

Immobilization of the Highly Dispersed Fullerene on the Surface of Cyclodextrin Modified Layered Double Hydroxides Film

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A novel method was studied for the immobilization of the fullerene on the surface of cyclodextrin modified layered double hydroxides film. The supramolecular structure, physico-chemical behaviour and thermal decomposition were characterized by XRD, UV-VIS, NMR and TG-DTA. The XRD results show that the basal spacing of the resulting C₆₀/CMCD-LDH film is similar with that of the CMCD-LDH film. Moreover, the UV-VIS result indicates the interaction between C₆₀ with inclusion host-CMCD, which confirmed the fullerene was only included by the CMCD on the surface of LDH. The thermal decomposition of C₆₀/CMCD-LDH was also investigated by TG-DTA measurements. Compared with the pure fullerene, the thermal stability of C₆₀/CMCD-LDH is reduced after highly dispersed and its combustion temperature decreased by 100 °C. Therefore, this work provides a novel dispersed fullerene based on functionalized CD/layered material composite. Furthermore, the schematic model of the inclusion structure has been proposed. Further investigation will focus on the photoelectrochemical and optical limiting properties of these fullerene-trapped layered double hydroxide materials.

Key Words: Fullerene, Layered double hydroxides, Carboxymethyl- γ -cyclodextrin, Highly dispersed, Film.

INTRODUCTION

Fullerenes have been extensively studied during the past decade¹⁻⁵ and a high number of organic derivatives and composites have been prepared and characterized. Due to the intriguing physical and chemical properties, fullerenes and their derivatives have been shown to be promising favourable magnetic, superconductivity, electrical, non-linear optics, ion-selective electrode, single-molecule devices and organic memory devices⁶⁻¹⁰. For many of the applications, it requires the preparation of fullerene-containing films on desired surfaces and the successful application of these devices relies greatly on the degree of the film order. Methods used to prepare fullerene containing films include solution casting¹¹, thermal evaporation^{12,13}, Langmuir and Langmuir-Blodgett films¹⁴ and self assembled monolayers (SAMs)¹⁵. By far the self assembled monolayers is the most effective method to organize a two-dimensional highly ordered fullerene-containing assembly on various substrates. Echegoyen *et al.*¹⁶ reported the first example of self assembly of [60] fullerene (C₆₀) derivative driven by the molecular recognition between the crown ethers linked to C₆₀ and the ammonium groups attached to the gold surfaces. Most recently, the work was extended to the noncovalent self

assembly of native C₆₀ *via* the interfacial supramolecular recognition by surface-attached host systems such as cyclotrivenylene derivatives¹⁷, calixarene derivatives¹⁸ and porphyrin derivatives¹⁹. Among the various hosts for fullerenes, cyclodextrins (CDs) have received considerable attentions since the time when pioneering work was performed by Anderson *et al.*²⁰ to embed C₆₀ from water by the selective complexation with γ -cyclodextrin. Recently, well-ordered arrays of complexes of C₆₀ and a γ -cyclodextrin derivative have been constructed on a gold surface²¹.

Layered double hydroxides (LDHs, also known as anionic clays), are a class of layered materials consisting of positively charged brucite-like layers and exchangeable interlayer anions, which have recently received increasing attention, owing to their versatility and usefulness in a wide range of technological applications such as catalysis²², functional materials²³⁻²⁶, two-dimensional solid-state nanoreactors²⁷, bioactive nanocomposites²⁸ and so on. Layered double hydroxides can be represented by the general formula [M²⁺_{1-x}M³⁺_x(OH)₂]^{x+}(Aⁿ⁻_{x/n})⁻mH₂O, where M²⁺ and M³⁺ are divalent and trivalent metal cations, such as Mg²⁺ and Al³⁺, respectively and Aⁿ⁻ is an anion, such as CO₃²⁻, SO₄²⁻ or NO₃⁻. The structure of LDHs is most clearly described by considering the brucite-like structure, M(OH)₂,

