlayer products. Figure 4 shows the optical absorption spectra of metanilic anion and the intercalated materials in the wavelength range ~240–800 nm. There are only two absorption bands at 262 nm and 269 nm in spectrum a. These are associated with the phenyl group of the metanilic monomer. No shift or intensity change of these two absorption bands was observed after the intercalation of the metanilic anion into the NiAl LDH in spectrum b. Following the addition of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, a weak absorption band (centered at 300 nm) correspond-

ing to the  $\pi_B-\pi_B^*$  transition appeared in spectrum c, indicating the occurrence of polymerization of the intercalated monomer; the polymerization occurred between the benzenoid units. The new absorption band centered at 550 nm in spectrum d can be attributed to charge transfer from the quinoid to the benzoid segments ( $\pi_Q-\pi_B^*$ ) (Kang *et al.*, 1998), which shifted hypsochromically to 510 nm in spectrum e. Moreover, the highly oxidized pernigraniline transmits at ~400 nm, which can also be observed in spectrum e. The  $\pi_Q-\pi_B^*$  transition demonstrates that quinonoid units formed in the polymeric products (0.02 g and 0.2 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), and the hypsochromic shift of this absorption band indicates that the oxidation state of the interlayer product was promoted remarkably. This result is quite consistent with the report on the study of the interconversion of polyaniline oxidation states by optical absorption spectroscopy (Albuquerque *et al.*, 2004). A similar optical spectrum has been observed for polyaniline films deposited from the vapor phase onto silica substrates, in which the optical spectrum was attributed to polyaniline units with chain length less than in 'conventional' polyaniline but greater than in five-ring oligomers (Luca and Thomson, 2000). Based on the comparison between our results and those in the literature, this optical spectrum of PANIS/LDH is therefore indicative of short chains of interlayer PANIS in this work.

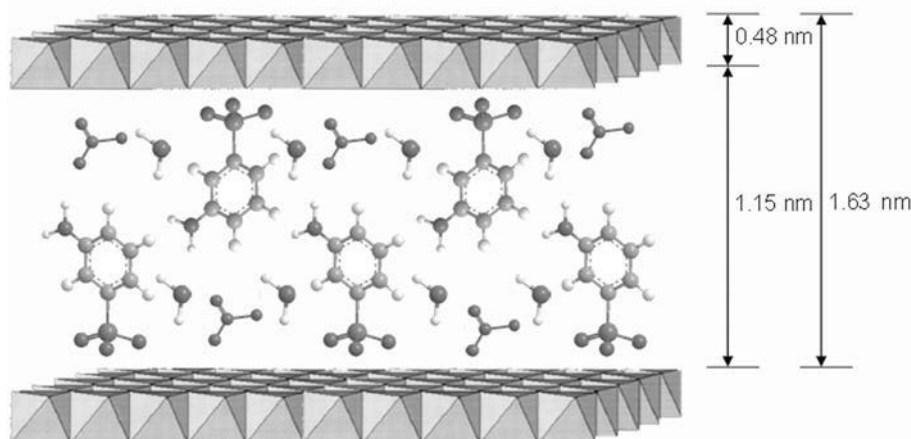


Figure 3. A schematic representation of the possible arrangement for NiAl-metanilic LDH.

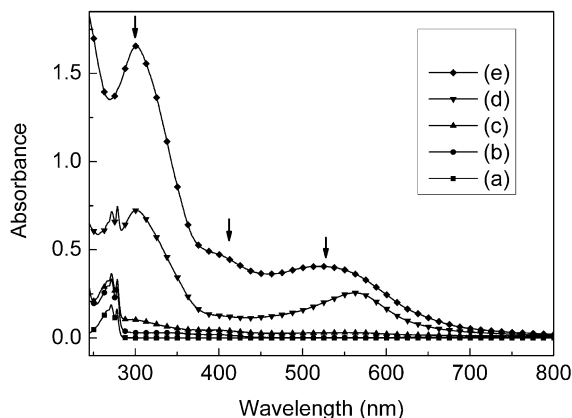


Figure 4. UV-vis spectra of metanilic acid (a), NiAl-metanilic LDH (b), and NiAl-metanilic LDH treated with 0.002 g (c), 0.02 g (d) and 0.2 g (e) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

