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Synthesis of α- and β-CoNi binary hydroxides nanostructures and luminol chemiluminescence study for H_2O_2 detection

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ABSTRACT

Herein, we firstly reported utilization of α- and β-CoNi hydroxides nanostructures as efficient catalyst for the luminol-H_2O_2 CL reaction. The catalysts were synthesized by hydrothermal method and characterized by XRD, FT-IR, FE-SEM/EDX, and UV–vis. The α-form had layered double hydroxide (LDH) structure witout trivalent cations in the metal hydroxide layer, while the structure of β-phase was similar to brucite. UV–vis spectra demonstrated that the partial oxidation of Co^{2+} and Ni^{2+} did not occur in the both catalysts. It was found that α- and β-CoNi could significantly enhance CL reaction of luminol-H_2O_2 at pH = 11. During study of experimental parameters the higher relative intensity of CL signal in the presence of α-Co-Ni hydroxide was observed. This may be due to the greater Co^{2+}/Ni^{2+} ratio in this catalyst than β-phase. Therefore, a facile and rapid method was developed to assay H_2O_2 using α-CoNi binary hydroxide as catalyst. Under optimum conditions, in the range 0.1–12 μM of H_2O_2 concentrations the CL intensity was linear and a detection limit (S/N = 3) of 0.05 μM for H_2O_2 was obtained. The relative standard deviation for 6 repetitive determinations was less than 2.9%. The proposed method was successfully applied to detect H_2O_2 in river water samples with recoveries of 97.3% and 106%.

1. Introduction

The importance of H_2O_2 is not covered by any chemists. It is one of the most common oxidants used in the chemical synthesis. In addition, treatment of organic pollutants from natural waters and wastewaters is performed in the presence of H_2O_2 as efficient oxidizing agent [1]. The other applications of H_2O_2 in fields of the tooth-whitening, bleaching, disinfectant and food industry have been reported [2–5]. Moreover, detection of H_2O_2 in water is important from the environmental point of view. Many methods including amperometry, potentiometry, fluorimetry, colorimetry and chemiluminescence for the analytical determination of H_2O_2 have been developed [6–10]. Among these methods, chemiluminescence has received increasing interest due to higher sensitivity, instrumental simplification, lower detection limit, low cost and no stray light [11]. Chemiluminescence is a phenomenon in which molecules that are excited by a chemical reaction return to the ground state with emit light. The CL emission has been used for analytical analysis in chemistry, industry, medicine, biotechnology and water treatment. However, no progress is observed in CL reaction without the presence of a suitable catalyst. The synthesis of layered materials with nanostructures as catalyst for analytical measurements and organic reactions has been intensively studied. Hydroxides cobalt and nickel are crystallized in two polymorphs, α and β [12,13]. The β-hydroxides are composed of neutral metal hydroxide layers similar to brucite-like structure, in which M^{2+} is surrounded octahedrally by six hydroxyl ions and each OH^- is surrounded by three metal cations. The layers are regularly stacked on top of each other along the [001] direction (c-*axis*) without intercalated species with basal spacing of 4.60 Å (Fig.1a). The α-hydroxides consist of positively charged layers of metal hydroxides that are separated by intercalated anions and water molecules in the gallery to restore charge neutrality. The structure of α-hydroxides is stabilized by strong electrostatic attraction between the positive layers and the interlayer anions and also by the presence of hydrogen bonds among the positive layers, anions, and interlayer water. Thus, α-hydroxides is expected to have a larger basal spacing (usually > 7 Å) than β-hydroxides (Fig.1b), depending on the incorporated anions [14]. The α-hydroxides are isostructural with hydrotalcite-like or LDHs without any distribution of trivalent cations over the octahedral layers. Although, LDHs have a positive charge on the hydroxide layers due to the isomorphous replacement of some M^{2+} cations by M^{3+}, Kamath et al. [15] suggested that the α-hydroxides of Co^{2+} and Ni^{2+} produce a positive charge via partial protonation of the hydroxyl ions. In the

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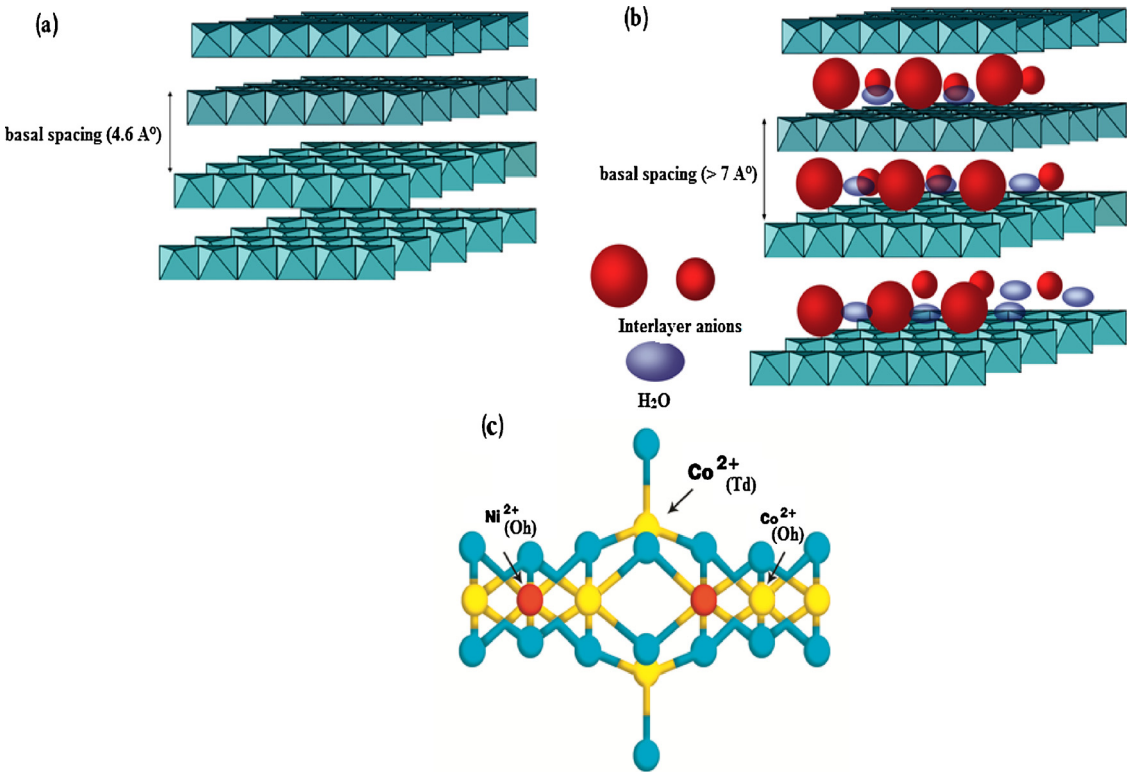