which consists of M^{2+} ions coordinated octahedrally by hydroxyl groups, with the octahedral units sharing edges to form infinite, charge-neutral layers. In the commonly observed powder form, LDHs have a house-of-cards structure involving edge-to-face particle interactions, which limits their research and application²⁹. The most effective solution to this problem may be preparation of LDHs film on substrates³⁰⁻³⁴. Jung and co-workers used the ultrasonification method to prepare monolayer of LDH films with a high packing density and a preferred orientation with the *c*-axis perpendicular to the substrate surface^{32,33}, whilst Sasaki and co-workers reported that the exfoliation of LDH in organic solvents (formamide, for instance) gives colloidal LDH particles which can be used as building blocks in the preparation of transparent oriented LDH films by layer-by-layer techniques³⁴. Our group has recently reported fabrication of NiAl-LDH film with the *c*-axis parallel to the substrate, by means of employing porous anodic alumina/aluminum as both substrate and sole source of aluminum^{30,35,36}.

In recent years, the immobilization of CDs with layered supports has attracted much attention. Modified CDs have been used as a "guest" molecule incorporating into layered hosts such as α -zirconium phosphate³⁷, montmorillonite³⁸ and layered double hydroxides^{39,40}. In previous work, the intercalation of sulfated β -CD into LDH as well as the structural characterization, thermal decomposition behaviour have been studied^{41,42}. Recently we have shown that when the internal surfaces of the layered anionic clay (Zn-Al LDH) are functionalized by anchoring anionic carboxymethyl β -cyclodextrin (CMCD) cavities, neutral guest molecule can be enantioselectively included within it^{35,36,43}.

In this study, the structured CMCD-LDH film was fabricated by the method of *in situ* crystallization on a porous anodic alumina/aluminum (PAO/Al) substrate. In this film, the *ab*-face of LDH microcrystals is perpendicular to the substrate and the LDH plates are exposed to the outside, which is favourable to include solute from solutions. Then the CMCD-LDH film was added into xylene solution of C_{60} and was heated for 72 h at 70 °C. It was found that the fullerene molecules were immobilized in the CMCD cavities on the surface of the CMCD-LDH film (schematized in Fig. 1). Therefore, we developed a novel method for the preparation of self assembly C_{60} on the surface of carboxymethyl- γ -cyclodextrin (CMCD) modified LDH (CMCD-LDH).

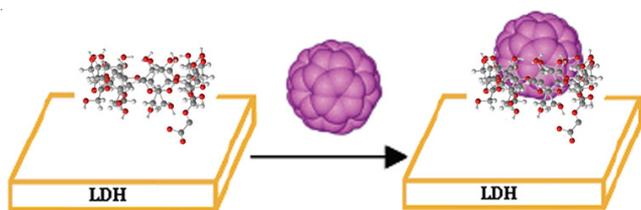


Fig. 1. Schematic representation for the immobilized fullerene in the CMCD cavities on the surface of LDH film

EXPERIMENTAL

All chemicals including $Zn(NO_3)_2 \cdot 6H_2O$, NH_4NO_3 , $NH_3 \cdot H_2O$, chloroacetic acid, γ -cyclodextrin and C_{60} were of analytical grade. γ -Cyclodextrin was purchased from Aldrich and the others from the Beijing Chemical Plant Limited.

Aluminum metal sheet was purchased from Shanghai Jing Xi Chemical Technology Co. Ltd., purity: > 99.5 %, thickness: 0.1 mm.

Preparation and characterization

Synthesis of carboxymethyl- γ -cyclodextrin, CMCD (4.7): CM- γ -CD was synthesized according to the procedure described in the literature⁴⁴ with some modifications. In brief, γ -CD (37.8 g) and NaOH (35.2 g) was dissolved in 200 mL of water and monochloroacetic acid (44.1 g) was added with gentle stirring. The mixture was heated at 90 °C for 3 h. The solution was then cooled in an ice bath and the pH was adjusted to 6.0 with concentrated hydrochloric acid. Furthermore, methanol was gradually added into the solution with stirring to obtain CMCD precipitation. The average number of carboxylate groups (4.7) per CMCD was calculated using 1H NMR⁴⁵.

