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Solid-solid intercalation and optical properties of VO-8-hydroxyquinoline decoration of layered silicate magadiite

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Coordination of vanadyl (VO^{2+}) ions with 8-hydroxyquinoline (8Hq) in the interlayer space of layered silicate magadiite (mag) was realized by solid-solid intercalation. Composition, structure and morphology of this compound were studied by X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). The obtained results indicate that the basal spacing of decorated mag increased after intercalation and suggest that VO-8Hq decorated into the interlayer of mag (VO-mag-8Hq) was successfully synthesized for the first time. Optical properties of VO-mag-8Hq were studied by ultraviolet-visible (UV-Vis) and photoluminescence spectroscopy (PL). The findings reveal that VO-8Hq complexes in the interlayer space exhibit extraordinary fluorescence properties and the confined space of mag influences the optical properties of VO-8Hq complexes.

Keywords: *magadiite; decoration; composite materials; multilayer structure; luminescence*

1. Introduction

Nanostructured inorganic-organic composites have been considered as one of the main research areas in materials science and technology for developing new functional and structural advanced materials [1–8]. Properties of the composites were determined not only by joining properties of host and guest components but also by composition, morphology, structure, connectivity of phases and interfacial properties [1]. Host-guest composites based on intercalation of guest molecules into inorganic layered hosts create a new class of superior functional materials, such as catalyst and molecular sieving materials, which have novel chemical and physical properties [9–11].

Recently, some inorganic layered materials including layered double hydroxides, clay minerals, graphite, etc., have been used for decorating organic substances in their interlayer spaces with the aim of synthesizing inorganic-organic

complexes for wide applications [12–16]. Magadiite (mag $Na_2Si_{14}O_{29} \cdot xH_2O$) from the phyllosilicate family, has a layered structure which consists of agglomerated particles with irregular shapes and partly sharp grain boundaries. Structure of mag is composed of one or multiple negatively charged sheets of SiO_4 tetrahedrons with abundant silanol-terminated surfaces. Negative charges in the layers of mag are counterbalanced by hydrated cations (Na^+ or H^+) in the interlayer spaces [17]. Mag has a high cation exchange capacity which can be applied to ion-exchange, whereby Na^+ can be replaced by other cations or large quaternary ammonium ions [3, 18–20]. Previous research demonstrated that mag could be a good candidate for synthesis of organic-inorganic composites [19, 21, 22]. 8Hq ligands (Fig. 1) and complexes with these ligands have attracted considerable attention because of their practical luminescence properties, especially in the use of organic light-emitting devices [23, 24]. In the past decades, vanadium oxides have received increasing attention due to their layered structures, novel chemical and physical

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properties, which make them promising for applications in catalysts, gas sensors, lithium ion batteries, optical switching devices, energy storage, and so on [25–33].

However, intercalation of vanadyl complexes with 8-hydroxyquinoline (8Hq) (denoted as VO-8Hq) in the interlayer space of the silicate mag has not been reported to the best of our knowledge. Herein, we report the decoration of 8Hq into the interlayer spaces of VO exchanged mag and its optical properties.
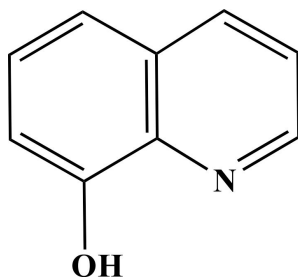

Fig. 1. The molecular structure of 8Hq.

2. Experimental

2.1. Materials

Sodium hydroxide (NaOH), vanadyl sulfate (VOSO$_4$·2H$_2$O), silica gel (40 wt.% Aldrich) and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without any further purification. Magadiite (mag) was synthesized via a hydrothermal reaction according to the literature [34] and slightly modified. In a typical synthesis, 27 g of silica gel (0.18 mol silica) was slowly added to 20 g (1.11 mol) deionized water containing 1.6 g (0.04 mol) NaOH under vigorous stirring. A continuous stirring was ensured in this process until a solid gel was formed in this step. After 1 h, the mixture was transferred into a teflon-lined stainless steel autoclave and maintained at 150 °C for 48 h. The solid product was washed repeatedly with deionized water to remove excess NaOH until pH ≈ 7 and dried at 80 °C overnight [35]. The chemical formula of the obtained mag can be expressed as Na$_2$Si$_{14}$O$_{29}$·H$_2$O. Its cation exchange capacity (CEC) is 2 meg/g [36].

