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Three Dimensional Nanowall of Calcein/Layered Double Hydroxide: Towards Electrogenerated Chemiluminescence Sensor

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This paper reports the fabrication of three-dimensional (3D) nanowall structure based on intercalation of Calcein into layered double hydroxide (LDH) by a modified solvothermal direct growth process, and explores its electrogenerated chemiluminescence (ECL) property for detection dopamine (DA). X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the Calcein/LDH nanowall film possess a preferential orientation with their *ab* plane perpendicular to the substrate. The nanowall film shows tunable luminous property by simple changing the amount of Calcein in the LDH interlayer, and the optimum fluorescence intensity occurs in the sample with x=1.25%. The stable and strong ECL signals suggested that this film possesses excellent operational and storage stability, which is essential to a sensor. The ECL intensity increased linearly with increasing DA concentration from 5.00×10^{-7} to 1.01×10^{-4} M. The detection limit was 3.52×10^{-7} M. The mechanism of ECL sensor indicates that the 3D micro-morphology of the Calcein/LDH nanowall film has a positive influence on the electrochemical property due to its high surface area and reduced interface resistance. Therefore, this work not only provides a preparation method for chromophore/LDH complex with 3D micro/nanostructure, but also systematically probed the structure-property relationship of the Calcein/LDH nanowall film. According to this strategy, the advanced sensors and devices with outstanding optical and electrochemical property can be achieved.

1. Introduction

Electrogenerated chemiluminescence (ECL) has the advantages of high sensitivity and selectivity, low background signal and cost, convenient to operate and setup, and versatility,[1,2] which shows wide application in the field of biosensors,[3–5] imaging,[6,7] lasing,[8] and organic light emitting diodes.[9,10] Generally, the ECL reagents are immobilized on a solid electrode surface, so as to reduce the reagent consumption, simplify the designing process, and realize the reversible sensor.[11,12] There are many immobilized techniques to be applied, including self-assembly, Langmuir-Blodgett, electrodeposition, electrospin, and so on. These methods are perfect for getting single layer and/or multilayer film modified electrode. However, the two-dimensional layered structure has a negative effect on mass and electronic transfer due to its dense stack. Therefore, the fabrication of electrode with hierarchical structure is the developing direction for highly efficient ECL sensors and devices.

In recent years, the three-dimensional (3D) electrode materials with micro/nanostructure, which could increase the rate of redox reaction and transfer rate of mass and electron due to its high surface area and reduced interface resistance, is subject to the unprecedented concern as nanotechnology and science continue to develop. Especially, the modified electrode by growing layered double hydroxides (LDHs) micro/nanostructure on surface of the conductive substrate has drawn great interests thanks to their higher redox activity, low cost and excellently environmental-friendly feature.[13,14] In addition, LDHs materials have been widely employed to fix chromophores through adsorption, intercalation, and assembly methods, resulting in ordered and anisotropic arrangement and enhanced optical behavior of the chromophores.[15,16] However, it was barely reported related to ECL property for the complex comprised by LDHs and chromophores with 3D micro/nanostructure. This results from the difficulty to intercalate chromophores into LDHs nanowall interlayer grown on rigid and inflexible conductive substrate. Therefore, the key to design ECL sensor based on 3D micro/nanostructure chromophore/LDH complex roots in how to intercalate chromophores into LDH nanowall interlayer, for the purpose of obtaining excellent optical and electrochemical property.

Herein, Calcein fluorescence molecule was chosen as the model ECL reagent to its high fluorescence efficiency and general application.[17] The preparation for intercalation of Calcein into LDH with 3D nanowall structure by a modified solvothermal direct growth process were reported, and explore its ECL sensor property for detection Dopamine (DA). The Calcein/LDH nanowall is approximately vertically aligned

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on the substrate, and its average height is 5 μm. The luminous property can be tuned by changing the amount of Calcein in LDH interlayer, and the optimum fluorescence intensity occurs in *x*=1.25%. The stable and strong ECL signals suggests that this film possesses potential cycling stability, which is very suitable for a sensor device. The ECL intensity increased linearly with increasing DA concentration from 5.00×10^{-7} to 1.01×10^{-4} M. The detection limit was 3.52×10^{-7} M. The mechanism testified that the emitter for ECL sensor to DA is Calcein molecule; the micro-morphology of the Calcein/LDH film has an impact on the electrochemical property. Therefore, we not only provide a preparation method for chromophore/LDH complex with 3D micro/nanostructure, but also systematically probed the structure-property relationship of the Calcein/LDH nanowall film. On the basis of the instance, the advanced ECL sensors and devices with high optical and electrochemical property can be designed.