#### FTIR spectroscopy

Figure 5 shows the FTIR spectra of NiAl- $\text{NO}_3$  LDH, NiAl-metanilic LDH and the three polymerization products. The broad bands around  $3448\text{ cm}^{-1}$  (Figure 5a) and  $3442\text{ cm}^{-1}$  (Figure 5b) correspond to the O–H-stretching vibration of surface and interlayer water in LDH. These vibrations occur at lower frequency than for the O–H in free water at  $3600\text{ cm}^{-1}$  (Li *et al.*, 2004). This suggests the formation of hydrogen bonding between interlayer water and the guest anions as well as the layer hydroxide groups. The absorption band at  $1384\text{ cm}^{-1}$  of the metanilic intercalated LDH (Figure 5b) is due to the stretching vibration of  $\text{NO}_3^-$ , and compared with the NiAl- $\text{NO}_3$  LDH precursor (Figure 5a); the relative intensity of this band decreased

remarkably. Three strong bands at 1599, 1484,  $1453\text{ cm}^{-1}$  and a weak one at  $1315\text{ cm}^{-1}$  were observed, all of which can be attributed to characteristic absorptions of metanilic anion (Liu *et al.*, 2004). Moreover, the broad band at  $1170\text{ cm}^{-1}$  was attributed to the presence of para-substituted aromatic C–H ( $\delta$  in plane) and the aromatic C–N ( $\nu$ ). The bands at 1110 and  $1035\text{ cm}^{-1}$  were characteristic absorptions of the symmetric vibration of S–C and S=O, respectively (Liu and Kanatzidis, 1995). The absorption bands of lattice vibrations appeared in the range  $400\text{--}650\text{ cm}^{-1}$ .

The FTIR spectra of the samples treated with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  reveal the different oxidation states of the interlayer polymer. The intensity of the absorption bands at 1599, 1484 and  $1454\text{ cm}^{-1}$  assigned to the vibration of  $-\text{B}-$  and  $-\text{Q}-$  became gradually weaker with increased  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration (Figure 5). This indicates that the degree of oxidation of the polymerization products increases with the quantity of oxidizing agent. The bands at 1523, 1474 and  $1431\text{ cm}^{-1}$  of the sample with 0.2 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Figure 5e) indicate that the polymerization product has almost a  $-\text{Q}-$  structure (Huber, 2003). Comparison of IR spectra between the original metanilic-intercalated LDH and its oxidation products reveals a sharp decrease in the bands at  $1170$  ( $\nu_{\text{C-H}}$  in plane), 1270 and  $1315\text{ cm}^{-1}$ , which point to a substantial decrease in the number of amino groups ( $-\text{NH}_2$ ). This further confirmed the formation of an interlayer polyconjugated system.

#### XPS determination

The XPS N 1s core level spectra of NiAl-metanilic LDH samples that were untreated and treated with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  are shown in Figure 6. The main banding

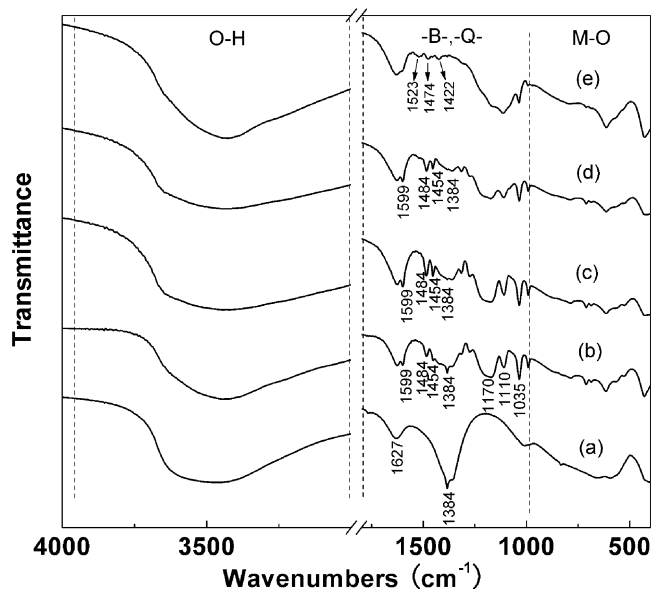


Figure 5. FTIR spectra for NiAl- $\text{NO}_3$  LDH (a), NiAl-metanilic LDH (b), and NiAl-metanilic LDH treated with 0.002 g (c), 0.02 g (d) and 0.2 g (e) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