Synthesis of CMCD-LDH film: The CMCD-LDH film was prepared by *in situ* crystallization on a porous anodic alumina /aluminum (PAO/Al) substrate. The porous anodic alumina film was fabricated by anodizing an aluminum metal sheet for 50 min in a thermostatic bath of 1M H_2SO_4 at 25 °C and with a current density of 20 mA cm^{-2} . In this experiment, PAO/Al was used as both the substrate and the sole source of aluminum. In a typical procedure, 0.01 mol of $Zn(NO_3)_2 \cdot 6H_2O$, 0.06 mol of NH_4NO_3 and 0.001 mol of CMCD were dissolved in deionized water to form a clear solution with a total volume of 100 mL and the pH was adjusted to 6.5 by adding diluted ammonia (1 % NH_4OH). The PAO/Al substrate was then placed vertically in the solution at 70 °C for 48 h, to obtain the CMCD-LDH microcrystals grown on the surface of the substrate. Finally, the substrate was taken out, rinsed with water and dried at room temperature. Based on the difference between the initial and final mass of the substrate, the weight of CMCD-LDH film per unit area of the substrate was calculated to be 3.06×10^{-2} kg/ m^2 .

Inclusion C_{60} by the CMCD-LDH film: C_{60} was included within the CMCD cavities of CMCD-LDH film by reaction with xylene solution. In a typical inclusion experiment, 0.10 g of C_{60} was allowed to equilibrate with CMCD-LDH film (1.5×10^{-3} m^2) in xylene (100 mL) by heated at 70 °C for 72 h. The film was washed thoroughly with xylene, centrifuged and dried at 70 °C for 20 h.

Characterization: Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer with Cu- K_{α} radiation ($\lambda = 1.5406$ Å). The operating voltage and current were 40 kV and 30 mA, respectively. The step used was $0.02^\circ s^{-1}$ in the 2θ range from 2-70°. The morphology of the CMCD-LDH film was investigated by using a scanning electron microscope (SEM: Hitachi S-4700). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vector²² spectrophotometer in the range 4000-400 cm^{-1} with 2 cm^{-1} resolution. An UV-vis spectrophotometer (Shimadzu UV-2501PC) was employed to measure the absorbance spectra of compounds in the 200-700 nm wavelength range. ^{13}C solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were run on a Bruker AV300 spectrometer operating at a frequency of 75.467 MHz for ^{13}C at a spinning rate of 5000 Hz with a 5 s

pulse delay. TG analysis was measured on a PCT-1A thermal analysis system with a heating rate of 10 °C/min under air atmosphere.

RESULTS AND DISCUSSION

Characterization of CMCD-LDH film

XRD: The CM- γ -CD intercalated LDH film (CMCD-LDH film) was synthesized by *in situ* crystallization on PAO/Al substrate as described in the experimental part. The XRD patterns of the CMCD-LDH film as well as the PAO/Al substrate are illustrated in Fig. 2. The sequence of strong (003), (006) reflections at low angle and the (012) reflection at high angle for the film (Fig. 2b) indicates formation of well-crystallized hydrotalcite-like LDH phase. The reflection can be indexed to a hexagonal lattice with R-3m rhombohedral symmetry, commonly used for the description of LDH structures. The interlayer distance of CMCD-LDH is 1.841 nm, which is similar with the CM- β -CD-LDH film³⁶. Taking into account the dimensions of the γ -cyclodextrin molecule and the rule of charge balance, the CM- γ -CD anions can only adopt a monolayer arrangement with their cavities axis perpendicular to the LDH layer. This is similar to the arrangement in our previous research of CM- β -CD-LDH film³⁶. In an LDHs, a positive charge on the layers necessitates the presence of charge-balancing anions in the interlayer and external surface. In this paper, it was found that the CMCD on LDH surface plays an important role in the inclusion of C₆₀.

