

A strategy to the ordered assembly of functional small cations with layered double hydroxides for luminescent ultra-thin films†

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Received 22nd March 2010, Accepted 26th May 2010

DOI: 10.1039/c0cc00522c

A cationic functional molecule (BNMA) was assembled with a positively-charged LDH monolayer through a polyanion (PVS) as the intermediary. The approach allows fine-tuning and ordered assembly of functional cations with LDH monolayers for designing and achieving novel organic–inorganic ultra-thin films.

Layered double hydroxides (LDHs) are an important class of anionic clay, which can be described by the general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^+ A^{n-}_{z/n} \cdot yH_2O$. Here, M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is an anion. These materials serve as important additives in the chemical industry and have also attracted considerable interest for their potential application in catalysis,¹ separation processes² and drug delivery.³ Unlike most cationic clay materials, such as montmorillonite, the important feature of LDHs is that synthesis allows the layered charge density and the elemental composition to be tuned over a wide range, which facilitates fine control of the properties of the host layer.⁴ Moreover, according to the demands of specific performances, researchers have rationally chosen and designed hundreds of suitable functional anions to assemble with LDHs for constructing new types of organic–inorganic hybrid materials.⁵ However, it is well known that only anionic species can be directly intercalated into the galleries of the positively-charged LDH layer, owing to the charge-balance rule. To date, the assembly of functional cations with LDH layers, to the best of our knowledge, has never been reported. This largely restricts the development of LDH-based functional materials and remains a stimulating challenge. Therefore, it is highly desirable to achieve an approach for the assembly of LDH layers and abundant functional cations to extend the field of layered composite materials with prospective applications based on the performance of the two parts.

Recently, much concern has focused on the ordered assembly of the exfoliated LDH monolayer and functional polyanions through the layer-by-layer (LBL) technique, and the resulting hybrid ultra-thin films (UTFs) combine the advantages of tunable organic–inorganic components and controllable

thickness at the nanoscale.⁶ The fabrication principle, through electrostatic assembly of these UTFs, inspires and enlightens us to challenge the goal of assembly of cations and LDH monolayers. Herein, we put forward a concept and develop a general and facile method to fabricate novel cation–LDH UTFs with a suitable polyanion as the carrier: Firstly, small functional cations are adsorbed onto the main chain of the polyanion, based on Coulombic interaction at the molecular level, yielding a cations@polyanion pair incorporating both negative charge and the functional behavior of the cation. Subsequently, the alternative layer-by-layer assembly of this cations@polyanion pair and LDH monolayer can be achieved for constructing one type of new UTF material. The cations@polyanion pair is analogous to the symbiotic relationship in biological systems, *i.e.*, their stable co-existence in the gallery environment is provided by the positively-charged LDH monolayer.

In this work, a photoactive divalent cation bis(*N*-methyl-acridinium) (BNMA, an important dye in the field of chemiluminescence) and an optically-inert polyanion polyvinylsulfonate (PVS), were chosen for the formation of a BNMA@PVS pair in solution with a certain ratio. The ion pairs act as an integrated structure with a negative charge to alternately assemble with exfoliated Mg–Al-LDH monolayers for the purpose of fabrication of (BNMA@PVS/LDH)_{*n*} (*n* = 4–32) UTFs (Scheme S1†), which shows long-range order and well-defined emission of yellow-green light. The UTFs exhibit better optical properties with longer fluorescence lifetimes and well polarized fluorescence, compared with the pristine BNMA sample. Molecular dynamic simulation studies indicate that the BNMA@PVS/LDH UTF is a stable system structurally dominated by electrostatic interactions, and the BNMA@PVS pair exhibits preferential orientation between the LDH monolayer, facilitating the enhancement of the optical properties of BNMA cations. The approach in this work allows ordered assembly and fine-tuning of the functional cations/LDH system, and thus provides great opportunities to design and prepare novel LDH composite materials by combining the controllable properties of both the host layer and the guest molecules.

UV-visible absorption spectra measurements for (BNMA@PVS/LDH)_{*n*} UTFs with varying numbers of assembly steps are shown in Fig. 1a. The intensities of the characteristic absorption bands of BNMA at 265 and 371 nm correlate linearly with the bilayer number, *n* (Fig. 1a, inset), demonstrating an ordered and regular film growth procedure. The fluorescence emission intensity at 510 nm also presents consistent enhancement with the increase of *n* (Fig. 1b). It can be seen that these films

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† Electronic supplementary information (ESI) available: Experimental and computational details, structure and morphology characterization of BNMA@PVS/LDH. See DOI: 10.1039/c0cc00522c

