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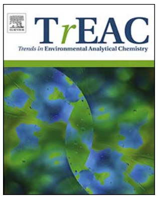

Review

Applications of layered double hydroxides based electrochemical sensors for determination of environmental pollutants: A review

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ABSTRACT

Layered double hydroxides (LDHs) are getting considerable attention as electrode modifiers in electrochemical sensing applications. They are unique materials because of their two-dimensional structures, highly tunable interior architecture, excellent ion exchange capabilities, reasonable interlayer spaces, and high porosities. They are easy to synthesize from commonly available inorganic precursors. In electrochemical sensing, they provide a stable environment for immobilization of the enzymes or other sensing materials. LDHs have been used both in pure form or in combination with other materials to address certain issues in electrochemical sensing. LDHs modified electrodes may also improve sensitivity and selectivity toward the detection of certain target analytes by pre-concentrating/accumulating target species. In this review, we provide an overview of recent advancements in LDH based electrochemical sensors for environmental analysis.

1. Introduction

A growing variety of sensors can have substantial impacts on quality of everyday life. Principal issues to consider while integrating any sensing platforms include cost-effectiveness, the potential for real time monitoring in terms of sensitivity and selectivity, and mainly the operational simplicity. In this regard, electrochemical sensors are among the promising technologies as they are simple, low-cost, sensitive and selective alternates of sophisticated instruments [1,2]. Different materials have been used as modifiers for bare electrodes to enhance their electrocatalytic activity toward detection of environmental pollutants [3].

Nanomaterials have attained considerable attention as electrochemical sensing materials due to their extraordinary properties, distinguishing performance and a wide range of materials. The widespread uses and applications of nanomaterials in electrochemical sensing are associated with their unique features of the large surface area, and excellent mechanical, chemical, physical as well as electrical properties [4]. The large surface area plays a vital role in enhancing the kinetics of electrochemical reactions as well as providing a huge number of active sites for the desired electrochemical reactivity [5]. Moreover, nanomaterials can be further functionalized with desired chemical moieties to enhance the selectivity toward target analytes.

Layered double hydroxides (LDHs) are two-dimensional nanostructured materials with unique physicochemical properties. They are the enthralling class of inorganic materials with adjustable chemical composition and structures. They are also identified as hydrotalcite or anionic clays. By composition, they consist of positively charged layers of metal hydroxides with charge-balancing anions and some water molecules situated in between the layers. They are denoted by the general formula $[M^{2+}1-xM^{3+}x\ (OH)_2]^{x+}\ (A^{n-}_{x/n})\ .mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations and $An-$ is the interlayer guest ions with n- valence. The values of x may differ between 0.22 and 0.33 [6]. From the structural point of view, LDHs have resemblance with brucite, $Mg(OH)_2$, in which Mg^{2+} is surrounded by six OH^- ions and the resulting octahedral structures are connected to each other forming an infinite two-dimensional layer. Brucite layers get positively charged by replacing some divalent ions with trivalent ions. This positive charge is then balanced or neutralized by localizing anions in the interlayer spaces. Water molecules are also intercalated in the interlayer spaces stabilizing the structure of resulting LDHs. (Structure of brucite and hydrotalcites is shown in Fig. 1. The stability of LDH structure comes from electrostatic interaction and hydrogen bonding between the layer and interlayer contents. The structures of LDHs are amenable to desired fine-tuning by changing the divalent and trivalent ions and intercalated anions. The selected di and trivalent ions should have their radii not significantly different from those of Mg^{2+} and Al^{3+}. LDHs are characterized by the unique features of being low-cost, non-toxic, high surface area, two-dimensional structure, replaceable intercalated anions, positively charged surface and tunable internal and