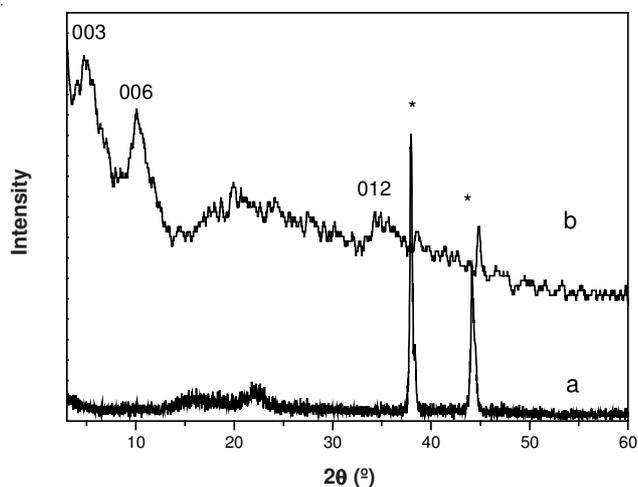


Fig. 2. XRD patterns of (a) the PAO/Al substrate, (b) the CMCD-LDH film. Asterisk denotes the reflections of Al substrate

Infrared spectroscopy: The FT-IR spectra of γ -CD, CM- γ -CD and the CMCD-LDH powder scraped from the film are shown in Fig. 3. In the infrared spectrum of the as-synthesized sodium salt of CMCD, a broad strong absorption band at 3386 cm⁻¹ is observed, which can be attributed to OH combination stretching vibrations of hydroxyl groups and physically adsorbed water. An absorption at 2928 cm⁻¹ is due to the stretching vibration of -CH₂. Two strong bands at 1604 and 1420 cm⁻¹ are attributed to the asymmetric and symmetric stretching vibrations of carboxylate -COO⁻, respectively. Bands

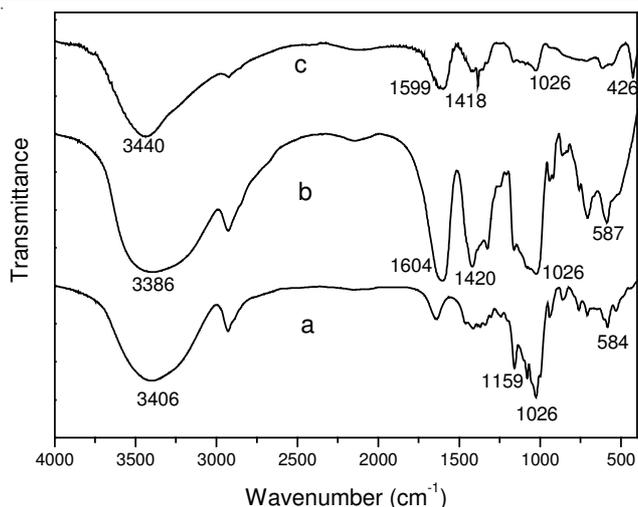


Fig. 3. FT-IR spectra of (a) γ -CD, (b) CMCD and (c) the CMCD-LDH powder scraped from the film

at 1160, 1026 cm⁻¹ are assigned to absorption of C-O, C-O-C of glucose units. In the case of the CMCD-LDH powder scraped from the film, most bands of CMCD show no obvious change upon intercalation into LDH (Fig. 3c). The asymmetric stretching band of -COO⁻ moves slightly toward to low frequency, at 1599 cm⁻¹. This spectral change may be related to the formation of hydrogen bonding between the carboxylate and the hydroxyl in LDH layer. Moreover, the metal-hydroxyl (M-OH) stretching modes of LDH layer appear at 426 cm⁻¹. That all indicate the formation of CMCD-LDH composition.

SEM and EDX: Furthermore, the morphology of the PAO/Al substrate and CMCD-LDH film was studied by scanning electron microscopy (SEM). The surface (Fig. 4A) of PAO/Al substrate shows that the PAO film has porous structure with pore diameter of *ca.* 20 nm. Fig. 4B exhibits the surface-view of the CMCD-LDH film after crystallization on the PAO/Al substrate at 70 °C for 48 h. The curved hexagonal faces of the LDH microcrystal can be clearly observed perpendicular to the substrate over the entire substrate surface. The edge-view of the CMCD-LDH film (Fig. 4C) demonstrates that only a monolayer of the LDH crystals with a thickness of *ca.* 1 μ m was assembled on the PAO/Al substrate. These images indicate that the *ab*-face of LDH microcrystals is predominantly perpendicular with respect to the substrate. This observation can be confirmed by energy dispersive X-ray (EDX) analysis, displayed in Fig. 4D. Along EDX line scanning over the LDH film and a part of the PAO/Al substrate, the Zn/Al distribution ranges from 1.2-2.0. At depths below 1 μ m, however, the Zn profile of the EDX rapidly decreases to almost zero, indicating the absence of the Zn species inside the substrate.