2.2. Synthesis

Fig. 2 shows synthetic process of VO-8Hq decoration of mag, which mainly comprised three steps. At the first step, H-mag was synthesized using mag under acidic conditions. Before ion-exchange of vanadyl (VO^{2+}) cations, H-mag was produced by adding synthetic mag to HCl (0.1 M), until pH was about 2, under magnetic stirring for 24 h. When the ion exchange reactions were finished, the resulting products were separated using a centrifugal separator and washed with deionized water several times until a negative AgNO$_3$ test was achieved. At the second stage, VO-mag was prepared by ion-exchange reaction between H-mag and VOSO$_4$ solution. 6 mL VOSO$_4$ (0.5 mol/L), 24 mL (1.33 mol) H$_2$O and 1.0 g (1.15 mmol) H-mag were added to a 50 mL round-bottom flask. The mixture was stirred at 60 °C. After 12 h, the products were separated by centrifugation, washed with distilled water (H$_2$O) repeatedly to remove excess ions and dried at 80 °C for 12 h. At the third stage, complexes of 8Hq with VO^{2+} in VO-mag were created by solid-solid intercalation [19] as follows: 0.0435 g (0.3 mmol) 8Hq was mixed with 0.3 g (0.32 mmol) VO-mag and ground manually using an agate mortar and a pestle at ambient environment for 15 min. After solid-solid reaction, the products were washed with n-hexane (C$_6$H$_{14}$) and ethanol (CH$_3$CH$_2$OH) three times repeatedly and dried at 60 °C for 24 h. Synthesized products were named as VO-mag-8Hq.

2.3. Characterization

Powder X-ray diffraction (XRD) was performed on a PANalytical - X'Pert^3 Powder diffractometer using monochromatic CuKα radiation. The amounts of exchange cations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Optima 2000DV ICP-OES) and an energy-dispersive X-ray spectrometer (EDS) attached to a scanning electron microscope (SEM, QUANTA450). X-ray photoelectron spectroscopy (XPS) was used to investigate the surface composition of the products performed on ESCALAB250Xi, Thermo Fisher Scientific. Fourier-transform infrared (FT-IR) spectra
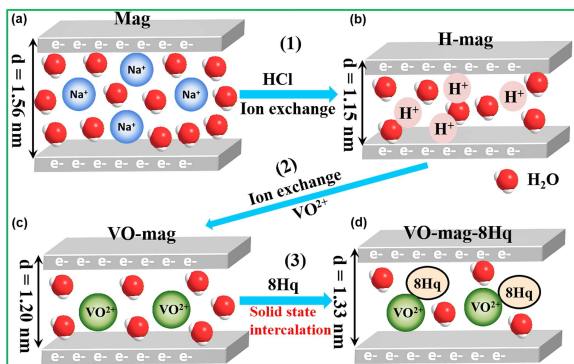
Fig. 2. Schematic illustration of synthesis of VO-mag-8Hq: (a) mag; (b) H-mag; (c) VO-mag; (d) VO-mag-8Hq. Basal spacing (d) was obtained from XRD patterns shown in Fig. 3.

of the samples were recorded by KBr disk method on a Nicole Avatar 360 FT-IR spectrometer (USA) over the spectral region of 400 cm^{-1} to 4000 cm^{-1}. The morphology and dimensions of the products were observed by field emission scanning electron microscopy (SEM, NOVA NanoSEM 450, FEI). Samples for SEM observation were gold-sputtered in order to get better morphology of the surface. Diffuse reflectance spectra (UV-Vis) of the solid samples were collected on an American HP-8453 scanning spectrophotometer using an integrated sphere. Photoluminescence spectra (PL) were characterized on a standard Jasco FP-6500 spectrofluorophotometer with the excitation at 400 nm.

3. Results and discussion

Fig. 2 displays the proposed process of 8Hq decorating interlayer of mag and Fig. 3 shows XRD patterns of various products. Basal spacing (d) of mag was evaluated as 1.56 nm (Fig. 3b). After exchanging with H$^+$, H-mag with d = 1.15 nm was obtained (Fig. 3c). VO-mag of the type of H-mag was synthesized by VO^{2+} exchanging with H-mag and its basal spacing increased to 1.20 nm (Fig. 3d). After intercalation of 8Hq into VO-mag, the basal spacing of VO-mag-8Hq increased to 1.33 nm (Fig. 3e). The increase of basal spacing indicates that the VO-8Hq complexes were successfully decorated into interlayer of mag. Changes of the basal

