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Anion-intercalated layered double hydroxides modified test strips for detection of heavy metal ions

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ABSTRACT

In this work, a novel approach for facile and rapid detection of heavy metal ions using anion-intercalated layered double hydroxides (LDHs) modified test strips is demonstrated. By intercalating $Fe(CN)_6{}^{4-}$ or S^{2-} anions into the interlayers of LDHs on the filter paper, various heavy metal ions can be easily detected based on the color change before and after reaction between the anions and the heavy metal ions. Upon the dropping of heavy metal ions solutions to the test strips, the colors of the test strips changed instantly, which can be easily observed by naked eyes. With the decrease of the concentration, the color depth changed obviously. The lowest detection concentration can be up to 1×10^{-6} mol L^{-1}. Due to the easily intercalation of anions into the interlayer of the LDHs on test trips, this procedure provides a general method for the construction of LDHs modified test strips for detection of heavy metal ions. The stability of the prepared test strips is investigated. Furthermore, all the results were highly reproducible. The test strips may have potential applications in environmental monitoring fields.

1. Introduction

The existence of heavy metal ions in natural water, soil and food has attracted much attention due to their danger to environmental and human health [1]. Many of these heavy metal ions (such as Pb^{2+}, Cd^{2+}, Fe^{3+} and Cu^{2+}) are carcinogens, which can accumulate in human body causing a wide variety of diseases [2,3]. Therefore, fast and effective detection of heavy metal ions is very important for environmental security and human health.

Various methods have been developed to detect heavy metal ions. For example, inductively coupled plasma/atomic emission spectrometry (ICP/AES), inductively coupled plasma mass spectrometry (ICPMS) and atomic absorption spectroscopy (AAS) offer an ultrasensitive and relatively accurate approaches to trace heavy metal ions [4–6]. However, these methods are expensive and time-consuming, generally not available for on-site testing by unskilled personnel. Furthermore, colorimetric method [7–9], fluorometric method [10–12] and electrochemical method [13] have been developed based on the specific reaction between the reagents and the metal ions. For example, by specific reaction of thymine and Hg^{2+} to form thymine–Hg^{2+}–thymine, Hg^{2+} ions can be sensitively detected [14]. Although these methods are accurate, most of them require complex and expensive organics or biomolecules. Therefore, it is highly necessary to develop a simple, portable and inexpensive method for fast detection of various heavy metal ions in aqueous media.

Recently, research interest has focused on test strips, because of their simple, portable, inexpensive, disposable, fast response advantages [15]. Various strategies for construction of test strips have been reported to detect the heavy metal ions [16]. Ratnarathorn et al. [17] reported the investigation of silver nanoparticles colorimetric sensing of Cu^{2+} by paper-based analytical devices, the detection principle is that paper devices coated with the modified Ag nanoparticles solution changed from yellow to orange and green–brown color after the addition of Cu^{2+} due to the nanoparticle aggregation. Takahashi et al. [18] obtained a membrane filter with firmly attached and uniform coatings of organic dye nanoparticles/nanofibers on them. Usually, signaling reagents, such as dithizone, 1-(2-thiazolylazo)-2-naphthol, 1-(2-pyridylazo)-2-naphthol, tetraphenylporphin, are necessary for the detection of heavy metal ions by attaching them on the surface of solid substrates. However, these reagents usually coated on the paper by soaking method, which easily led to the leakage of reagents, resulting in low reliability and sensitivity of the detection. Furthermore, these methods usually detect one heavy metal ion due to the specific reaction between the signaling reagents and the target heavy metal ions. How to construct a stable test strip capable of rapidly detecting several heavy metal ions is still a great challenge, which may have promising applications in real life.

Layered double hydroxides (LDHs) have been widely studied in many important fields such as catalysis, separation, biomedicine, owing to their special layered structure [19]. The general formula

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of LDHs can be expressed as $[M^{II}_{1-x}M^{III}_{x}(OH)_2][A^{n-}_{x/n}]\cdot mH_2O$ (M^{II} denoted as divalent metal ions and M^{III} denoted as trivalent metal ions respectively, A^{n-} denoted as anions), which consists of positively charged brucite-like hydroxide sheets and charge-balancing interlayer anions. [20,21] The interlayers are connected by relatively weak hydrogen bonding. Therefore, anions can enter or get out of the interlayers under certain conditions. Such anion-exchangeable ability enables the LDHs to be widely applied in anion adsorption materials with large adsorption capacity [22]. For example, in our previous research [23], Br intercalated Co–Ni LDHs nanosheets showed adsorption capacity of 195 mg g^{-1} for methyl orange, much higher than that of commercial activated carbon (20–80 mesh) with 140 mg g^{-1}. The intercalated anions can be further exchanged out of the interlayer of LDHs, which can react with metal ions to form products with different colors [24,25]. Developing test strips according to this principle will be facile to detect various heavy metal ions in practical life. However, as far as we know, the anions intercalated LDHs modified filter papers as test strips for heavy metal ions has not been reported.

