

자외선 차단 효과를 갖는 신기능성 물질 설계

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The Synthesis and Characterization for Design a Novel Functional Material with UV Block

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Introduction

More frequent reports of skin cancer have made people increasingly aware of the danger of prolonged exposure to ultraviolet (UV) rays, which account for about 6% of the terrestrial sunlight and, under excessive doses, is proved to cause erythema, certain skin cancers, keratitis, and cataracts. Textiles and sunblocking creams are the common choices to shield against UV radiation, although UV radiation also weathers and degrades the textiles. Consequently, new UV-blocking agents have been developed to add to or to improve the UV-protective function of textiles, plastic films, and other related products [1]. There are both organic and inorganic UV blockers. The organic blockers are also called UV absorbers because they mainly absorb UV rays. Inorganic UV blockers are usually certain semiconductor oxides such as TiO₂, ZnO, SiO₂, and Al₂O₃, for example. Compared with the existing organic UV absorbers, the inorganic UV agents are more preferred because of their unique features including, among others, nontoxicity and chemical stability under both high temperature and UV-ray exposure.

However, the material architecture of UV-blocking function of inorganic materials is remained so important projects to researchers. Until now investigators have been believed that TiO₂ loading methods on matrix materials provides good UV protection by reflecting and/or scattering most of the UV-rays through its high refractive index [2,3]. Others believe that it absorbs UV radiation because of its semiconductive properties [4,5].

Therefore, we are selected to layered double hydroxides (LDHs) with a advantage of the high adsorption ability, high surface area, high anion exchange capacity and interlayer

reaction. Layered double hydroxides known as anionic clay are a family of compounds which deserve much attention in recent years [6]. These are a class of layered compounds derived from the structure of mineral brucite, $Mg(OH)_2$. LDHs can be described by general formula $[Mg_{1-x}Al_x(OH)_2] (An-x/n)\cdot H_2O$ ($0.2 \leq x \leq 0.33$) and positively charged. The mineral forms the LDH structure of Mg with Al. A large number of reviews have been published to illustrate the diversity of these reactions.

The aim of this work is the synthesis and characteristics for design a new functional material with UV block effect. In other words, to design a novel functional compound intercalated the titanate in HTlc using organic tetrabutyl orthotitanate (TBOT) as precursor.

Experimental

HTlc was prepared using a mixture solution with $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ added basic solution of NaOH and Na_2CO_3 with vigorously stirring and keep up constant between the pH range 9-10 for 24hr at room temperature by co-precipitation method. On the other hand, Ti-HTlc series are prepared through aging with stirring at mild temperature using TBOT in solutions adjusted to pH=8-12, respectively.

Results and Discussion

The characterization of titanium intercalated in hydrotalcites (HTlc), with change pH, is very important because they determine their catalytic properties and particularly the acid-base properties. The powder XRD patterns of the HTlc and four Ti-HTlc series, HTlc and Ti-HTlc-n ($n=1-5$), are showed in Fig. 1. Generally, the basal peak of HTlc is made up 003, 006 and 012 planes. The basal peak is due to the diffraction of the space between the adjacent layers in the HTlc. The ionic radius of the metal cations as well as the metal oxygen bond lengths (1.90 Å for Al-O and 1.95 Å Ti-O) lead to some difference in the peaks position for the XRD patterns. We could assume the intercalation of titanate into HTlc by the shift and a new low-intensity peak at $2\theta \approx 18.3^\circ$ and 25.4° , respectively.

The existence of intercalation titanium in HTlc was can confirm by FT-IR spectra analysis shown in Fig. 2. The broad band around 3441 cm^{-1} is due to the OH stretching mode of layer hydroxyl groups hydrogen bonded interlayer water molecules. The bands between $1614-1645\text{ cm}^{-1}$ and 1370 cm^{-1} are due to the vibration mode H_2O molecules and CO_3^{2-} anion, respectively. The weak band around $1037-1050\text{ cm}^{-1}$ is presumed to the bending mode of titanium oxide. These can be due to the presence of some Ti atoms in an octahedral environment corresponsive in Ti-O-Ti bonds as part of small TiO_2 regions.

A specific surface area, pore volume and pore diameter using N_2 absorption-desorption isotherms shown in Table 1. The values for the specific surface areas pore volume and pore diameter are calculated following the BET method. The largest surface area, $444.3\text{ m}^2/\text{g}$, is shown in Ti-HTlc-2 sample but the maximum pore volume and pore diameter amongst the

titanium-containing samples are Ti-HTlc-4 sample, 0.73 mL/g and 118.7 Å, respectively. These facts we could find that a pore size and volume was possible fully according to pH control.

Conclusion

This work provided the information that we can utilize advantage with flexible interlayer space as layered materials such as layered double hydroxides (LDHs) with positive charge on the surface. Moreover, the particle and pore sizes of these materials are adjustable by diverse variable such as reaction temperature, pH and contents ratio. The analysis showed that intercalation of titanate in HTlc at XRD pattern, 18.3° and 25.4°, and FT-IR peak of Ti-O-Ti bond around 1037-1050 cm⁻¹). Ti-HTlc-n series has the possibility to apply to materials with UV blocking effect.

