

Intercalated methylene blue between calcium niobate nanosheets by ESD technique for electrocatalytic oxidation of ascorbic acid



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ABSTRACT

A hybrid assembly of cationic methylene blue (MB) with calcium niobate ($\text{Ca}_2\text{Nb}_3\text{O}_{10}$) nanosheets was fabricated by electrostatic self-assembly deposition (ESD) method. The obtained MB– $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanocomposites were characterized by a variety of analytical techniques such as XRD, FTIR, SEM and TG–DTA. Interlayer spacings determined from XRD patterns reveal that MB^+ cation form an inclined monolayer arrangement with its long molecular axis being tilted approximately 46° against $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheets. The intercalated MB cations showed a fine diffusion-controlled electrochemical redox process and exhibited excellent electrocatalytic activity towards ascorbic acid (AA) oxidation in neutral media. Differential pulse voltammetry studies demonstrated that the intercalation nanocomposite detects AA linearly over a concentration range of 1.0×10^{-4} M to 8.3×10^{-3} M with the detection limit of 4.6×10^{-5} M at a signal-to-noise ratio of 3.

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1. Introduction

Methylene blue (MB), a water-soluble cationic dye molecule belongs to the phenothiazine family, has been widely studied since its synthesis in 1876. MB possesses high electroactivity [1], which makes it be widely used as electron transfer mediator. To overcome the water-soluble disadvantages, MB has been immobilized in various matrices such as α -zirconium phosphate [2], barium phosphate [3], silica gel modified with niobium oxide [4], mordenite-type zeolite [5], Ag nanoparticle-doped sol–gel film [6], for the detection of various reagents.

On the other hand, layered metal oxide semiconductors (LMOs) are a kind of amazing materials with unique two-dimensional structure. Structural, textural, and compositional modifications of LMOs have been investigated to develop new materials with tailored properties, such as catalysis [7,8], photocatalysis [9,10], electrooxidation [11] and photoluminescent behaviors [12] etc. The electrocatalytic activities of LMOs can be promoted by introducing electron mediators such as MB between the host nanosheets [13],

therefore, it is promising to utilize such kind of nanocomposite in construction of electrochemical sensors. Our research group has succeeded in the intercalation of MB into $\text{K}_4\text{Nb}_6\text{O}_{17}$, KTiNbO_5 , KLaNb_2O_7 by the ion-exchange method [14–16]; the nanocomposites exhibit excellent electrochemical behaviors. However, because of the mass transfer limitation, a whole intercalating process for layered oxides always takes several days and even weeks.

Two-dimensional LMOs nanosheets, which are obtained by exfoliating bulk layered compounds, have aroused considerable interests [17]. It has been proven that utilization of 2D nanosheets with typical dimensions of less than a few nanometers in thickness and micrometer-order lateral sizes as building blocks to design various “nano”-systems is quite effective [18,19]. Among the diverse fabrication techniques, ESD based on the electrostatically driven self-assembly provides a quick and reliable way to hybridize a range of guest species including transition metal complex [20–22], transition metal ions [23,24], inorganic nanoparticles [25–28] with the exfoliated LMOs nanosheets. However, the examples of exploration in the utilization of ESD technique to achieve intercalative hybridization between LMOs nanosheets and organic dyes are still limited [29].

In the present work, we have reported the direct coassembly of Dion–Jacobson type perovskite ($\text{KCa}_2\text{Nb}_3\text{O}_{10}$) nanosheets and MB^+ cations to fabricate lamellar nanocomposites for the first time. The

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assembly of MB⁺ cations into the interlamellar space of calcium niobate host can be finished in a few minutes at room temperature without complicated instruments. The electrochemical behaviors of MB–Ca₂Nb₃O₁₀ hybrid thin film were studied. The electrocatalytic properties to the oxidation of ascorbic acid (AA) on the intercalation compound modified GC electrode have been investigated utilizing cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

2. Experimental

2.1. Preparation of MB–Ca₂Nb₃O₁₀ hybrids

KCa₂Nb₃O₁₀ was prepared by calcining a mixture of K₂CO₃, CaCO₃, and Nb₂O₅ (K:Ca:Nb = 1.1:2:3) at 1473 K for 12 h [30,31]. The exfoliated nanosheets of calcium niobate were obtained following the previously reported method [22,32]. 2 g of the powder sample was treated three times with 80 mL of HNO₃ aqueous solution (5 M). The protonated product (0.4 g) was then dispersed into equivalent molar of tetrabutylammonium hydroxide (TBAOH) aqueous solution (100 mL) and vigorously stirred at room temperature for one week. The resulting colloidal suspension was centrifuged at 2000 rpm for 30 min to remove the unexfoliated particles, and the supernatant nanosheets suspension was used in the flocculation reaction. MB–Ca₂Nb₃O₁₀ nanocomposites were prepared by the mixing of 3.84 mM MB aqueous solution and the exfoliated Ca₂Nb₃O₁₀ suspension (12 mL). Different volumes (3, 4, 6, 8 or 12 mL) of MB solution were involved in the reaction, noted hereafter as Ca₂Nb₃O₁₀/MB_{4.0}, Ca₂Nb₃O₁₀/MB_{3.0}, Ca₂Nb₃O₁₀/MB_{2.0}, Ca₂Nb₃O₁₀/MB_{1.5} and Ca₂Nb₃O₁₀/MB_{1.0}. The flocculent precipitate was centrifuged, washed with distilled water, and then dried in vacuum at 50 °C overnight.