Herein, we designed a novel test strip for detection of heavy metal ions by modifying the filter paper with anion intercalated LDHs. $Fe(CN)_6{}^{4-}$ and S^{2-} anions were used to intercalate into the interlayer of LDHs on the filter paper. The prepared anions intercalated LDHs modified test strips were used to detect a range of heavy metal ions, furthermore, the stability of the test strip were investigated. The prepared test strips should be valuable for rapid, on-site screening of heavy metal ions in environmental monitoring fields.

2. Experimental section

2.1. Materials

All agents including $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 6H_2O$, $CuCl_2\cdot 2H_2O$, $Pb(CH_3COO)_2\cdot 3H_2O$, $FeCl_3\cdot 6H_2O$, $3CdSO_4\cdot 8H_2O$, $K_4Fe(CN)_6\cdot 3H_2O$, Na_2S were analytical grade and used without further purification. The deionized water was used in all the experimental processes.

2.2. Synthesis of Mg–Al LDHs modified test strips

To synthesize Mg–Al LDHs modified test strips, firstly, the filter paper with 4 cm length and 3 cm width was immersed into NaOH solution for 6 h and then washed with deionized water three times. Secondly, 0.01 mol of $Mg(NO_3)_2\cdot 6H_2O$ and 0.005 mol of $Al(NO_3)_3\cdot 6H_2O$ were dissolved in 100 ml of deionized water. After that, the pretreated filter papers were added into the above solution. Then, a suitable volume of NaOH solution was dropped into the filter paper immersed solution to adjust the pH to 10, the solution was transferred into a 120 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 12 h, and then allowed to cool to room temperature naturally. The final filter paper was washed with absolute ethanol and deionized water several times respectively and finally air-dried at room temperature.

2.3. Synthesis of $Fe(CN)_6{}^{4-}$ and S^{2-} intercalated LDHs test strips

Typically, intercalation of $Fe(CN)_6{}^{4-}$ into LDHs test strips was performed by ion-exchange with $Fe(CN)_6{}^{4-}$ anions. LDHs test strips were then immersed into 200 mL of $K_4Fe(CN)_6$ aqueous solution (0.25 M) for 24 h to promote complete transformation. The test strips were washed with absolute ethanol and deionized water several times respectively and finally air-dried at room temperature. Then the test strips were cut into 10 pieces. The S^{2-} intercalated LDHs test strips were prepared by the same method.

2.4. Characterization

The structure and morphology of products were examined with field emission scanning electron microscopy (FESEM; Hitachi S-4800). FT-IR spectra in transmission mode were recorded using a Nicolet Impact 400D FTIR spectrometer (4000–400 cm^{-1}, 4 cm^{-1} resolution, KBr pellet). Photographs were taken using a Canon G11 digital camera.

2.5. Detection of heavy metal ions

The detection experiment was carried out as following: firstly, $Fe(CN)_6{}^{4-}$ and S^{2-} intercalated LDHs modified test strips with the same size were prepared for use. Then, several heavy metal ion solutions including Cu^{2+}, Fe^{3+}, Pb^{2+} and Cd^{2+} solutions with different concentrations were provided for further detection. After that, 50 μL of the heavy metal ion solutions were dropped on the surface of the test strips. The detection effect was evaluated by observing the color depth of the test strip after dropping heavy metal solutions on it.

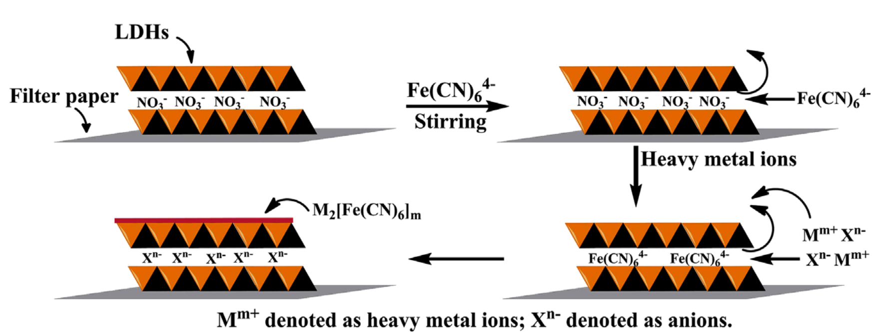
2.6. The real sample detection

Tap water (derived from the Taian City Water Company) was selected to verify the practicability of the prepared anions intercalated LDHs modified test strips. The water sample was detected by the standard addition method using Cu^{2+} as an example.

3. Results and discussion

3.1. The mechanism for the design of the test strips and the detection of heavy metal ions

The anions intercalated Mg–Al LDHs modified test strips for design and detection of heavy metal ions are schematically



Scheme 1. Illustration of the concept for the formation of Mg–Al LDHs modified test strips and detection of heavy metal ions.