2. Materials and methods

2.1 Materials

N, N-bis (carboxymethyl) aminomethylfluorescein (Calcein), and Dopamine (DA) were purchased from Sigma-Aldrich Company. Analytical grade chemicals including $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, C_2H_5OH, phosphate buffer solution and acetone were used without further purification. The deionized and decarbonated water was used in all the experimental processes.

2.2 Fabrication of the Calcein/LDH nanowall film

The fabrcation of the Calcein/LDH nanowall was carried out by using a modified solvothermal direct growth process reported previously.[18] $Mg(NO_3)_2{\cdot}6H_2O$ (2 mmol), $Al(NO_3)_3{\cdot}9H_2O$ (1 mmol), NH_4F (10 mmol) and urea (70 mmol) were dissolved in 100 mL of deionized water. Then Calcein (*a* mol) were dispersed in salt solution with stirred thoroughly for 1 h, in which $x = a/n(\mathrm{Al}) = 0.1\%$, 1.25%, 10%, and 100%, respectively. The ITO substrates were cleaned in an ultrasonic bath by succesive using detergent, deionized water, acetone, ethanol and deionized water for 10 min each. Subsequently, the cleand ITO substrate was immersed into the above solution at 80 ˚C for 7 h. The substrate coated with the Calcein/LDH nanowall film was then withdrawn from the solution, and washed fully with deionized and decarbonated water and dried at 20 ˚C.

2.3 Techniques

A scanning electron microscope (SEM ZEISS) was used to study the morphology of ECL sensor with 20 kV accelerating voltage. The structue was studied by appling X-ray diffraction patterns (XRD) with a Rigaku 2500 VB2+PC diffractometer (40 kV, 50 mA, and Cu Kα radiation λ = 0.154056 nm), step-scanned with a scanning rate of 2 °/min, and a 2ϑ angle ranging from 2 to 70°. The Fourier transform infrared (FTIR) spectra were recorded using a Vector 22 (Bruker) spectrophotometer in the range 4000–500 cm^{-1} with 4 cm^{-1} resolution. The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer with the excitation wavelength of 490 nm, and the emission spectra range in 500–700 nm were recorded with 3 nm of excitation and emission slits. The film fluorescence image was observed by using an OLYMPUS-BX51 fluorescence microscope equipped with an Andor iXON electron amplifying CCD camera (DU-885K-C00). The exposure value is 10 ms. The ECL analyzer system was applied to detect DA with a model MPI-E at 800 V. The electrochemical (EC) measurements were performed using a CHI 660B electrochemical workstation. A conventional three-electrode system was used in both of ECL and EC process, including a working electrode (modified ITO glass), a auxiliary electrode (platinum foil), and a reference electrode (saturated Ag/AgCl). All measurements were carried out in 50 mM phosphate buffer solution with pH 7.

3. Results and discussion

3.1 Morphology and structure

Figure 1A shows top-view SEM observations of the Calcein/LDH nanowall film, from which uniform hexagonal plate-like microcrystals were observed with diameter of 0.5–1 μm and thickness of 30 nm. The Calcein/LDH film has a vertical wall network structure composed by interconnected and intersected nanoplatelet building blocks, which caused by a "heterogeneous nucleation growth" mechanism.[19] This nanostructure can further be observed from high-magnification SEM (Figure S1). A representative cross-sectional SEM image (Figure 1B) shows that the Calcein/LDH nanowall film with an average height of 0.5 μm is approximately vertically arranged on the substrate. Figure 1C illustrates the XRD patterns of the bare ITO substrate, Calcein/LDH film on ITO, and corresponding powder sample scraped from ITO substrate. The Calcein/LDH film on ITO substrate shows a series of reflection at 34.8 °, 39.2 °, 61.1 ° and 62.4 ° compared