Characterization of C₆₀/CMCD-LDH film

XRD: The powder XRD patterns of CMCD-LDH film and C₆₀/CMCD-LDH film are displayed in Fig. 5. Both the patterns indicate formation of well-crystallized hydrotalcite-like phase. Compared with the CMCD-LDH film, it was found that the gallery height of the C₆₀/CMCD-LDH remains the same upon including C₆₀ (Fig. 5b). This indicated that the

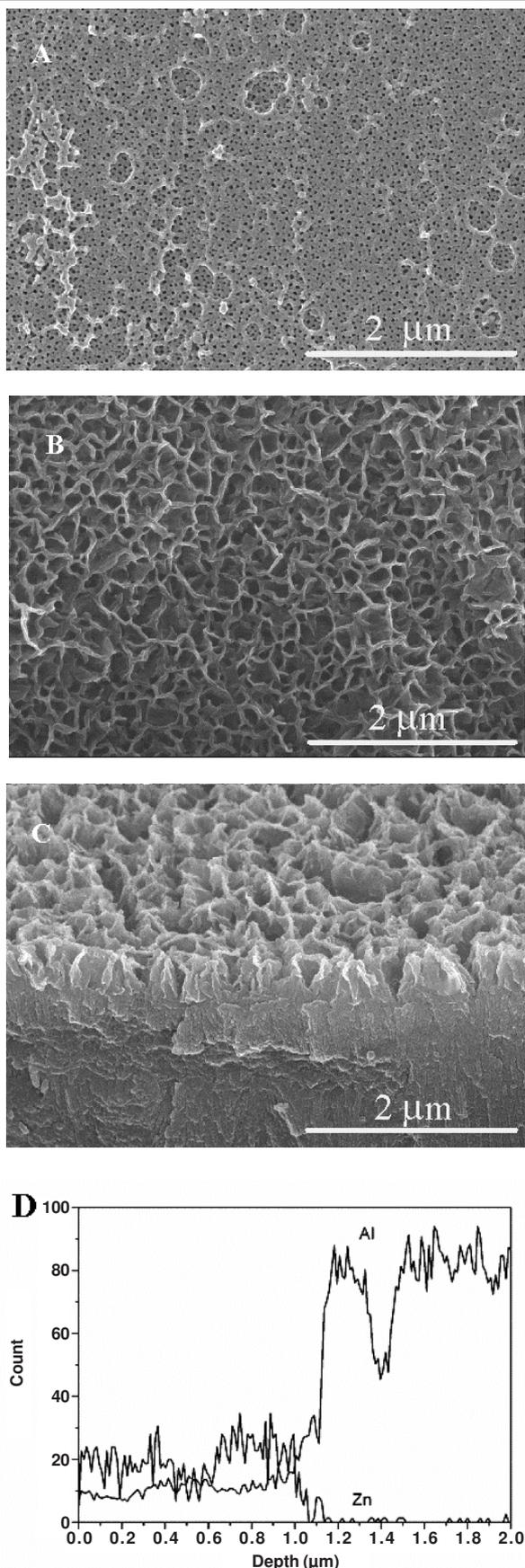


Fig. 4. SEM images of (A) the PAO/Al substrate, (B) surface-view of the CMCD-LDH film on PAO/Al substrate, (C) edge-view of the CMCD-LDH film, (D) the energy dispersive X-ray line scan of the edge-view of the film