Fig. 1. Structure of (a) brucite-like β-CoNi binary hydroxide and (b) hydrotalcite-like (LDH) α-CoNi binary hydroxide. (c) Schematic representation of Co^{2+} ions in octahedral and tetrahedral sites and Ni^{2+} ions in octahedral sites.

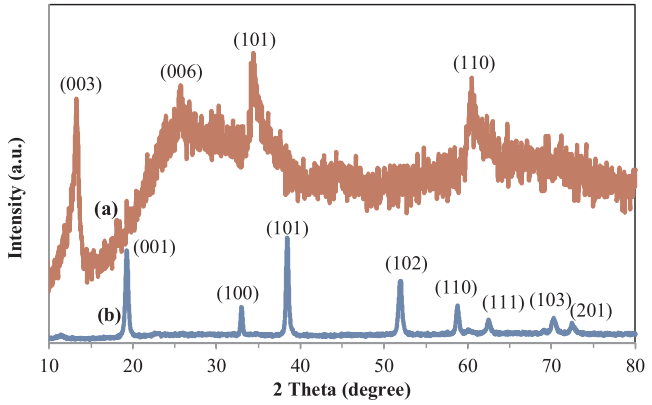

Fig. 2. XRD patterns of (a) α- and (b) β-CoNi binary hydroxides.

present study, α- and β-CoNi binary hydroxides nanostructures were synthesized by hydrothermal method and used as catalyst for the luminol-H_2O_2 CL reaction. Over the past two decades, there has been growing interest in the use of hydroxides cobalt and nickel as supercapacitor electrode materials and rechargeable alkaline batteries [16,17]. However, according to our survey, no report has obtained from catalytic property of these compounds in the luminol-H_2O_2 CL reaction. To date, various types of transition metals catalysis, such as complexes, metal oxide nanoparticles, noble metal nanoparticles and semiconductor nanoparticles have been developed for the luminol-H_2O_2 CL reaction [18–21]. Among theses, it is well-established that Co^{2+} as efficient catalyst for CL reaction in the luminol-H_2O_2 system can be used [22]. It is reported that in α-hydroxide, Co^{2+} ions can adopt either octahedral (Oh) or tetrahedral (Td) sites and Ni^{2+} ions occupy octahedral sites only (Fig.1c) [23]. However, all cations have octahedral configuration in β-hydroxide. In our work, Co^{2+}/Ni^{2+} ratio in the metal hydroxide layer affects the sensitivity and catalytic activity of α-

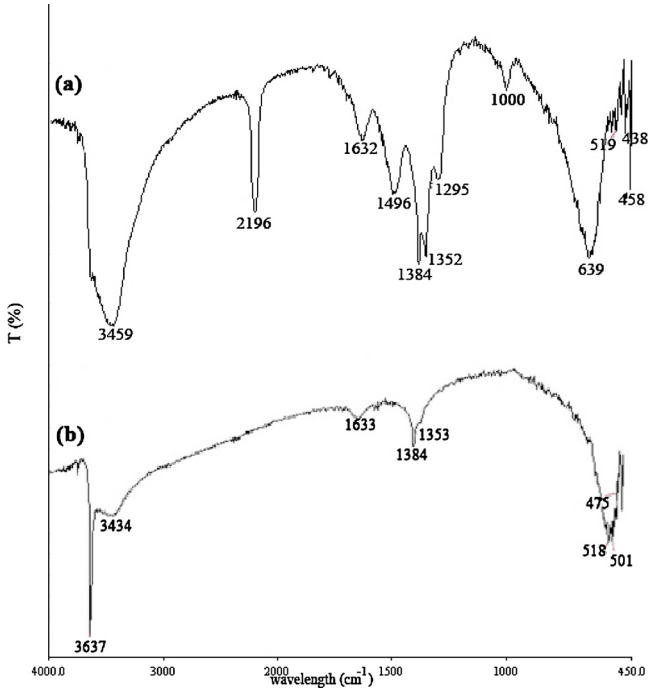

Fig. 3. FT-IR spectra of (a) α- and (b) β-CoNi binary hydroxides.

and β-CoNi binary hydroxides. The results showed that α-phase has higher activity and is a better sensor for H_2O_2 detection using proposed method. The limit of detection was obtained to be 0.05 μM. Efficiency of the proposed method was evaluated by determination of H_2O_2 in river water samples.