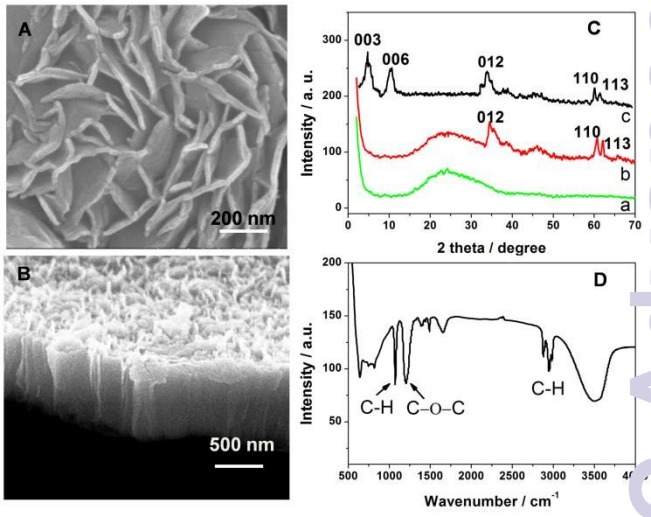

Figure 1. (A) Top-view SEM images and (B) cross-sectional SEM image of the Calcein/LDH film on ITO substrate. (C) XRD patterns of (a) bare ITO substrate, (b) the Calcein/LDH film and (c) the Calcein/LDH powder. (D) FT-IR spectrum of the Calcein/LDH film.

to bare ITO, corresponding to [012], [015], [110] and [113] reflections peaks, respectively. This result demonstrates successful growth of the Calcein/LDH nanowall on the ITO substrate. In case of the powder sample occurs two new reflections at 5.1 ° and 10.3 °, corresponding to the [003] and [006] of an randomly stacked-LDH phase, respectively. The absence of [00*l*] reflections for the Calcein/LDH nanowall film indicates a preferential orientation of LDH crystallites with their *ab* plane perpendicular to the substrate. Moreover, the [003] and [006] reflection peaks of the Calcein/LDH nanowall shift to low angle compared with MgAl-CO_3-LDH nanowall, demonstrating Calcein was intercalated into LDH interlayer (Figure S2). In order to further clarify Calcein intercalation, the control experiment was carried out by adsorbing Calcein on the surface of the MgAl-CO_3-LDH nanowall film. Figure S3 displays the ECL intensity of Calcein/LDH nanowall film is 30 fold higher than that of Calcein adsorbed LDH film, demonstrating the absorption amount of Calcein on the LDH surface is very few which can almost be omitted. In addition, the appearance of vibration of C–H and C–O–C for the Calcein/LDH nanowall film in FT-IR spectrum further confirms the intercalation of Calcein, consistent with the results of XRD (Figure 1D).

3.2 Fluorescence performance

Figure 2A shows the fluorescence emission spectra for the Calcein/LDH (*x*%) nanowall film with different amount of Calcein in the interlayer of LDH. Figure 2B displays the fluorescence intensity increase at first to a maximum and then decrease as the increasing of Calcein amount. The optimal luminous intensity present in the sample with *x*=1.25% with an emission peak of 510 nm. The corresponding fluorescent microscopic photographs shows uniform and strong green fluorescence (insert in Figure 2A). The fluorescence intensity increases by one order of magnitude for the sample of the Calcein/LDH (*x*=1.25%) nanowall film compared with Calcein solution (10^{-5} mol·L^{-1}). A red-shift from 510 to 530 nm was observed along with progressively decreasing intensity as *x* increases from 1.25% to 100%, which can be attributed to the change in the aggregation state of interlayer Calcein molecule. This result indicates the fluorescence emission wavelength and intensity of the Calcein/LDH nanowall film can be simply tuned by controlling the amount of Calcein in LDH matrix. It is noted that the maximum emission intensity of the nanowall film almost is equal to the parallel film (Figure S4). This demonstrates the structure and morphology have no influence on fluorescence property of the Calcein/LDH film with same chemical composition. Furthermore, the Calcein/LDH nanowall film shows optimum fluorescence emission at pH=7–8 due to the equilibrium between different fluorescence forms of Calcein in the LDH gallery (Figure S5). Thus, the ECL performance was evaluated at pH=7.4, so as to obtain ECL sensor and device with excellently sensory property which can be used at physiological condition.

3.3 Electrogenerated chemiluminescence sensor

Dopamine (DA) is one of the most important biogenic amines, which has a vital role to play in the renal, central nervous, cardiovascular and hormonal systems as well as in drug addiction.[20,21] Several diseases will occur with abnormal levels of DA, including Parkinson,[22] hypertension and heart failure.[23] Thus, it is absolutely crucial to detect DA content with rapidity and sensitivity, so as to obtain timely and effective therapy. Various methods have been applied to determine the DA content, such as high performance liquid chromatography (HPLC),[24,25] fluorescence spectrum,[26,27] ion chromatography,[28] and ECL spectrum.[29] Among them, the ECL method has attracted extensive concerns due to remarkable simplicity, rapidity, high sensitivity and easy controllability.[30]