2.2. Characterization

Zeta potentials of the exfoliated colloidal suspension were measured using a Malvern Zetasizer Nano instrument. X-ray diffraction patterns were obtained with a RINT 2000 diffractometer (Rigaku), using Cu K α radiation ($\lambda = 0.154$ nm) with 2θ from 2° to 50°. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrometer with the use of KBr pellets. Scanning electron micrograph (SEM) images were taken with a JSM-5600 apparatus (JEOL) operating at 15 kV for the Au-coated samples. TG–DTA measurements were carried out using Netzsch STA49F3 apparatus at a heating rate of 10 °C min⁻¹ under air atmosphere.

Electrochemical measurements were performed on a CHI660C electrochemical workstation, with a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The glassy carbon electrode (GCE, area 0.03 cm²) was polished with 1.0 and then 0.3 μ m alumina to obtain a mirror-like surface and used as the working electrode. The modified electrode designated as MB–Ca₂Nb₃O₁₀/GCE was prepared by coating 6 μ L MB–Ca₂Nb₃O₁₀ aqueous suspension on GCE and dried for at least 12 h.

3. Results and discussion

Owing to the insertion of bulky TBA cations between the layers after acid exchange, layered host undergo osmotic swelling and exfoliated into Ca₂Nb₃O₁₀ nanosheets [33]. A zeta potential (ζ) of –52.2 mV was measured for calcium niobate nanosheets colloidal suspension, which shows the dispersion is stable and well-dispersed. For the samples with addition of MB, supernatant liquid was collected and measured. As shown in Fig. 1, a progressive increase of MB volume increases the zeta potential of

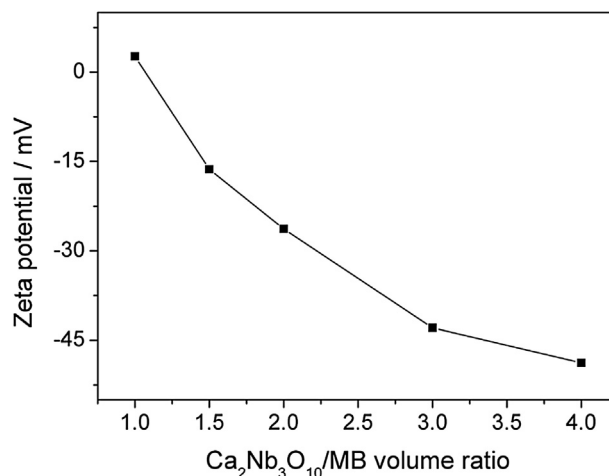


Fig. 1. The relationship between zeta potential and Ca₂Nb₃O₁₀/MB volume ratio.

Ca₂Nb₃O₁₀ nanosheets gradually. A ζ value of –26.3 mV was measured for Ca₂Nb₃O₁₀/MB_{2.0}, suggesting the mixed solution is unstable. It can be observed a large number of blue flocculent precipitates were formed and settled down to the bottom of the container quickly. Similar phenomenon was also observed in the cases of Ca₂Nb₃O₁₀/MB_{1.5} and Ca₂Nb₃O₁₀/MB_{1.0}. When the volume ratio of MB solution to host nanosheets suspension reaches 1, coassembly of negatively charged Ca₂Nb₃O₁₀ nanosheets with MB, even leads to the charge inversion of Ca₂Nb₃O₁₀ surface. Zeta potential measurements confirms that the process used for preparing MB–Ca₂Nb₃O₁₀ nanocomposites is based on the self-assembly by electrostatic interaction of negatively charged Ca₂Nb₃O₁₀ nanosheets with MB⁺ ions.

The restacking products by mixing colloidal calcium niobate exfoliated suspension and MB aqueous solution with the different volume ratios were isolated from the reaction mixture. XRD patterns of these restacking products are shown in Fig. 2, together with KCa₂Nb₃O₁₀ and the protonated form. The strong and sharp reflection peaks suggest that the original KCa₂Nb₃O₁₀ is well crystallized. An exchange of K⁺ with H⁺ causes the (00l) peaks move to higher angles, corresponding to the hydrated form (HCa₂Nb₃O₁₀·1.5H₂O) [34]. XRD patterns of the three restacking products give a series of symmetric and well-defined peaks corresponding to (00l) reflections. The (001) peaks were located on almost the same 2θ angle of ~3.3°, indicating a basal spacing of ~2.66 nm. By subtracting the thickness of Ca₂Nb₃O₁₀ slab (1.44 nm) [17], the net interlayer height of MB–Ca₂Nb₃O₁₀ can be calculated as 1.22 nm. Since the molecular dimension of MB is 1.70 × 0.76 × 0.325 nm [35], it is postulated here that MB forms monolayer coverage with its long molecular axis being tilted approximately 46° against the host nanosheets (see Fig. 3). The reaction is extremely fast, and is complete within a few minutes since the interlayer of calcium niobate is completely open and there is no steric restrict for the immobilization of guest moieties. And we are delighted to find that the restacking products exhibit relatively high crystallinity, evidencing the regular organization of the host nanosheets and dye cations during the rapid self-assembly process, which is not common for the ESD method.

The intercalation of MB into KCa₂Nb₃O₁₀ is further confirmed by IR spectra. In Fig. 4, characteristic absorption peaks of MB locate at 1604 cm⁻¹ and 1494 cm⁻¹ (stretching vibrations of the aromatic rings), 1400 cm⁻¹ (C–N stretching), 1358 cm⁻¹ (–CH₃ symmetric deformation) [36,37]. Similar bands also appear in the IR spectrum of restacking product (Fig. 4c), with some red shift to 1597, 1487,

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