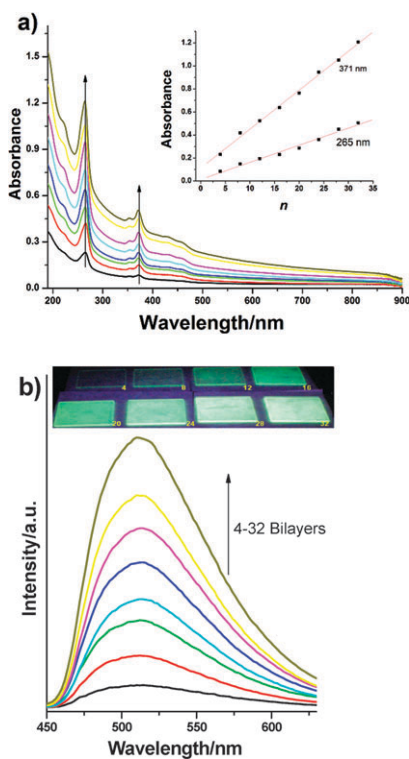


Fig. 1 (a) UV-vis absorption spectra, (b) fluorescence spectra of the $(\text{BNMA@PVS/LDH})_n$ ($n = 4-32$) UTFs. The insets in (a) and (b) show the plots of absorbance at 265 and 371 nm vs. n , and optical photographs under 365 nm UV irradiation, respectively.

exhibit uniform and increasing bright luminescence upon increasing the bilayer number under UV light irradiation (the inset of Fig. 1b), with the color coordinates (CIE 1931) mainly located in the yellow-green region (ESI: Table S1†). Compared with the pristine BNMA solution (Fig. S1†), no obvious red or blue shift in the absorption and fluorescence spectra was found for the as-prepared UTFs with different bilayers, suggesting no formation of BNMA aggregation occurs throughout the whole assembly processing. X-ray diffraction (XRD, Fig. S2 and Table S2†) shows that the UTFs are significantly ordered and that the periodic layered structure grows in the perpendicular direction with a period of *ca.* 1.3 nm corresponding to the thickness of one BNMA@PVS/LDH unit. The XRD reflection intensity also increases upon increasing the bilayer number. The Fourier transform infrared (FT-IR) spectra shows that the peak positions of the BNMA@PVS/LDH UTF are nearly unchanged compared with those of the pristine BNMA sample (Fig. S3†).

A top-view scanning electron microscope (SEM) image for $(\text{BNMA@PVS/LDH})_8$ UTF (Fig. 2a) shows that the film surface is continuous and uniform, and a film thickness of *ca.* 15 nm can be estimated by observing the side-view SEM image (Fig. 2b). The atomic force microscopy (AFM) image (Fig. 2c) reveals morphology and roughness information of the UTF, from which it can be seen that the film surface is smooth enough, with a root-mean-square roughness of 6.618 nm. Using fluorescence microscopy (Fig. 2d), the UTF shows a green color with a homogeneous brightness over its entire area, indicating that the BNMA chromophores are

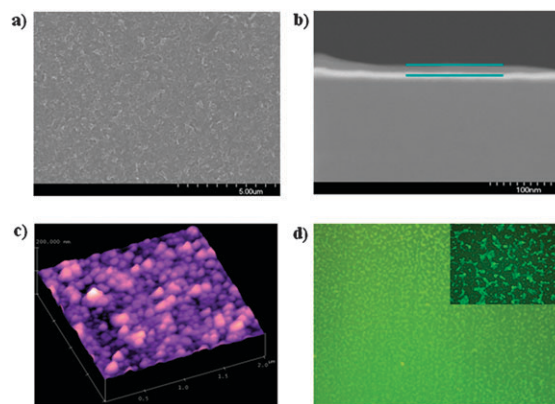


Fig. 2 The morphology of $(\text{BNMA@PVS/LDH})_8$ UTF for (a) top-view SEM image, (b) side-view SEM image, (c) tapping-mode AFM image, and (d) fluorescence microscope image multiplied by 50-fold and 1000-fold (the inset plot).

distributed uniformly throughout the whole film. Moreover, the as-prepared UTFs with different bilayer numbers were further monitored by SEM and AFM (Table S3 and Fig. S4†). AFM shows that the films are microscopically uniform and smooth, with the roughness less than 14 nm in each case, and the side-view SEM images reveal an approximately linear growth of the thickness of *ca.* 1.5 nm for per $(\text{BNMA@PVS/LDH})_1$ bilayer growth, which is very close to the basal spacing obtained by XRD. This confirms that the multilayer film has a uniform and periodic layered structure, in accordance with the assembly behavior observed by UV-vis absorption and fluorescence spectra.