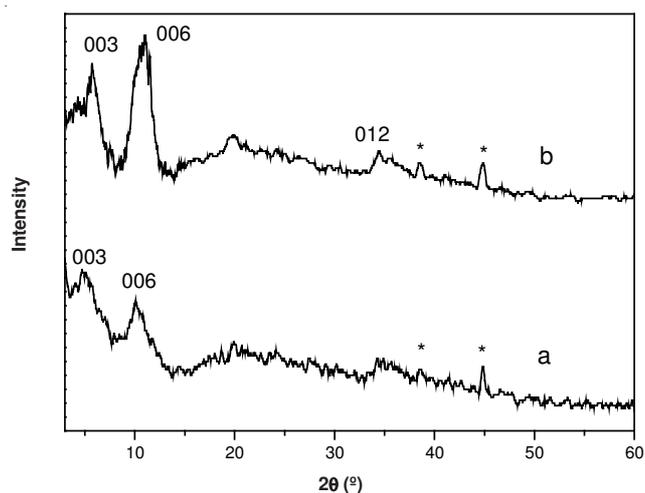


Fig. 5. Powder XRD patterns of (a) CMCD-LDH film, (b) C₆₀/CMCD-LDH. Asterisk denotes the reflections of Al substrate

fullerene molecules can't be included in the CMCD in the LDH interlayer. The explanation for this unusual behaviour is that the C₆₀ molecule is too large to diffuse into the CMCD-LDH interlayer region. It was guessed that C₆₀ was immobilized on the surface of LDH by the recognition of CMCD cavities and this will be further confirmed in the next section.

SEM: Moreover, the morphology of C₆₀/CMCD-LDH film was shown in Fig. 6. It can be seen that after inclusion of C₆₀, the curved hexagonal faces are still perpendicular to the substrate. The LDH microcrystals can be clearly observed and covered almost the entire substrate surface. This observation indicated that the inclusion of C₆₀ hardly affected the crystals of CMCD-LDH film.

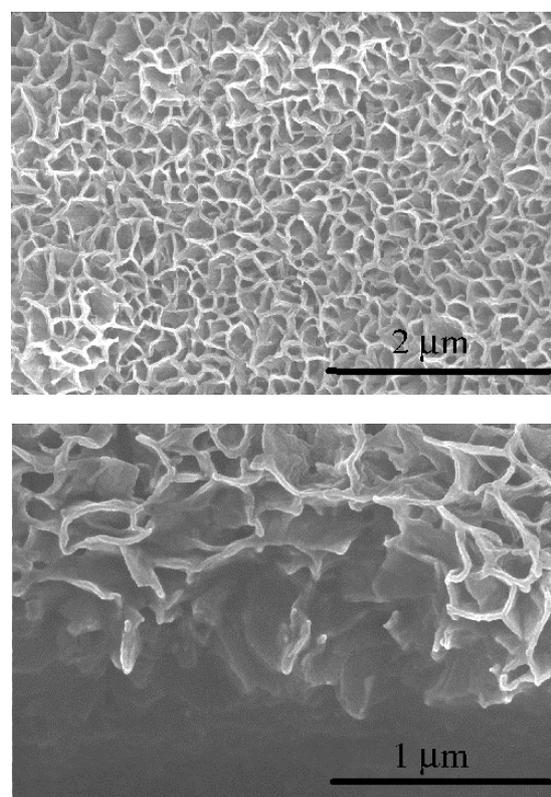


Fig. 6. SEM images of C₆₀/CMCD-LDH

UV-VIS: Fig. 7 shows the UV-VIS spectra of C_{60} /CMCD-LDH film as well as the corresponding reference samples. It was found that the spectrum of solid C_{60} powder displays broad bands appearing at 240 and 322 nm, in accord with the literature⁴⁶. Moreover, the peak maxima position of physical admixture of C_{60} and NO_3 -LDH are very close to those of C_{60} powder. It indicated that the C_{60} is hardly adsorbed on the surface of hydrophilic LDH layer. In the case of C_{60} /CMCD, the absorption bands of C_{60} obviously move to longer wavelength (270 and 343 nm respectively). Furthermore, it was found that the absorption bands of C_{60} /CMCD-LDH centered at 260 and 343 nm are very close to those of C_{60} /CMCD, which confirms that C_{60} is embedded in the cavity of CMCD attached to LDH surface. The red-shift of UV bands is considered as clear evidence for the formation of an inclusion complex. The spectral shifts indicate that the excited states of the caged C_{60} are subject to electronic changes resulting in a more stable structure upon encapsulation. In this report, the red shift of the UV spectrum is considered as a clear evidence for the formation of inclusion complex.