3.3.1 Stability

The Calcein/LDH nanowall film was used as the electrode at anode to detect DA concentration. Firstly, the stability was tested in order to guarantee the usability of the nanowall film in the practical detection applications. Figure 3 shows the E[illegible] signal–time curve of film in 10^{-6} mol·L^{-1} DA + 0.1 mol·L^{-1} PBS (pH 7.4) at 100 mV·s^{-1} under continuous potential scanning 1[illegible] cycles. The ECL signal exhibits no obvious change with low relative standard deviation (RSD = 0.57%) of the peak height, demonstrating the good operational stability of the sensor. After 1 month, the ECL sensor stored in PBS of pH 7.4 at 4 °[illegible] still retained about 97% of its initial intensity response (Figure S6). The stable and strong ECL signals suggested that this sensor possesses good cycling stability, which is very suitable for determination of DA.

3.3.2 Detection of DA

Figure 4A shows the more the appearance of DA, the larger ECL intensity of the Calcein/LDH nanowall film. The ECL intensity increased linearly with increasing DA concentration in

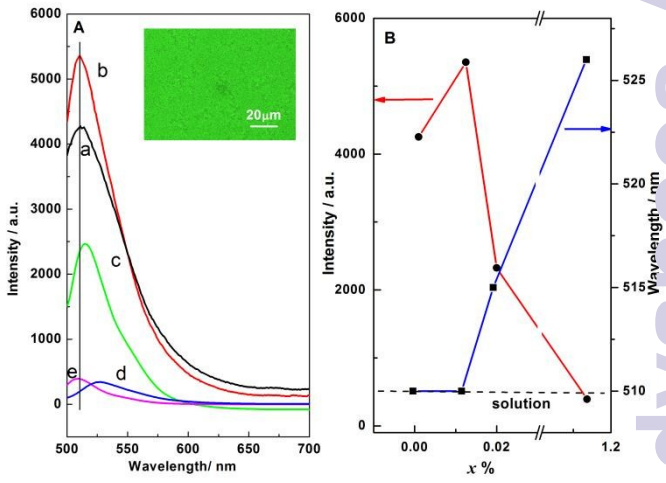

Figure 2. (A) The photoemission spectra of the Calcein/LDH (*x*%) nanowall film f[illegible] (a)~(d) *x* = 0.1%, 1.25%, 10%, and 100%, respectively and (e) pristine Calcein in solution with the excitation wavelength of 490 nm. The inset plot shows the fluorescent microscopic photographs for *x* = 1.25% (40×/0.75 dry objective). (B) Fluorescence intensity at the maximum emission peak and emission wavelength at the maximum emission peak varying with the increase of Calcein content in the Calcein/LDH (*x*[illegible]) nanowall film.

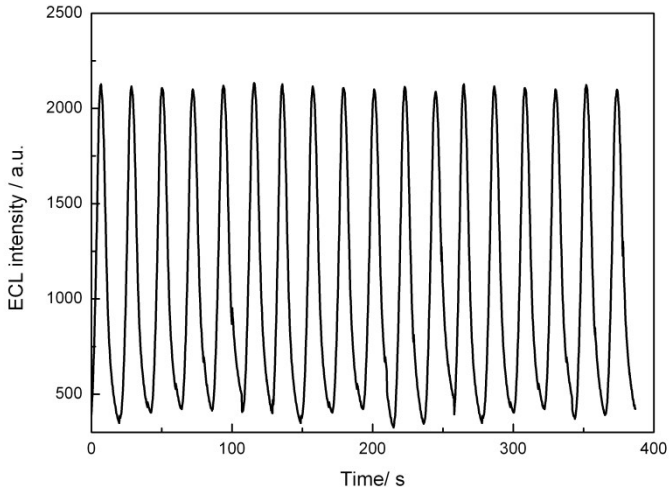

Figure 3. The ECL stability of proposed sensor in 10^{-6} mol·L^{-1} DA + 0.1 mol·L^{-1} PBS (pH 7.4) at 100 mV·s^{-1}.

the range 5.00×10^{-7} to 1.01×10^{-4} M, with the following linear regression equation: I = 98.3+1.88×10^{6} c (M), R^2 = 0.9987. The detection limit was 3.52×10^{-7} M based on the signal to noise ratio of 3. A control study between our work and other reported DA chemosensors was performed (Table 1). It can be seen that the ECL sensor of Calcein/LDH nanowall film displays a wide linear range response and low detection limit based on the comparison to references.[31–34] The ECL enhancement mechanism possibly attribute to the superior electrochemical property of the Calcein/LDH vertical nanowall film, which will be testified by the following electrochemical measurement (3.4.1 section). Moreover, the selectivity of the film has been also carried out and shown in Figure S7. It can be observed that AA has no effect on detection for DA in the mixture solution of DA and AA even if the concentration of AA is 500 fold higher than that of DA. Based on above results, we can conclude that the film shows a high selectivity for DA, which can be potentially used in practical application.

