

Synthesis and electrochemical properties study of novel intercalation compound of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with cationic methylene blue

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Published in Micro & Nano Letters; Received on 9th July 2013; Revised on 11th October 2013; Accepted on 17th October 2013

A functional layered nanocomposite, $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$, was prepared by the intercalation of methylene blue (MB) into the layered material, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, by a guest-exchange method using the $n\text{-PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ intercalation compound as an intermediate. The resultant nanocomposite was characterised by powder X-ray diffraction and infrared. Electrochemical studies reveal that the target hybrid retains the good redox activities of MB^+ cation and has potential utilisation in electrocatalytic reactions.

1. Introduction: Two-dimensional layer materials have attracted considerable attention because of their unique structures and applications in massive fields such as photocatalysis, ion-exchange, intercalation and electrochemical activity [1–4]. To the best of our knowledge, perovskite structure transition metal oxides such as niobium-based semiconductor materials are mostly layer-structured. Most importantly, KNb_3O_8 , $\text{KNb}_4\text{O}_{17}$, KTiNbO_5 and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ exhibit unique electronic and optical properties [5–7]. With the unique structures and properties, the Dion-Jacobson phases material, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (shown in Fig. 1), has recently been a focus of researchers' attention, a substantial number of functional organic compounds can be inserted into the layer material because of its ion-exchange property.

The thiazine cationic dye, methylene blue (MB), has been widely used in electrochemical biosensors and electrochemical determinations as a catalyst-mediator or redox indicator by virtue of its redox potential [8]. It is a positively charged water-soluble redox dye. However, the low molecular weight water-soluble property of MB

may affect its stability as biosensors [9]. Therefore MB has been reported to be inserted into layered materials such as zirconium phosphate and layered manganese oxide to overcome this shortcoming. To date, there is no printed literature on the combination of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with MB.

2. Experimental: The layered material, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, was prepared by the solid-state reaction of stoichiometric quantities of a high-purity mixture of K_2CO_3 , CaCO_3 and Nb_2O_5 at 1250°C for 24 h [10]. The intercalation compound of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ with MB^+ is difficult to prepare by a direct reaction because of the bulkiness of MB, thus a two-step intercalation with $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ as a precursor was taken to prepare the nanocomposite $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$. $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ was prepared as follows: first, 2 g of the powder $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was treated with 6 M HNO_3 for 72 h at room temperature three times to obtain calcium niobate acid $\text{HCa}_2\text{Nb}_3\text{O}_{10}$. Then, 1.0 g $\text{HCa}_2\text{Nb}_3\text{O}_{10}$ was stirred with 20 ml of 50% *n*-propylamine aqueous solution at 60°C for three weeks and white $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ powder was obtained. The target nanocomposite was prepared by mixing 0.5 g $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ with 5 mM MB^+ aqueous solution in a 50 ml glass ampoule for four weeks at 70°C . Finally, the resultant sample was centrifuged and washed with distilled water several times to obtain the blue violet powder $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$.

3. Results and discussion: We have employed a two-step ion exchange method and successfully inserted MB^+ into the layered material. The XRD patterns of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, $\text{HCa}_2\text{Nb}_3\text{O}_{10}$, $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ and $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ are shown in Fig. 2. From Fig. 2 (a) and (b), we can see that the interlayer spacing changes from 1.48 to 1.55 nm after the protonation of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$. The sharp peak exhibits that the sample has a high crystallinity and all the peak indices shown matched well with the reported patterns [11]. The two-step intercalation compound, $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$, has a d_{002} value of 2.26 nm, which indicates that H_3O^+ in the interlayer was exchanged by PrNH_3^+ . As shown in Fig. 2 (c) and (d), $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ was successfully prepared under reflux at 70°C , resulting in the decrease of the interlayer distance from 2.26 to 1.71 nm. Considering the molecular size of MB ($1.70 \times 0.76 \times 0.325$ nm) and the thickness of the $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ layer, it is postulated here that MB^+ forms a monolayer coverage with its long molecular axis perpendicular to the host layer.