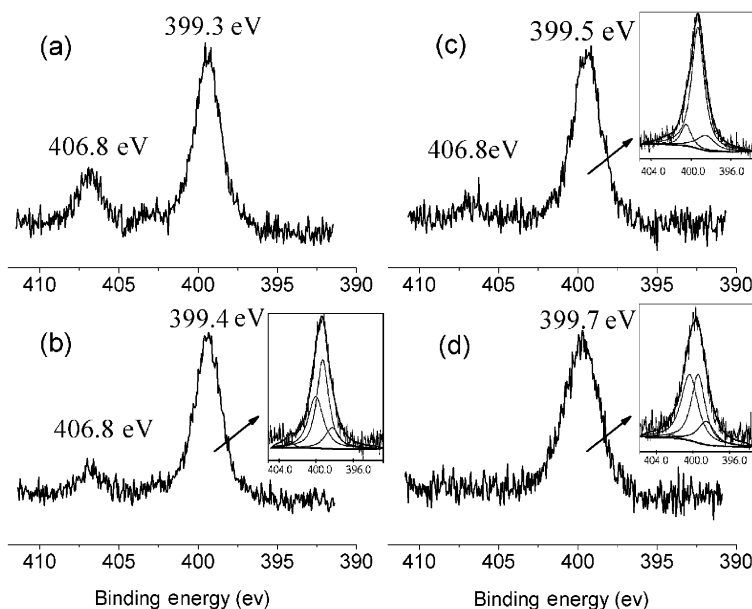


Figure 6. XPS N 1s spectra and peak-curve fit for NiAl-metanilic LDH (a), and NiAl-metanilic LDH treated with 0.002 g (b), 0.02 g (c) and 0.2 g (d) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

energy moved from 399.3 eV in NiAl-metanilic LDH (Figure 6a) to 399.7 eV after treatment with 0.2 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Figure 6d) and the FWHM (full width at half maximum) increased from 1.84 to 2.35 eV. It is reasonable to deduce that the chemical environment of N in the metanilic monomer has changed remarkably due to the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and interlayer PANIS with different oxidation states formed after treatment with different quantities of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

The aniline polymers have the general formula  $[(-B-NH-B-NH-)_y (-B-N=Q=N-)_{1-y}]_x$  (Stejskal *et al.*, 1996), in which *B* and *Q* denote the  $\text{C}_6\text{H}_4$  rings in the benzenoid and quinonoid forms, respectively. Thus, the neutral intrinsic redox states can vary from that of the fully oxidized pernigraniline (PNA,  $y = 0$ ), to that of the fully reduced leucoemeraldine (LM,  $y = 1$ ). The 50% intrinsically oxidized polymer has been termed emeraldine (EM,  $y = 0.5$ ). In particular, the proportions of quinonoid imine ( $=N-$ ), benzenoid amine ( $-NH-$ ), and positively charged nitrogens corresponding to a particular oxidation and protonation level of the polymer

can be quantitatively differentiated in the properly curve-fitted N 1s core level spectrum (Chen and Wen, 2003).