spacing are closely related to the peculiar arrangements of metal chelates between the layers, which could be attributed to the β-type packing between the silicate sheets [37].
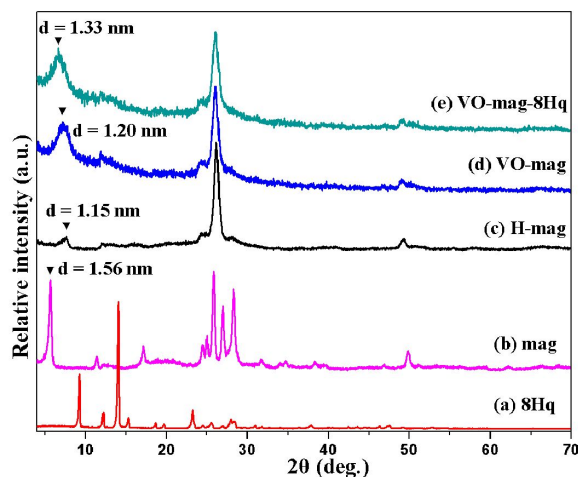

Fig. 3. XRD patterns of various samples.

Fig. 4 shows the FT-IR spectra of 8Hq, VO-mag and VO-mag-8Hq. VO-mag-8Hq exhibits the bands ranging from 1600 cm^{-1} to 1300 cm^{-1} originating from 8Hq. The peaks located at 1562 cm^{-1}, 1502 cm^{-1}, 1472 cm^{-1} and 1383 cm^{-1} were assigned to benzene ring stretching of 8Hq. This finding further demostrated that 8Hq was complexed in VO-mag-8Hq in agreement with the XRD results. The morphology of VO-mag-8Hq was observed by SEM (Fig. 5b). VO-mag-8Hq kept the original shapes of mag (Fig. 5a), however, platelets became disordered in some extent, which may have resulted from the grinding process.

To further confirm the composition of VO-mag-8Hq, corresponding tests including ICP-AES, EDS, elemental mapping and XPS were carried out. Fig. 6 shows EDS spectra of VO-mag-8Hq, and the elements such as C, N, O, Si and V are distinctly observed. Fig. 7 shows elemental mapping images of VO-mag-8Hq, and reveals that all elements are homogeneously distributed, suggesting that 8Hq was successfully decorated VO-mag. Fig. 8 depicts XPS spectra, which reveal that VO-mag-8Hq consists of C, N, O, Si and V elements, in agreement with the observations
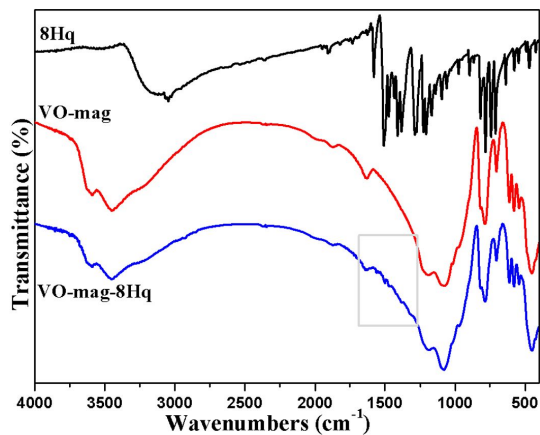
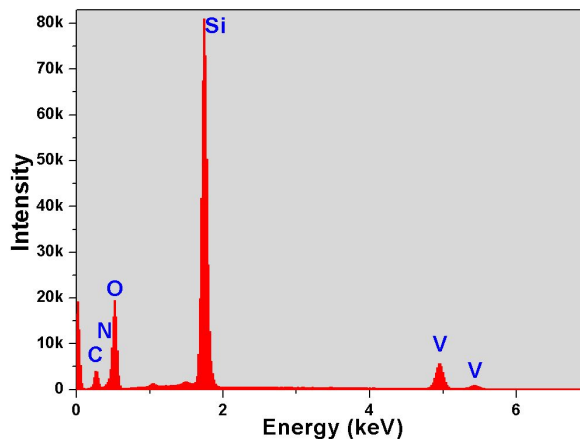Fig. 4. FT-IR spectra of 8Hq, VO-mag and VO-mag-8Hq.
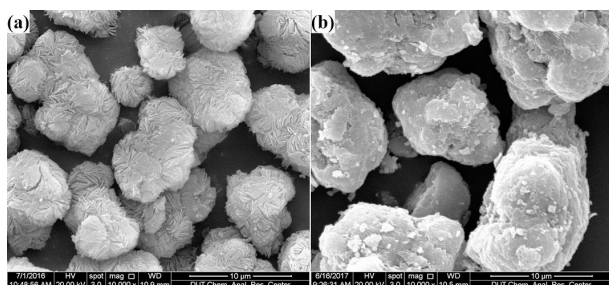

Fig. 6. EDS spectrum of VO-mag-8Hq.