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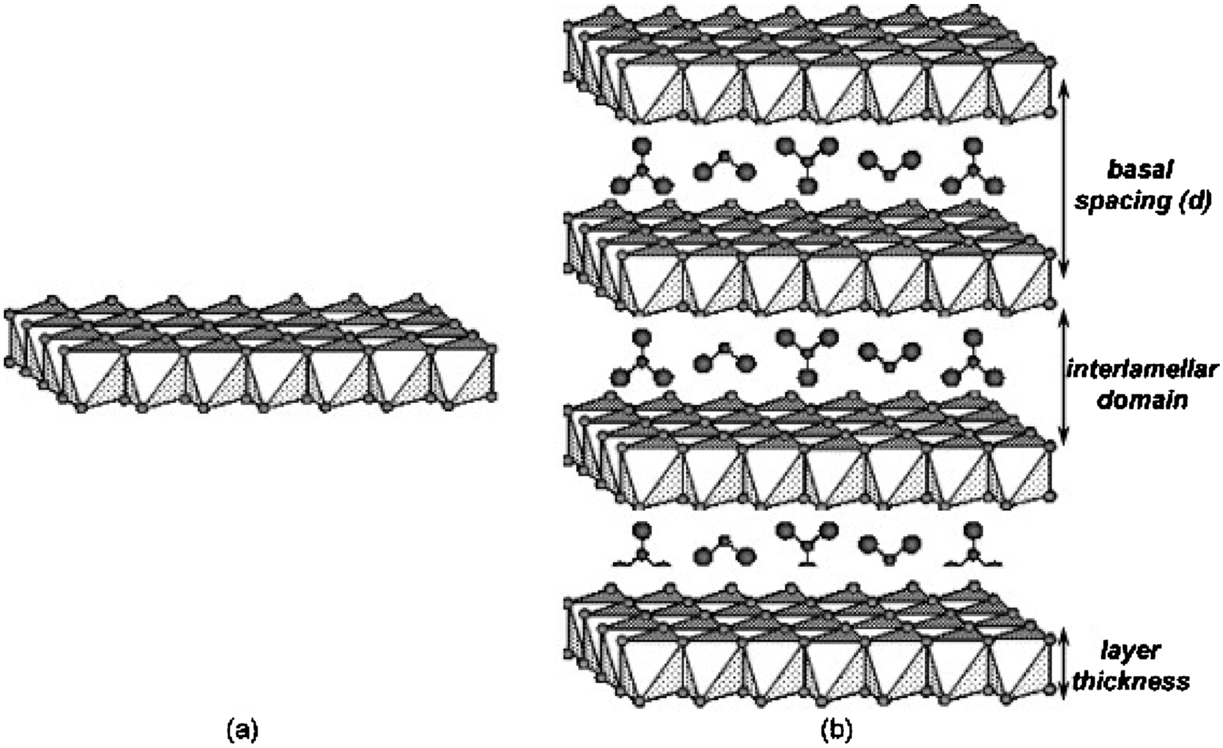

Fig. 1. Schematic structural representation: (a) brucite; (b) hydrotalcite. Reproduced with permission from [16]. Copyright (2007) Elsevier B.V.

external architecture [7]. Their unique applications emerge from their highly porous structure, large anion exchange capacities, and water-resistant structures. LDHs have been extensively used in catalysis [8], flame retardants [9], fuel cells [10], drug delivery [11], adsorption [12], analytical extractions [7,13,14], and in many other areas [15].

Several studies have shown that LDHs are emerging materials for chemical modification of electrode surfaces. Generally, in trace and ultra-trace analysis, such materials allow analytes to confine into a minimal volume near the electrode during preconcentration step leading to low limits of detection (LODs). LDHs can improve sensitivity and selectivity of detection as they allow to immobilize electrocatalytic reagents [17].

Due to industrial revolution and urbanization, human environment is severely contaminated by inorganic and organic pollutants [18,19]. This contaminated environment poses serious health risks to human, wild life, and aquatic organisms. Various national and international environmental agencies have defined allowable limits of these toxic pollutants in different environmental compartments. A range of analytical instruments has been developed over the years for determination of environmental pollutants. Despite their high sensitivity, selectivity, and efficiency, they are not suitable for low-resources set up as their prices are too high to afford. Moreover, analysis time is dependent on the nature and physical state of the matter. In the case of complex environmental samples, long and tedious sample procedure is required. The requirement of the expert technician and the high cost of consumables and routine maintenance also limit the scope of such instruments in low resource setups. Although considerable efforts have been made on miniaturization of such instruments, still their portability for field applications is a challenge. Therefore, simple, cost-effective, sensitive, selective and portable instruments are required to tackle the worldwide demand for monitoring of environmental pollutants [3]. Electrochemical sensors can be a simple and low-cost alternative to the sophisticated instruments.

The features, advancements and applications of LDH modified electrodes have been described in other review articles [17,20,21]. Most of the review articles are general and cover different directions of applications. This review article is dedicated to applications of LDH-modified electrochemical sensors for environmental monitoring. The recent advancements in LDH materials, synthesis procedures, and coating strategies are also discussed in brief. The review has been classified based on the studied pollutants.

2. Attractive features of LDH modified electrodes

Due to following unique features, LDHs are attractive candidates as electrode modifiers [20,22,23].

- They are easy to prepare using a variety of synthesis routes.
- They can be synthesized from low cost precursors.
- Due to porosity, they provide high mobility of the analyte and the reaction products.
- Due to positively charged layers, they can have good interactions toward polar or negatively charged molecules.
- The positively charged LDH layers are neutralized by exchangeable anions.
- Due to high water content, they provide biocompatible environment for the entrapped molecules.
- They provide a surface that can retain enzyme activity for longer period of times.
- They possess good hydrolytic and the chemical stabilities.
- They allow facile loading of catalysts.
- LDHs facilitate to enhance selectivity and the sensitivity of the electrochemical sensors.
- LDHs in electrochemical sensing play one or more of the following roles.
  - ○ Electrocatalysts
  - ○ Adsorbents for stripping analysis
  - ○ A surface for immobilization of other modifiers or biomolecues