The XPS N 1s core level spectra of the oxidized samples (Figure 6b–d) show four contributions which can be assigned to  $\text{C}=\text{N}$  (398.3 eV),  $\text{C}-\text{N}$  (399.3 eV),  $\text{C}=\text{N}^+$  (400.6 eV) and  $\text{C}-\text{N}^+$  (402.8 eV) based on the binding energy of core electrons, respectively (Kang *et al.*, 1998). The relative area ratios of the four components as well as their respective binding energy are given in Table 3. According to the results of previous XPS studies on chemically and electrochemically synthesized polyaniline, the oxidation level of the three products can be estimated by calculating the ratio of quinonoid imino ( $=N-$ ) total peak area to benzenoid amino ( $-NH-$ ) total peak area and the protonic ratio can be obtained by dividing the total peak area of  $\text{C}-\text{N}$  by the total peak area of  $\text{C}-\text{N}^+$  (Nascimento *et al.*, 2004). It can be seen from Table 3 that the samples treated with different amounts of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  are in different oxidation states and protonation levels. Increasing

Table 3. XPS semi-quantitative analysis of NiAl-metanilic LDH treated with different amounts of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

Samples	Color	— (At.%) —		Relative peak area (%)				$=N-/-N-$	$\text{N}^+/\text{N}$
		N 1s	S 2p	$\text{C}-\text{N}^+$ (402.8 eV)	$\text{C}=\text{N}^+$ (400.6 eV)	C-N (399.3 eV)	C=N (398.3 eV)		
Sample 1	green	3.0	3.4	1	11	75	13	0.32	0.14
Sample 2	blue	2.2	4.0	2	35	49	14	0.96	0.59
Sample 3	violet	2.1	5.3	1	45	38	16	1.56	0.85

Samples 1, 2 and 3 refer to NiAl-metanilic LDH treated with 0.002 g, 0.02 g and 0.2 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , respectively.

treatment with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  resulted in increased ratios of  $[\text{=N-}]/[\text{-NH-}]$  and  $[\text{N}^+]/[\text{N}]$  from 0.32 to 1.56 and 0.14 to 0.85, respectively. Thus, the quantity of oxidizing agent had a significant effect on the state of the polymerization products in this work. Furthermore, the colors of the 0.002 g, 0.02 g and 0.2 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  treated samples were green, blue and violet, respectively, consistent with a change in their oxidation states.

As shown in Figure 6a, the peak at 406.8 eV that is generally attributed to the nitrogen of nitrate was rather strong, indicating the coexistence of  $\text{NO}_3^-$  and the  $m\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$  monomer between the host layers. However, this peak decreased significantly along with the occurrence of oxidative polymerization. It became weaker with increased oxidation, and almost disappeared following the 0.2 g  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  treatment (Figure 6d). This agrees with the results of the elemental analysis (Table 1), further confirming that the interlayer co-existing  $\text{NO}_3^-$  was exchanged by the persulfate anions gradually during a process of interlayer polymerization. The relative atomic concentrations calculated from corresponding photoelectron peak areas are presented in Table 3. It can be seen that the percentage of N content decreased from 3.4 to 2.1% along with the increase in the percentage of S from 3.2 to 5.3%. A deduction can be obtained from the data listed above that  $\text{S}_2\text{O}_8^{2-}$  anions exchanged the co-existing nitrate anions in LDH and initiated the polymerization of the interlayer monomer. This might be due to the greater affinity of  $\text{S}_2\text{O}_8^{2-}$  for LDH layers than that of  $\text{NO}_3^-$ . Additionally, the absorption band at  $1384\text{ cm}^{-1}$  assigned to the presence of nitrate species decreased along with the polymerization reaction (Figure 5b–e), providing further evidence for this conclusion.

**Possible mechanism of polymerization.** Based on the experimental data above, the oxidative polymerization of the metanilic anion between the sheets of NiAl LDH can be interpreted as follows: The  $m\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3^-$  anions intercalated in NiAl LDH are in an interpenetrating arrangement. Water molecules and co-existing nitrate anions occupy the interlayer interstices. Following the addition of an oxidizing agent,  $\text{S}_2\text{O}_8^{2-}$  intercalated into the host layer by ion-exchange with  $\text{NO}_3^-$  and initiated the oxidative polymerization of the

interlayer monomer. According to the much earlier work of Mohilner *et al.* (1962), the aniline oxidation products obtained in neutral or acid media have a predominantly ‘head to tail’ arrangement. The oxidation state of the PANIS formed in the interlayer was enhanced along with an increase of the oxidizing agent, and the change in color of the three polymeric products confirms the corresponding promotion in the oxidation states. In summary, the interlayer oxidative polymerization of metanilic anion monomer is shown in Figure 7.