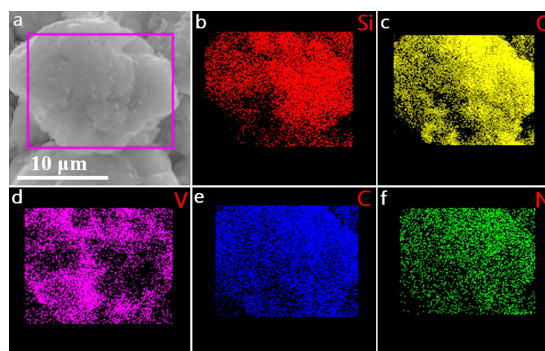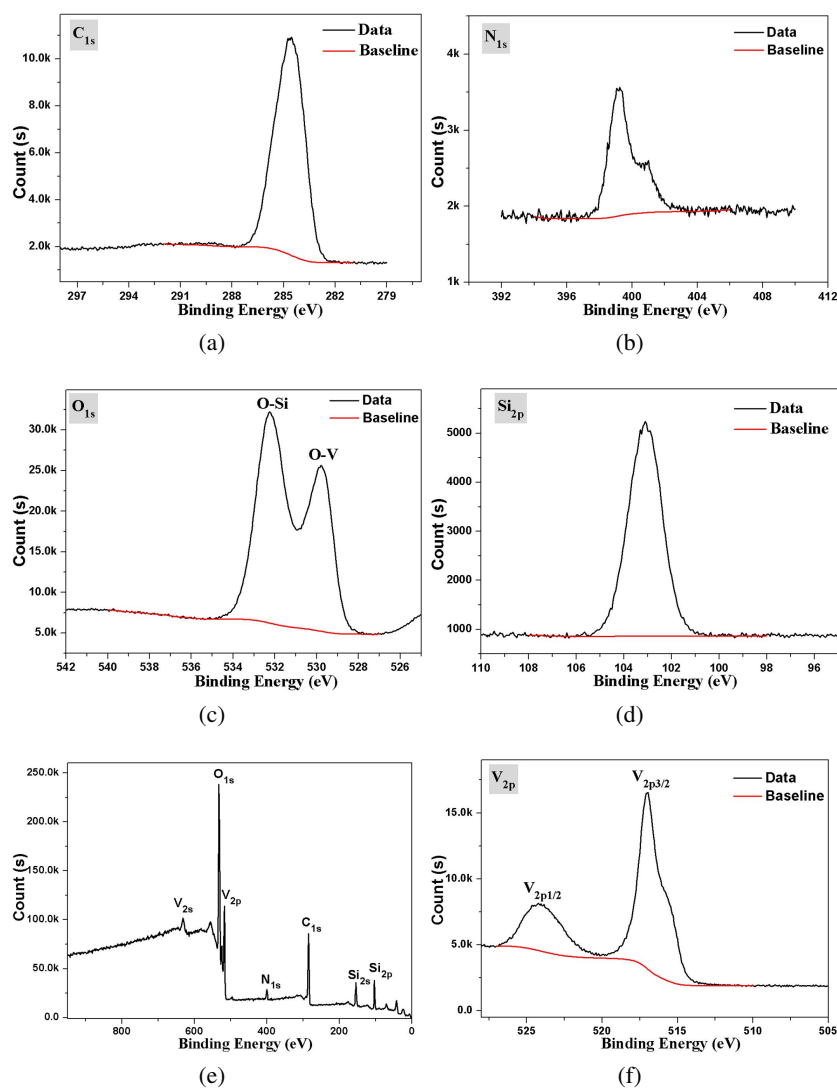Fig. 5. SEM images of (a) mag and (b) VO-mag-8Hq.

Fig. 7. A SEM image (a) and its corresponding elemental mapping images of VO-mag-8Hq (b-f): (b) element Si; (c) element O; (d) element V; (e) element C; (f) element N.

of EDS and elemental mapping. The binding energies of C_{1s}, N_{1s} and Si_{2p} are centered at 284.6 eV, 399.2 eV and 103.1 eV, respectively. O_{1s} signal (Fig. 8b) is divided into two peaks. Binding energy at 529.8 eV corresponds to VO structure, and the peak at 532.3 eV can be attributed to Si–O bond in mag [38, 39]. V_{2p} spectrum splits off two peaks $V_{2p3/2}$ (516.8 eV) and $V_{2p1/2}$ (524.2 eV). Atomic ratio of C/N obtained from XPS is 9.3, which is close to value the C/N = 9 in 8Hq. The amounts of V in decorated mag were evaluated by ICP-AES, and the percentage of V is 3.82 wt.% (30.1 mol%) in VO-mag-8Hq. Quantitative exchange with VO^{2+} did not occur owing to its exchange ability. Based on above analyses, 8Hq decorating VO-mag was successfully synthesized and the quantity of 8Hq was ca. 10.4 wt. % (29.5 mol%) (as shown in Table 1).