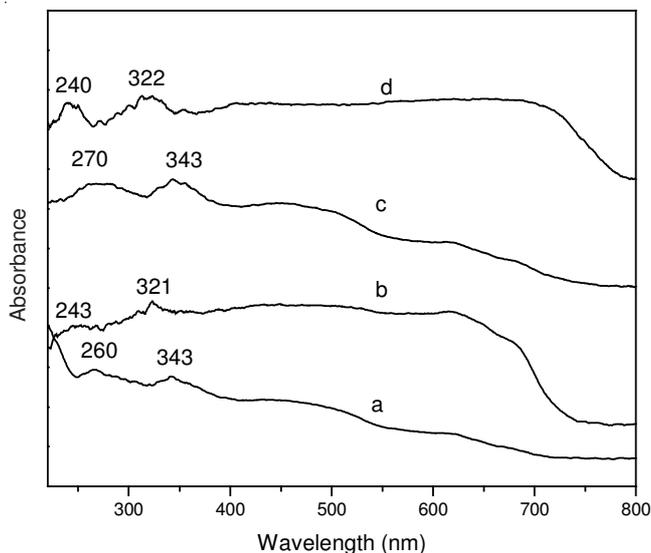


Fig. 7. UV-VIS spectra of (a) C_{60} /CMCD-LDH, (b) physical mixture of C_{60} and NO_3 -LDH, (c) C_{60} /CMCD, (d) C_{60} powder

^{13}C NMR: Supporting evidence for inclusion of C_{60} by surface CMCD was provided by solid-state ^{13}C NMR spectroscopy. The spectrum of the C_{60} gives a relatively sharp peak at *ca.* 143.3 ppm, which is close to the chemical shift of C_{60} in solutions (*ca.* 143.2 ppm). Moreover, the broader peaks in the range 50-110 ppm (Fig. 8) are assigned to the carbon atoms of cyclodextrin. After the inclusion by CMCD, the chemical shift of the resonance absorption lines moved downfield and was observed at 143.1 ppm (C_{60}), which is consistent with the presence of the interaction between C_{60} with inclusion host-CMCD.

TG-DTA: Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) also confirms the inclusion of C_{60} by the CMCD cavities on the surface of LDH film. Fig. 9 displays the TG-DTA profiles for C_{60} /CMCD-LDH film.