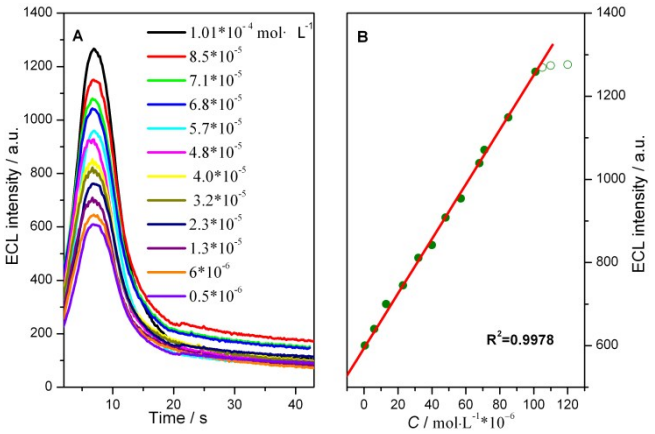

Figure 4. (A) The ECL of the Calcein/LDH nanowall film modified electrode in 0.1 mol·L^{-1} PBS (pH = 7.4) in the presence of DA with various concentrations (from 0.5×10^{-6} to 1.01×10^{-4} M). Scan rate: 100 mV s^{-1}. (B) The plot of ECL intensity *vs.* DA concentration.

Table 1 Comparison of the present method for the determination of DA with the other reported methods.

Electrodes	Method	Linear range (μM)	Detection limit (μM)	Ref.
SWCNT/Fe_2O_3/graphite	SWV[a]	3.2–31.8	0.36	31
Ag_2SeDs/PEI/MWCNTs/GCE	ECL	0.5–19.5	–	32
BSA[b]-stabilized Au nanocluster/ITO	ECL	2.5–47.5	–	33
CdSe quantum dots/ITO[c]	ECL	0.5–70	0.50	34
Calcein/LDH nanowall film/ITO	ECL	0.5–101	0.35	This work

[a]SWV, square wave voltammetry. [b]BSA, bovine serum albumin. [c]ITO, indium tin oxide.

3.4 The relationship of structure-property

3.4.1 Electrochemical behavior

Both of the Calcein/LDH parallel film and vertical nanowall film show similar optical behavior based on the results from the fluorescence spectra. Thus, for the sake of explanation the enhanced reason of ECL property, the electrochemical behavior of different film modified electrodes were studied shown in Figure 5. It can be found that both electrodes modified by the Calcein/LDH parallel film and vertical nanowall film moved the oxidation peak of DA to lower potential with a shift of 650 mV compared with bare ITO electrode, parallel and vertical MgAl-NO_3-LDH modified electrodes. The lower oxidation potential of DA can be attributed to the appearance of Calcein molecule, which facilitates the electron transfer of DA oxidation. It is important to note the oxidation peak current (i_{pa}) of vertical Calcein/LDH nanowall film modified electrode increased two times compared with the parallel film modified electrode. This result indicates that the micro morphology of the Calcein/LDH film has an impact on the electrochemical property, in which the 3D nanowall structure is more favorable for electron and mass transfer than parallel film, subsequent speeding up the catalysis oxidation of DA significantly.

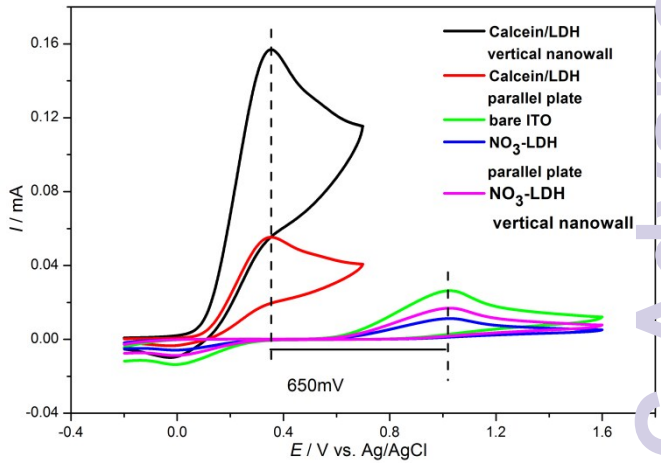

Figure 5. Cyclic voltammograms obtained with different electrodes in 10^{-6} mol·L^{-1} DA + 0.1 mol·L^{-1} PBS (pH 7.4) at 100 mV·s^{-1}.