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Table 1. Surface area, pore volumes and pore diameter of the HTlc and Ti-HTlc series by BET measurement.

Sample	Surface area (m ² /g)			Pore volume(mL/g)		Pore diameter(Å)	
	S _{mic} ^a	S _{ext} ^a	S _{BET} ^b	V _{mic} ^c	V _{total} ^d	D _{ads} ^e	D _{ave} ^f
HTlc	12.0	63.0	75.0	0.08	0.08	8.7	10.8
Ti-HTlc-1	84.4	125.8	210.3	0.03	0.38	71.9	72.5
Ti-HTlc-2	-65.5	509.8	444.3	0.04	0.41	29.9	36.9
Ti-HTlc-3	-36.5	323.2	286.7	0.02	0.71	83.2	99.1
Ti-HTlc-4	-38.6	284.2	245.5	0.02	0.73	98.2	118.7

^aSurface area due to micropores (S_{mic}) and surface area due to external surface(S_{ext}) in a sample based on the t-plot method.

^b Surface area of a sample (S_{BET})calculatedwiththeBETmethod.

^c Micropore volume (V_{mic})inasamplebasedonthet-plotmethod.

^d Total pore volume (V_{total})obtainedbyN₂adsorptionatp/p₀ ≈ 1.0.

^e Adsorption pore diameter (D_{ads}).

^f Average pore diameter (D_{ave}).

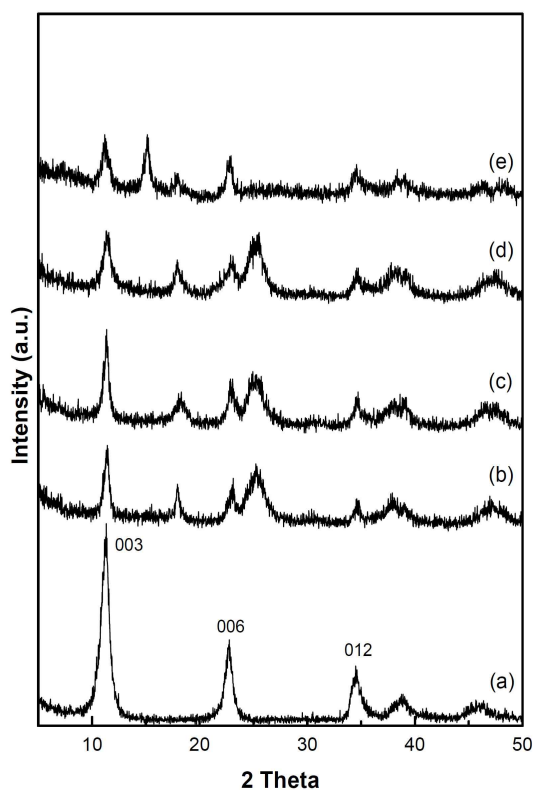


Figure 1. PXRD pattern of the HTlc and Ti-HTlc series: (a) HTlc, (b) Ti-HTlc-1, (c) Ti-HTlc-2, (d) Ti-HTlc-3 and (e) Ti-HTlc-4.

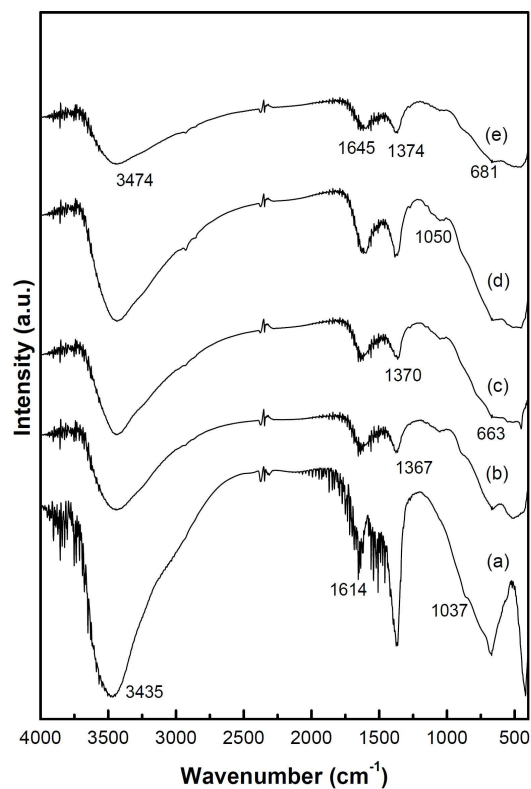


Figure 2. FT-IR spectrum of the HTlc and Ti-HTlc series: (a) HTlc, (b) Ti-HTlc-1, (c) Ti-HTlc-2, (d) Ti-HTlc-3 and (e) Ti-HTlc-4.