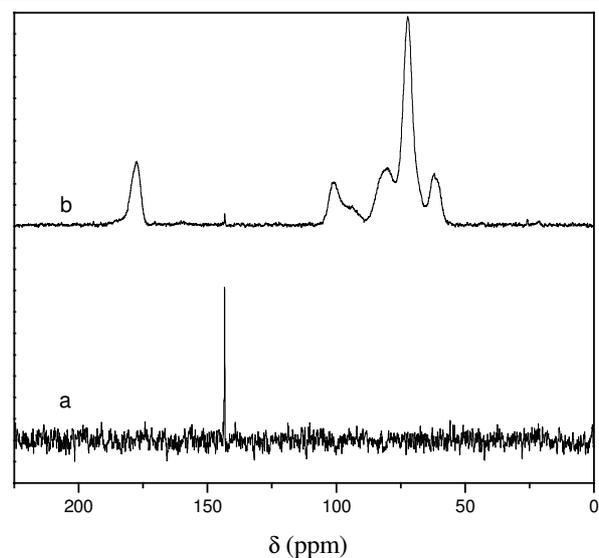


Fig. 8. ^{13}C MAS NMR spectra of (a) C_{60} powder, (b) C_{60} /CMCD-LDH

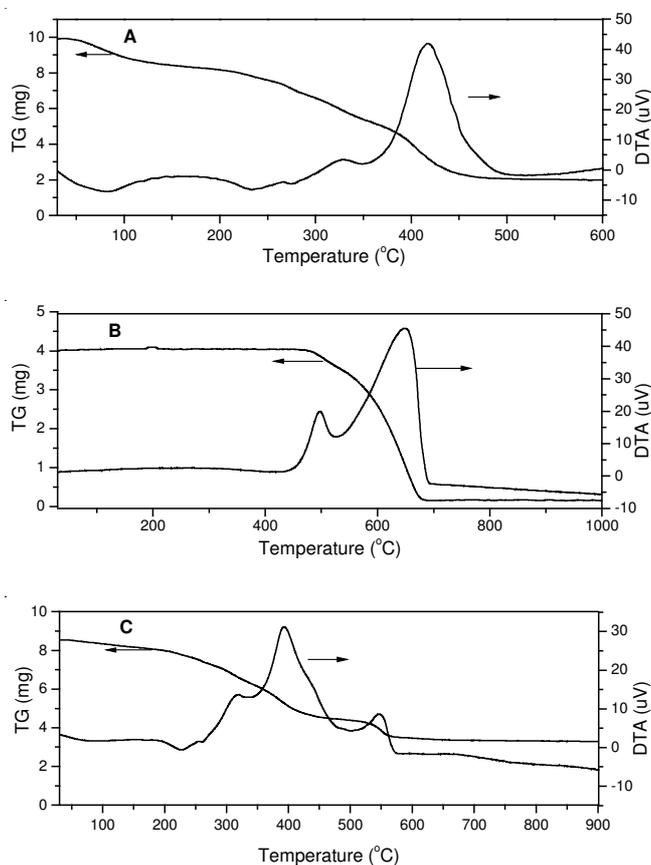


Fig. 9. TG and DTA curves for (A) CMCD-LDH, (B) C_{60} , (C) C_{60} /CMCD-LDH

The thermal decomposition of the CMCD-LDH complex (Fig. 9A) was characterized by three steps, which is in good agreement with the literature⁴⁷. The TG curve together with the corresponding DTA curves for the sample of C_{60} are shown in Fig. 9B, which undergoes a progressive weight loss in two steps with the increase of temperature. Associated with the weight loss, up to two exothermic peaks can be observed (at 495 and 647 °C) in its DTA curve recorded in an oxidizing atmosphere.

The TG and DTA curves of the C₆₀/CMCD-LDH sample are shown in Fig. 9C, in which three weight loss steps were observed. The first one from room temperature to 150 °C corresponds to the removal of surface adsorbed water and interlayer water molecules. The second one (250-500 °C), involving a gradual weight loss, is a result of the decomposition of CMCD ions and dehydroxylation of the brucite-like layers. The third one with a sharp weight loss in the temperature range 500-600 °C and a corresponding exothermic peak at 548 °C in the DTA curve is due to combustion of C₆₀, which indicates that the C₆₀ is included in the product. Compared to the decomposition of pure C₆₀, the combustion temperature of included C₆₀ is decreased by some 100 °C. This significant decrease in thermal stability of C₆₀ may be a result of the highly dispersed after inclusion in the CMCD cavities on the surface of CMCD-LDH film.

Conclusion

The highly dispersed fullerene immobilized on the surface of CMCD modified LDH film has been studied in this work. We have demonstrated a facile method for the preparation of oriented CMCD-LDH film with curved hexagonal microstructure on a PAO/Al substrate. The as-prepared CMCD-LDH film show excellent inclusion ability for fullerene and the fullerene molecules was immobilized in the CMCD cavities by noncovalent interaction on the surface of CMCD-LDH film. The XRD results show that the basal spacing of the resulting C₆₀/CMCD-LDH film is similar with that of the CMCD-LDH film, moreover, the UV-VIS results show the interaction between C₆₀ with inclusion host-CMCD, which all indicated the inclusion of fullerene by CMCD on the surface of LDH. A schematic model of the inclusion structure has been proposed. The thermal decomposition of C₆₀/CMCD-LDH was investigated by TG-DTA measurements. Compared with the pure fullerene, the thermal stability of C₆₀/CMCD-LDH is reduced after highly dispersed and its combustion temperature decreased by 100 °C. Therefore, this work provides a novel dispersed fullerene based on functionalized CD/layered material composite, further investigation will focus on the photoelectrochemical and optical limiting properties of these fullerene-trapped LDH materials.

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