It is illuminating to further compare the photophysical and electric properties of BNMA@PVS/LDH UTFs with the pristine BNMA sample. Analysis of the fluorescence lifetimes (see Fig. S5 and Table S4†) reveals that the fluorescence lifetime of BNMA-PVS@LDH UTF is prolonged by 12.5–13.6-fold (4.61–5.03 ns) compared with the pristine powder (0.37 ns). This remarkable increase is related to the uniform dispersion of the BNMA cations between LDH monolayers, with the existence of PVS polyanions. Both the isolation effect imposed by the rigid LDH monolayers and the interaction between PVS polyanion and BNMA prevent the formation of chromophore aggregation. As a result, better photoemission behavior can be obtained for the UTF system. Moreover, anisotropic photoluminescence spectroscopy demonstrates that the UTFs exhibit strongly polarized fluorescence with an anisotropy value⁷ of 0.15–0.2 (Fig. 3), whereas no polarization was found for the pristine BNMA powder and solution. The UTFs also show a luminescence anisotropy decay effect in the range of the fluorescence lifetime (Fig. S6 and Table S5 †). This observation reveals that the ordered assembled BNMA@PVS/LDH UTFs result in an enhanced optical performance compared with the pristine chromophore, and that the UTFs are potentially good candidates for polarized luminescence materials. Furthermore, these UTFs exhibit semiconductor properties, with the turn-on voltage increasing with the increase of the bilayer number, compared with the pristine BNMA (Fig. S7†), demonstrating that the electrical resistance of the UTF system can be tailored by incorporation of the LDH.

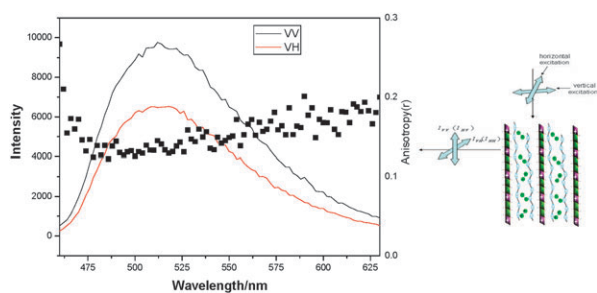


Fig. 3 Polarized fluorescence profiles with glancing incidence geometry in the VV, VH modes and anisotropic value (r) for the (BNMA@PVS/LDH)₃₂ UTF.

To further understand the geometric structures of this new type of UTF system, molecular dynamic (MD) simulation⁸ was employed for an idealized BNMA@PVS/LDH structural model. The computational basal spacing is *ca.* 1.47 nm, in good agreement with the experimental observation obtained by XRD and SEM. Typical snapshots of the BNMA@PVS/LDH system are shown in Fig. S8†. The organic ions are found to adopt an ordered arrangement with a preferred orientation in the as-prepared UTF, with the most probable angle of the N–N axis in the BNMA, with respect to the layers, being 15°, and the most probable angle of the line joining the terminal carbon atoms of PVS, relative to the LDH monolayer, being 2° (Fig. S9†). This ordered arrangement is responsible for the enhancement of the anisotropy of light-emission for the photoactive cations, as revealed by the polarized photoemission. Additionally, the distance of the terminal carbon atoms in PVS reduced by *ca.* 69% compared with that in the fully extended form, suggesting that the polyanions are flexible enough to be confined between the LDH monolayers. Moreover, the absolute electrostatic energy of the system is much larger than its van der Waals interaction, demonstrating that the driving force for the UTF assembly is mainly dominated by the Coulomb interaction.

In summary, we have demonstrated the first example of assembly of functional cations (BNMA) with the positively-charged LDH monolayer using the LBL technique, by means of incorporating the polyanion (PVS) as a carrier. The resulting BNMA@PVS/LDH UTFs have a periodic long-range ordered structure and well-defined yellow-green photoluminescence. In contrast to the pristine BNMA, prolonged luminescence lifetime and polarized photoemission have been achieved for the UTF system, demonstrating that they are

potential candidates for light-emitting materials. An MD simulation study shows that the BNMA molecules adopt a preferred orientation inclined almost parallel to the LDH monolayers which is responsible for the enhanced polarization of the photoemission behavior of the UTFs. Moreover, it can be expected that, by using the co-assembled LBL method described here, numerous cationic species can be assembled with LDH monolayers for designing and fabricating organic–inorganic functional materials based on the symbiotic relationship between the polyanion and the small cation. As an example, we have fabricated another UTF system by assembly of the monovalent cation rhodamine 6G and LDH monolayers by the same approach (Fig. S10†). Further work is underway for the assembly of LDH-based multicolored UTF systems employing red/green/blue luminescent cations.

Notes and references

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- (a) D. P. Yan, J. Lu, M. Wei, J. Ma, D. G. Evans and X. Duan, *Chem. Commun.*, 2009, 6358; (b) D. P. Yan, J. Lu, J. Ma, M. Wei, D. G. Evans and X. Duan, *J. Mater. Chem.*, 2010, **20**, 5016; (c) D. P. Yan, J. Lu, M. Wei, D. G. Evans and X. Duan, *J. Phys. Chem. B*, 2009, **113**, 1381. r can be expressed as the formula: $r = (I_{VV} - GI_{VH}) / (I_{VV} + 2GI_{VH})$, where $G = I_{HV} / I_{HH}$, determined from the aqueous solution. I_{VH} stands for the luminescence intensity obtained with vertical excitation polarized and horizontal detection polarization, and I_{VV} , I_{HV} and I_{HH} are defined in a similar way.
- See the references in the ESI†.