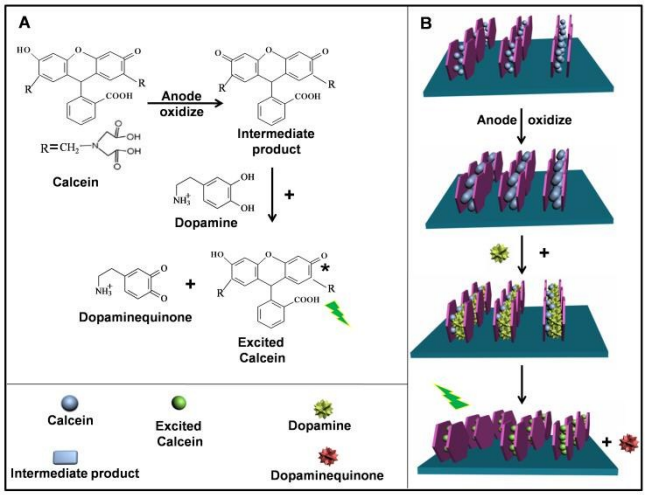

Figure 6. (A) The reaction pathway and (B) model pattern of the detection for DA using the Calcein/LDH nanowall film as modified electrode.

3.4.2 The ECL mechanism

The CL spectra of the ECL peak for the Calcein/LDH nanowall film was measured by inserting filters at wavelengths of 440, 460, 480, 530, 550, 570, and 620 nm under CV conditions. The ECL emission maximum at a wavelength of approximately 511 nm, which is almost equal to that of the fluorescence spectrum of Calcein, implies Calcein is the emitter. Therefore, the redox reaction between Calcein and DA can be deduced based on the results obtained from this work.[24] The reaction pathway and model pattern for the detection of DA by the Calcein/LDH nanowall film modified electrode can be represented in Figure 6. Firstly, the intermediate product (oxidized form of Calcein) was formed by oxidizing Calcein at anode owe to the appearance of hydroxyl group in host layers of LDH; Secondly, the reduced form of excited state Calcein (Calcein*) and dopaminequinone DA occur caused by the reaction between oxidized form of Calcein and DA; Finally, the fluorescence was emitted resulting from reduced form of Calcein* returns to the ground state.

4. Conclusions

Summary, the Calcein/LDH nanowall film was prepared by intercalating Calcein into LDH interlayer through a modified solvothermal direct growth process on ITO substrates, which demonstrates extraordinary ECL sensor property for detection DA molecule. Both of the cross-sectional SEM image and absence of [00*l*] reflections certify that a preferential orientation of the Calcein/LDH nanowall film with their *ab* plane perpendicular to the substrate. The fluorescence emission wavelength and intensity of the nanowall film can be tuned by controlling the amount of chromophore in LDH nanowall. The structure and morphology have no influence on fluorescence property of the Calcein/LDH film. In addition, the film modified electrode was used as ECL sensor to detect DA concentration, which shows high operational stability (RSD=0.55% in 18 cycles), storage stability (retained about 97% of its initial response after 1 month), broad linear range (from 5.00×10^{-7} to 1.01×10^{-4} M), and low detection limit (3.52×10^{-7} M). The study of structure-property shows the 3D micro-morphology of the Calcein/LDH film has a positive impact on the electrochemical property, which is more favorable for electron and mass transfer. Moreover, CL spectra confirmed the emitter is Calcein during the detection for DA. Therefore, this work not only provides a method to fabricate fluorescence film with 3D mirco/nanostructure based on chromophore and LDH, but also further confirmed the correlation between structure and property (fluorescence and electrochemistry) of the Calcein/LDH film. According to this strategy, other ECL sensors and devices with hierarchical structure and extraordinary performance can be obtained by virtue of tunability of LDH and the variety of chromophore molecules.