UV-Vis spectra of 8Hq and VO-mag-8Hq are presented in Fig. 9a. The bands belong to π-π* transition of aromatic ring in 8Hq located at 300 nm to 360 nm [40]. As for VO-mag-8Hq, this band became board and centered at 300 nm to 450 nm owing to the coordination of Hq with VO^{2+} in various sites of mag [41, 42]. Consequently, the band observed for VO-mag-8Hq (Fig. 9a) can be attributed to VO-8Hq formed in the interlayer spaces of mag. In PL spectra of VO-mag-8Hq, a luminescence peak appears at around 485 nm, which is consistent with value of 8Hq (484 nm) [23]. The observations confirm the formation of VO-8Hq complexes in the interlayer of mag. Molecular structure and packing of VO-8Hq formed in mag is a reason of tiny difference in PL spectra.

Table 1. Results of calcination of VO-mag and VO-mag-8Hq at 500 °C for 2 h in air.

Samples	m_1 [g] (room temperature)	m_2 [g] (500 °C for 2 h in air)	m_3 [g] (weight loss)	Weight loss [%]
VO-mag	0.2063	0.1948	0.0115	5.6
VO-mag-8Hq	0.2056	0.1727	0.0329	16.0
				10.4

Fig. 8. XPS spectra of VO-mag-8Hq: (a) survey spectrum; (b) core-level spectrum of O_{1s}; (c) core-level spectrum of Si_{2p}; (d) core-level spectrum of C_{1s}; (e) core-level spectrum of N_{1s}; (f) core-level spectrum of V_{2p}.

4.   Conclusion

In summary, we demonstrated that 8Hq was successfully decorated into the interlayer spaces of VO-mag. The organic intercalation was done by solid-solid reaction and *in situ* complex formation method at room temperature. Basal spacing of VO-mag-8Hq increased after intercalation in comparison to VO-mag. It suggests that the decoration of VO-8Hq into the interlayer of mag has
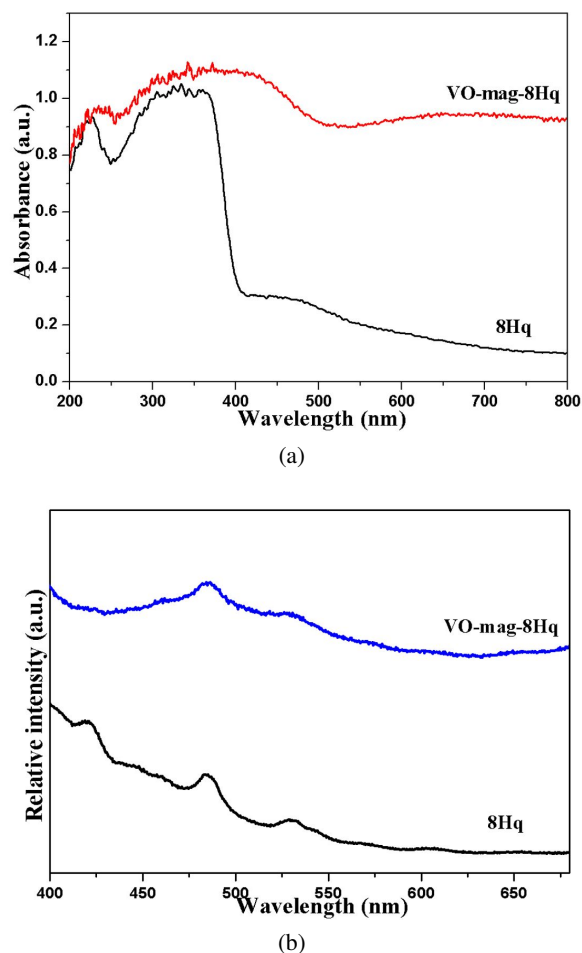
Fig. 9. UV-Vis (a) and PL (b) spectra of VO-mag-8Hq.

been successfully performed for the first time. VO-8Hq complexes in the interlayer space exhibited special fluorescence properties and the confined space of mag influenced the optical properties of VO-mag-8Hq. Due to easy operation of solid-solid reaction, present reactions and their products are useful for practical applications. Further studies on synthesis of intercalated compounds with controlled structures and functions using 8Hq ligand and different metal cations are in development.

Acknowledgements

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