The scanning electron microscopy (SEM) images of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ are shown in Fig. 3 (a); we can see that the original $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ consists of a plate-like texture reflecting its layered

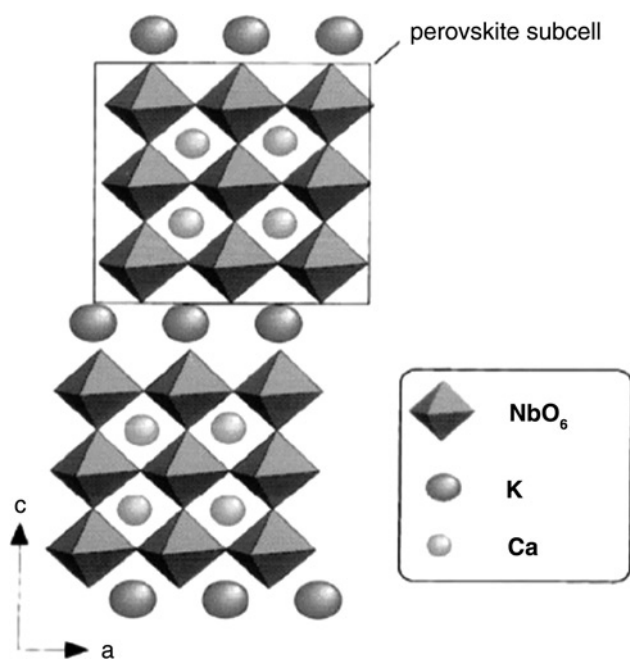


Figure 1 Schematic structure of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$

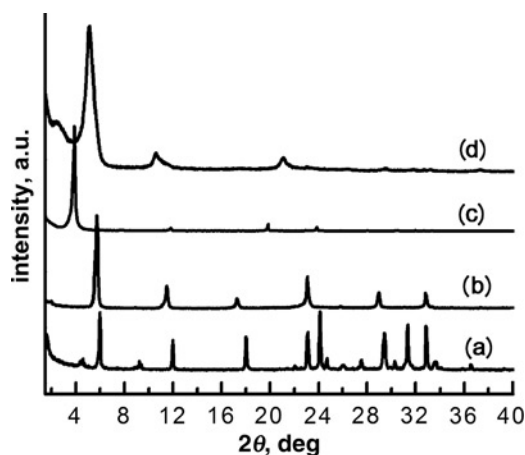


Figure 2 XRD patterns

- (a) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$
- (b) $\text{HCa}_2\text{Nb}_3\text{O}_{10}$
- (c) $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$
- (d) $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$

structure. The resulting product $n\text{-PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ and $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ retains the layered structure after the intercalation as shown in Fig. 3 (b) and (c).

The Fourier transform infrared spectroscopy (FTIR) spectrum of $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ (Fig. 4) further indicates the synthesis of the intercalation composite because of the absorption bands of MB^+ . The infrared spectrum of the nanocomposite exhibited no absorption bands attributable to the propylammonium ions of the intermediate [12], whereas the characteristic absorption bands of MB^+ were observed at 1609, 1496, 1402 and 1360 cm^{-1} [13].

In the aqueous solution, MB exhibits typical maximum absorbance peaks at about 612 and 666 nm, ascribed to the monomers and dimers, respectively [14], as shown in Fig. 4 (a). In comparison, in the UV spectrum of the $\text{MB}-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ film (Fig. 5 (b)), the two absorption bands appeared at broadened 600 and 677 nm. Similar phenomena have already been reported by many groups that have worked with this kind of immobilisation reaction [9, 13, 15]. The broadened peak at 600 nm is ascribed to the dimerised MB^+ , and the adsorption band at 677 nm is believed to be the MB monomer; the differences in adsorption wavelength are because of the influences by the host layer [16].