Acknowledgements

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References

1 L. R. Faulkner, A. J. Bard, Electroanalytical Chemistry, A. J. Bard, (Ed.), Marcel Dekker, New York, 1977, pp 1–95.
2 M. M. Richter, *Chem. Rev.*, 2004, **104**, 3003–3036.
3 X. Ou, X. R. Tan, X. F. Liu, H. M. Chen, Y. Fan, S. H. Chen, S. P. Wei, *RSC Adv.*, 2015, **5**, 66409-6641.
4 C. A. Marquette, L. J. Blum, Chemiluminescence and Bioluminescence: Past, Present and Future, A. Roda (Ed.), Royal Society of Chemistry, 2010, pp 488–510.
5 H. J. Wang, J. Zhang, Y. L. Yuan, Y. Q. Chai, R. Yuan, *RSC Adv.*, 2015, **5**, 58019-58023.
6 X. M. Lin, L. Y. Zheng, G. M. Gao, Y. W. Chi, G. N. Chen, *Anal. Chem.*, 2012, **84**, 7700–770.
7 J. Y. Zhou, G. Z. Ma, Y. Chen, D. J. Fang, D. C. Jiang, H. Y. Chen, *Anal. Chem.*, 2015, DOI 10.1021/acs.analchem.5b00542.
8 V. G. Kozlov, V. Bulovic, P. E. Burrows, S. R. Forrest *Nature*, 1997, **389**, 362–364.
9 X. H. Zhu, J. Peng, Y. Cao, J. Roncali, *Chem. Soc. Rev.* 2011, **40**, 3509–3524.
10 M. Shen, J. Rodríguez-López, J. Huang, Q. Liu, X. H. Zhu, A. J. Bard, *J. Am. Chem. Soc.*, 2010, **132**, 13453–13461.
11 Q. K. Kong, M. Li, C. Ma, H. M. Yang, S. G. Ge, M. Yan, J. H. Yu, *RSC Adv.*, 2015, **5**, 70345–70351.
12 L. Mao, R. Yuan, Y. Q. Chai, Y. Zhuo, Y. Xiang, *Biosens. Bioelectron.*, 2011, **26**, 4204–4208.
13 H. Maki, M. Takigawa, M. Mizuhata, *ACS Appl. Mater. Interfaces*, 2015, **7**, 17188–17198.
14 F. Z. Zhang, L. Guo, S. L. Xu, R. Zhang, *Langmuir*, 201 **31**, 6704–6712.
15 D. P. Yan, J. Lu, M. Wei, D. G. Evans, X. Duan, *J. Mater. Chem.*, 2011, **21**, 13128–13139.
16 Q. Wang, D. O'Hare, *Chem. Rev.*, 2012, **112**, 4124–41 5.
17 H. Diehl, J. L. Ellingboe, *Anal. Chem.*, 1956, **28**, 882–884.
18 J. W. Zhao, M. F. Shao, D. P. Yan, S. T. Zhang, Z. Y. Lu, X. Li, X. Z. Cao, B. Y. Wang, M. Wei, D. G. Evans, X. Du *J. Mater. Chem. A*, 2013, **1**, 5840–5846.

19 H. Y. Chen, F. Z. Zhang, S. Fu, X. Duan, *Adv. Mater.*, 2006, **18**, 3089–3093.
20 C. Wang, R. Yuan, Y. Q. Chai, Y. Zhang, F. X. Hu, M. H. Zhang, *Biosens. Bioelectron.*, 2011, **30**, 315–319.
21 X. M. Feng, C. J. Mao, G. Yang, W. H. Hou, J. J. Zhu, *Langmuir*, 2006, **22**, 4383–4389.
22 Z. Zhelev, R. Bakalova, I. Aoki, D. Lazarova, T. Saga, *ACS Chem. Neurosci.*, 2013, **4**, 1439–1445.
23 K. T. Homan, J. J. G. Tesmer, *ACS Chem. Biol.*, 2015, **10**, 246–256.
24 F. D. P. Ferreira, L. I. B. Silva, A. C. Freitas, T. A. P. Rocha-Santosa, A. C. Duarte, *J. Chromatogr. A.*, 2009, **1216**, 7049–7054.
25 B. Ferry, E. -P. Gifu, I. Sandu, L. Denoroy, S. Parro, *J. Chromatogr. B.*, 2014, **951–952**, 52–57.
26 Y. Sakaguchi, H. Yoshida, T. Hayama, M. Itoyama, K. Todoroki, M. Yamaguchi, H. Nohta, *J. Chromatogr. A.*, 2011, **1218**, 5581–5586.
27 V. S.-Y. Lin, C. Y. Lai, J. G. Huang, S. A. Song, S. Xu, *J. Am. Chem. Soc.*, 2001, **123**, 11510–11511.
28 C. L. Guan, J. Ouyang, Q. L. Li, B. H. Liu, W. R. G. Baeyens, *Talanta*, 2000, **50**, 1197–1203.
29 L. L. Xue, L. H. Guo, B. Qiu, Z. Y. Lin, G. N. Chen, *Electrochem. Commun.*, 2009, **11**, 1579–1582.
30 W. J. Miao, *Chem. Rev.*, 2008, **108**, 2506–2553.
31 A. S. Adekunle, B. O. Agboola, J. Pillay, K. I. Ozoemena, *Senser. Actuat. B: Chem.*, 2010, **148**, 93–102.
32 R. Cui, Y. P. Gu, L. Bao, J. Y. Zhao, B. P. Qi, Z. L. Zhang, Z. X. Xie, D. W. Pang, *Anal. Chem.*, 2012, **84**, 8932–8935.
33 L. L. Li, H. Y. Liu, Y. Y. Shen, J. R. Zhang, J. J. Zhu, *Anal. Chem.*, 2011, **83**, 661–665.
34 X. Liu, L. X. Cheng, J. P. Lei, H. X. Ju, *Analyst*, 2008, **133**, 1161–1163.