## CONCLUSIONS

The controlled chemical oxidative polymerization of a metanilic anion monomer within the interlayer of NiAl LDH was performed using, for the first time, ammonium persulfate as the oxidizing agent. Powder XRD was used to determine the structural change of NiAl- $\text{NO}_3$  LDH and the intercalated materials. The expansion of the basal spacing gave evidence that metanilic anions were intercalated into the LDH interlayer regions successfully. The progressive contraction of the basal spacings of the structure upon increased oxidation implies the occurrence of interlayer polymerization.

The UV-vis spectra give strong evidence for the intercalation and polymerization of metanilic anion in NiAl LDH and provide information regarding the oxidation states of the interlayer products. The absorption bands centered at 300 and 550 nm are indicative of  $\pi_{\text{B}}-\pi_{\text{B}}^*$  and  $\pi_{\text{Q}}-\pi_{\text{B}}^*$  transitions, respectively. The hypsochromic shift of the  $\pi_{\text{Q}}-\pi_{\text{B}}^*$  transition absorption indicates that the oxidation state of the interlayer product was increased remarkably with an increase in the quantity of oxidizing agent. The characteristic absorption bands of the aniline and sulfonic anions in FTIR spectra demonstrate the intercalation of metanilic anion compared with the NiAl- $\text{NO}_3$  LDH precursor. The changes in the characteristic absorption bands assigned to the vibration of  $-\text{B}-$  and  $-\text{Q}-$  indicate that the oxidative degree of the polymerization products increased along with increasing quantity of oxidizing agent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

X-ray photoelectron spectroscopy was used to determine the chemical compositions, the chemical environment changes of the N atom and the quantitative

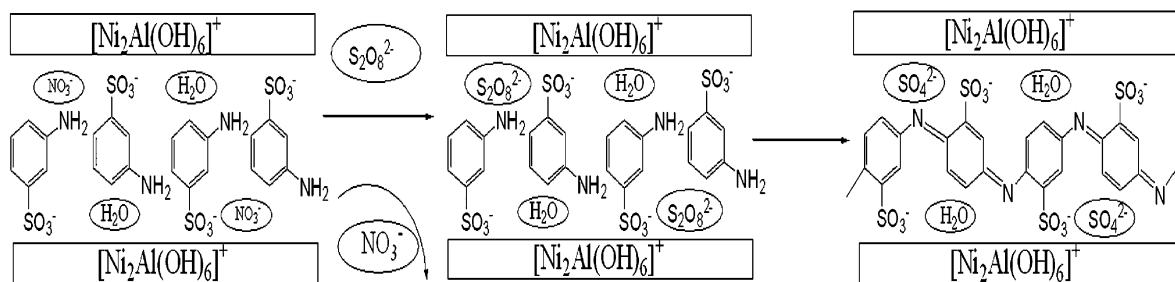


Figure 7. The interlayer oxidative polymerization of the metanilic monomer by the oxidizing agent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

evaluations of the various oxidation states of interlayer PANIS. The oxidation level  $[=N^-]/[-NH-]$  and the protonic ratio  $[N^+]/[N]$  with increased treatment with  $(NH_4)_2S_2O_8$  confirms that the quantity of oxidizing agent has a significant effect on the oxidation states of the polymerization products. In addition, the decrease of the relative atomic concentration of N along with the increase of S indicates that  $S_2O_8^{2-}$  anions exchanged for  $NO_3^-$  anions in the LDH interlayer and initiated the polymerization of interlayer monomer. Therefore, the study of the polymerization of metanilic anion in a restricted environment between LDH sheets may have applications for a novel nanoreaction vessel for confined chemical reactions.

#### ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation Key Project of China (Project No. 90306012), the National Natural Science Foundation Major International Joint Research Program (Project No. 20620130108), the Beijing Nova Program (No. 2004A13), and the Program for Changjiang Scholars and Innovative Research Team in the University (PCSIRT).

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(Received 25 November 2005; revised 15 March 2006; Ms. 1118 ; A.E. Peter J. Heaney)