MB is a well-known intercalator, and the intercalator was supposed to give high electrochemical signals in the nanocomposite such as $\text{MB}^+-\text{V}_2\text{O}_5$ [14] and $\text{MB}^+-\text{Nb}_6\text{O}_{17}$ [13]. The electrochemical characteristics of 0.01 mM MB in solution and the $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ film on a glass carbon electrode (GCE) in 0.1 M phosphate buffer solution (PBS) at 100 mV s^{-1} scan rate were investigated by cyclic voltammetry. A couple of well-defined

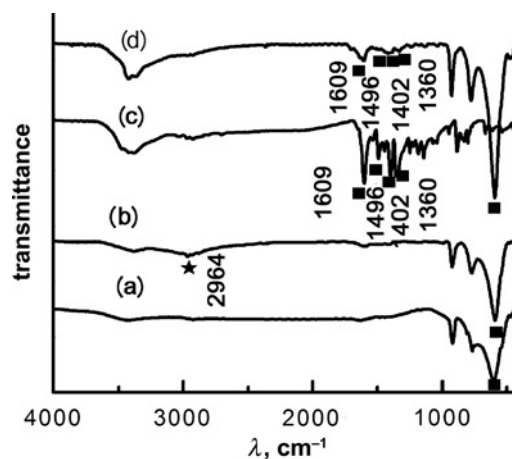


Figure 4 FTIR spectra

- (a) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$
- (b) $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$
- (c) MB
- (d) $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$

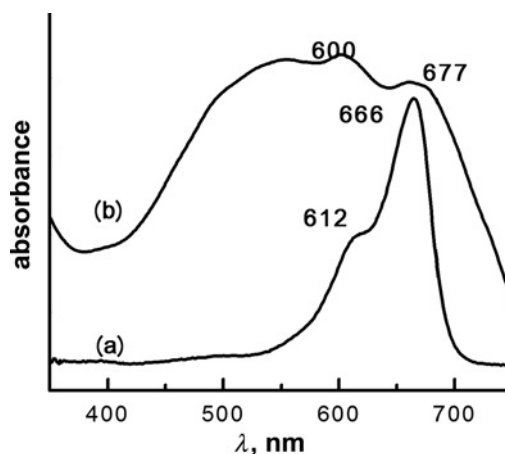


Figure 5 UV-vis absorption spectra

- (a) MB aqueous solution
- (b) $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ hybrid film

oxidation/reduction peaks appear in Fig. 5 (a) with redox potentials at -0.257 and -0.188 V for MB in PBS, the midpoint potential $E_m = (E_{pa} + E_{pc})/2 = -0.223\text{ V}$. The peak separation ΔE_p is 71 mV. The electrochemical behaviour of the $\text{MB}-\text{Ca}_2\text{Nb}_3\text{O}_{10}$ hybrid film on GCE in Fig. 6a (b) are very similar to that of 0.01 mM MB in solution. The redox potentials of the nanocomposite modified

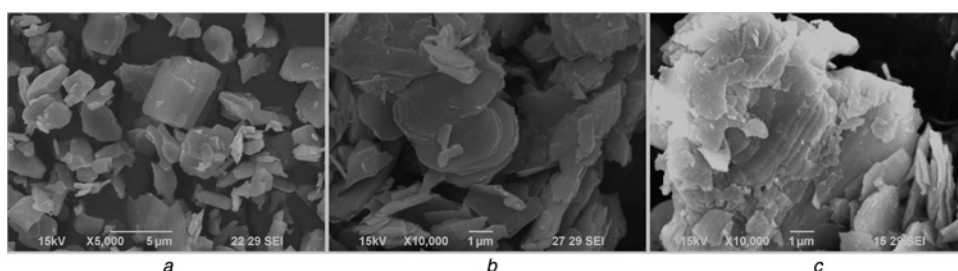


Figure 3 SEM images

- a $\text{KCa}_2\text{Nb}_3\text{O}_{10}$
- b $\text{PrNH}_3^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$
- c $\text{MB}^+-\text{Ca}_2\text{Nb}_3\text{O}_{10}$