A table of contents entry

Three Dimensional Nanowall of Calcein/Layered Double Hydroxide: Towards Electrogenerated Chemiluminescence Sensor

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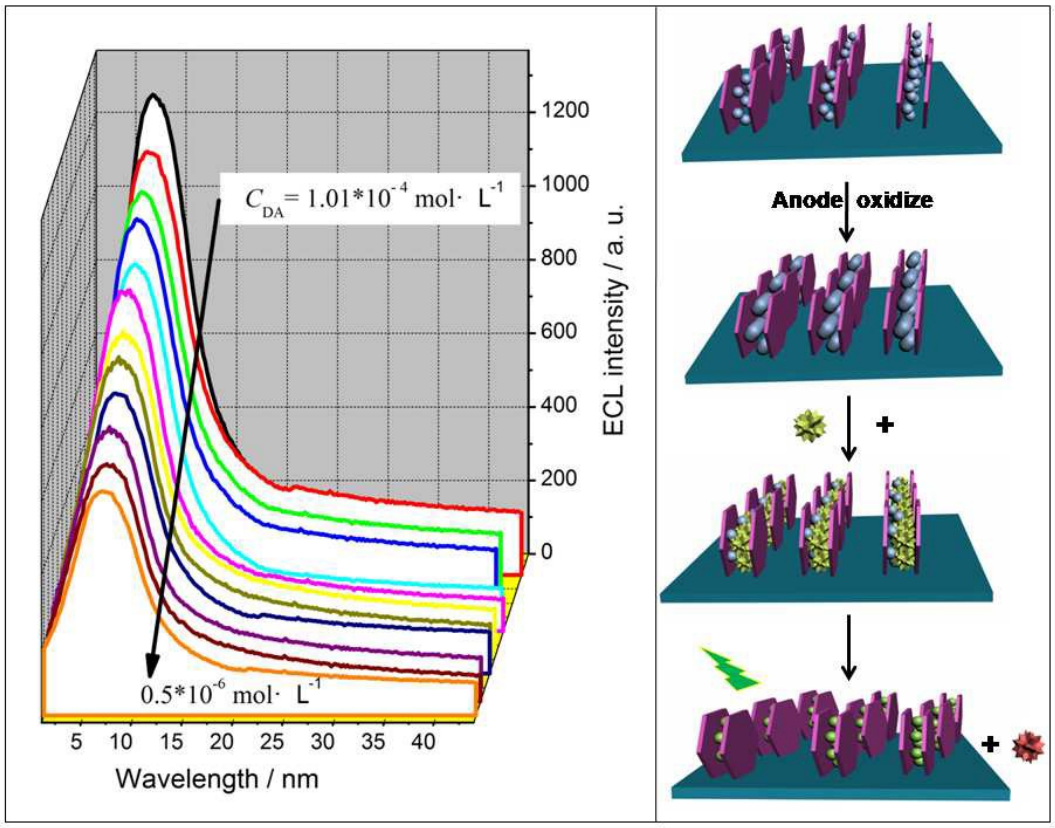

This paper reports fabrication of Calcein intercalation into layered double hydroxide with 3D

nanowall, and explores its electrogenerated chemiluminescence property.