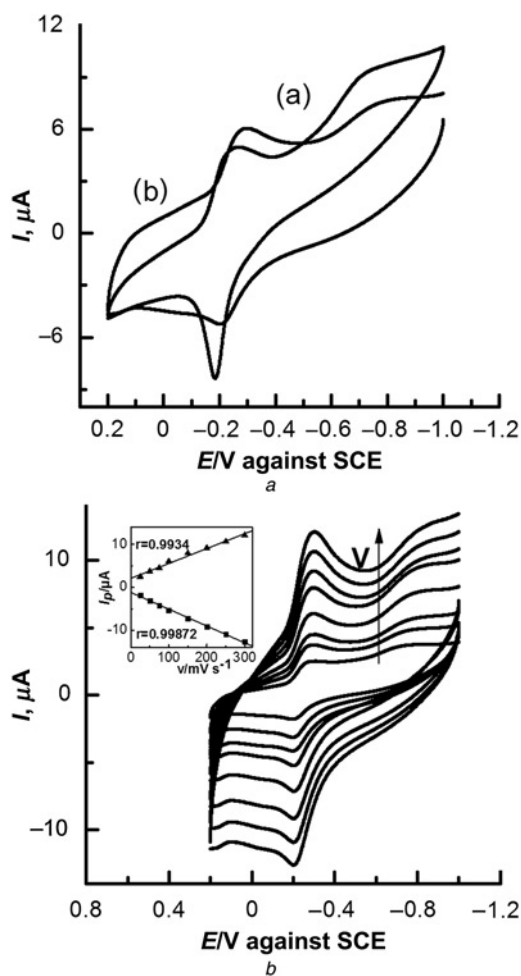


Figure 6 Cyclic voltammograms

a Cyclic voltammograms of (a) 0.01 mM MB and (b) MB⁺-Ca₂Nb₃O₁₀ modified electrode in 0.1 M PBS solution at a scan rate of 100 mV s⁻¹
 b Cyclic voltammograms of MB⁺-Ca₂Nb₃O₁₀ thin film in 0.1 M PBS (pH=7.0) at scan rates of 25, 50, 75, 100, 150, 200, 250 and 300 mV s⁻¹, respectively

Inset shows relationship between peak current and scan rate

electrode are at -0.202 and -0.267 V with an E_m of -0.235 V and ΔE_p of 65 mV. There is a negative shift for E_m and ΔE_p , which is mostly attributed to the influence of the semiconductor layers (calcium niobate sheets). It is reported that in Ca₂Nb₃O₁₀ layers, there exist two near-regular NbO₆ octahedra and two very distorted NbO₆ octahedra [17], different Nb-O distances will lead to less interaction between the host layer and the guest cation, which makes the hybrid capable of processing high ionic conductivity, thus the electrochemical activities of the hybrid will also be improved. Moreover, delaminated inorganic sheets tend to have a higher degree of freedom and a larger surface area, which will facilitate adsorption of the MB⁺ ions on their surface [8] and increase the electrochemical stability of the intercalate. To confirm this explanation, the BET surface area of KCa₂Nb₃O₁₀ and MB⁺-Ca₂Nb₃O₁₀ were measured, which are 7.22 and 9.247 m²g⁻¹, respectively. It is obvious that the surface area is greatly increased through intercalation of MB⁺, and one can predict that the electrochemical activities will also be greatly improved by increasing the active interfacial area.

Figure 6b shows the CV curve of MB⁺-Ca₂Nb₃O₁₀ in 0.1 M phosphate buffer solution (PBS) at different scan rates, which shows a couple of sensitive oxidation/reduction peaks with redox potentials at -0.202 and -0.267 V. The anodic peak shifts positively and the cathodic peak shifts negatively by increasing the scan rate

from 25 to 300 mV s⁻¹ as shown clearly in Fig. 4. The inset reveals that the cathodic and anodic peak currents (I_c and I_a) are proportional to the scan rate, suggesting a surface-controlled redox electrode process [18].

4. Conclusion: The functional layered nanocomposite, MB⁺-Ca₂Nb₃O₁₀, was synthesised by the guest-guest exchange method with a precursor PrNH₃⁺-Ca₂Nb₃O₁₀. To our best knowledge, this work is the first to report the synthesis of MB⁺-Ca₂Nb₃O₁₀. The excellent electrochemical activity of the MB⁺-Ca₂Nb₃O₁₀ hybrid film has also been investigated. We predict that the novel MB⁺-Ca₂Nb₃O₁₀ nanocomposite has potential applications as an electrode modifying material.

5. Acknowledgments: This work is supported by the Natural Science Foundation of Jiangsu Province (BK2011399) and the Jiangsu Marine Resource Development Research Institute Foundation (JSIMR10E06). The authors are grateful to the China Postdoctoral Science Foundation (no. 20110491384). This work is also funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

6 References

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