



## Research paper

# Synthesis of nanosized LDHs by Au colloidal nanoparticles as nuclei and its application for electroanalysis



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## ABSTRACT

Nanosized Ni–Al LDHs were synthesized via a hydrothermal method by using Au colloidal nanoparticles as nuclei for LDH growth, designated as Au/Ni–Al LDHs. Transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy were used to characterize the structure and morphology. N<sub>2</sub> physisorption was performed to measure the specific surface area. Electrochemical impedance spectroscopy and cyclic voltammetry were introduced to investigate the electrochemical properties of Au/Ni–Al LDHs. The average size of Au/Ni–Al LDHs was small as 10 ± 0.2 nm, and the high BET surface area was obtained. The conductivity was improved as Au/Ni–Al LDHs modified glassy carbon electrode (GCE), compared to Ni–Al LDHs modified GCE. Ascorbic acid was used as a model molecule to study the electroanalytical properties of Au/Ni–Al LDHs modified GCE. The results exhibited that high sensitive detection was obtained.

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## 1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and solvation molecules. A general formula for the most widely studied LDHs are expressed as  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot mH_2O]$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent metal ions, respectively;  $A^{n-}$  is an intercalate anion;  $x$  is the molar ratio,  $M^{3+}/(M^{2+} + M^{3+})$  (Cavani et al., 1991; Khan and O'Hare, 2002; Wang and O'Hare, 2012). LDHs have been extensively synthesized and studied for decades. There are a large number of synthesis approaches including co-precipitation (Carteret et al., 2011; Wang et al., 2013), hydrothermal method (Zhu et al., 2012; Wang and Yang, 2013), mechanochemical method (Iwasaki et al., 2012; Zhang et al., 2012), urea hydrolysis (Faour et al., 2012; Huang et al., 2012), and electrodeposition (Gong et al., 2009; Y. Wang et al., 2010). Thanks to the high surface area, layered structure, anion exchange capacity and tunable basic properties, LDHs have exhibited promising applications in many aspects, such as adsorbent (Liang et al., 2010; Wang et al., 2013), anion exchange (Wang et al., 2008), catalysts (Baliarsingh et al., 2013; Chen et al., 2014), anode materials (Wang and Yang, 2013), electrochemical sensors (Yin et al., 2011; Hai and Zou, 2015), magnetism (Abellán et al., 2015), energy storage and conversion (Shao et al., 2015), etc. The common issue in all these studies

is to seek a better control of the size, shape, and crystallinity of LDH particles, enabling more efficient products for the potential applications. LDHs with small size have advantages of relatively large surface area, fast electron transfer capacity, and potential use for precise research such as cellular drug delivery. There were a few reports proposing a fast nucleation and a subsequent hydrothermal method (Xu et al., 2006; Huang et al., 2012). But the nuclei they used were LDHs nuclei themselves, and the lateral size of the products obtained were not small enough, either. Apart from the relatively large sized LDHs particles obtained in the aqueous system, some reports were presented using a co-precipitation method in the presence of non-aqueous methanolic solvent (Gardner et al., 2001; Abellán et al., 2014), which leads to nanometric LDHs particles with small lateral dimensions.

Ascorbic acid (AA, vitamin C) is an essential vitamin, well known for stimulating the immune system, preventing illness, and playing an important part in the function of connective tissue. There have been a lot of studies on detection of AA (Weng and Hsiao, 2011; Y. Wang et al., 2014). Electrochemical methods have proved to be relatively convenient, fast and stable, and have shown high sensitivity and excellent flexibility (Sartori and Fatibello-Filho, 2012).

In this paper, Au colloidal nanoparticles were introduced to serve as the nuclei for LDHs growth via a hydrothermal method and small size of LDHs were obtained with the average size of 10 ± 0.2 nm, which designated as Au/Ni–Al LDHs. As comparison, raw Ni–Al layered double hydroxides (Ni–Al LDHs) were obtained following the same procedure only in the absence of Au colloidal nanoparticles. Compared to Ni–Al LDHs, the BET specific surface area and conductivity were improved as Au/Ni–Al LDHs. The electroanalytical properties of Au/Ni–Al LDHs

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modified glassy carbon electrode (Au-LDHs/GCE) were carried out by using AA as a model molecule. The results exhibited that more sensitive detection was obtained compared to Ni–Al LDHs modified glassy carbon electrode (LDHs/GCE).

## 2. Experimental

### 2.1. Reagents

AA was purchased from Sigma-Aldrich. Stock solution of AA (10 mM) was freshly prepared daily by dissolving a suitable amount of reagent in water. A Tris–HCl buffer supporting electrolyte solution (0.05 M Tris adjusted to pH 7.0 with 0.1 M HCl) was chosen for the AA determination. All solutions were prepared using ultra-pure water (resistivity > 18 M $\Omega$  cm) supplied by a Milli-Q purification system (Millipore). All other chemical reagents not mentioned were of analytical grade and used as received.

### 2.2. Preparation of Au/Ni–Al LDHs

First, Au colloidal nanoparticles were prepared using the borohydride reduction method using chloroauric acid as raw material and tri-sodium citrate as capping agent according to the literature (Jana et al., 2001; Gao et al., 2003). Briefly, a 25 mL aqueous solution containing  $4.0 \times 10^{-4}$  M HAuCl<sub>4</sub> and  $1.2 \times 10^{-4}$  M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> were prepared first. Then, ice cold aqueous NaBH<sub>4</sub> solution (1.0 mL, 0.1 M) was added all at once under stirring. The solution was then placed in the 4 °C refrigerator for 3 h to degrade any remaining NaBH<sub>4</sub> by reaction with water.

Next, Au/Ni–Al LDHs were prepared by a modified nucleation and a subsequent hydrothermal treatment (Xu et al., 2006). A certain volume of Au colloidal nanoparticles prepared above were dispersed into the mixed basic solution containing 0.15 M NaOH and 0.013 M Na<sub>2</sub>CO<sub>3</sub>. After being sonicated for 20 min, mixed salt solution containing Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2 M) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.1 M) was quickly added under vigorous stirring and keep stirring for 5 min. The volume ratio of Au colloidal nanoparticles, mixed basic solution, and mixed salt solution was 2:4:1. This aqueous suspension was then reacted in a 100 mL Teflon-lined stainless steel autoclave at 100 °C for 16 h. After air-cooling, a stable homogeneous suspension was obtained. Au/Ni–Al LDHs were collected with high speed centrifugation (10,000 rpm), followed by rinsing with ultra-pure water for several times, and drying at 50 °C. For comparison, raw Ni–Al LDHs were prepared following the same procedure as above only in the absence of Au colloidal nanoparticles. The yields for raw Ni–Al LDHs and Au/Ni–Al LDHs were 51% and 77%, respectively, which were calculated according to the formulas obtained below through measurements.

### 2.3. Electrode modification

Prior to modification, the bare GCE was polished with 0.3  $\mu$ m alumina powder on fine abrasive paper and then cleaned ultrasonically in ethanol and ultra-pure water. The colloidal suspension (1 mg mL<sup>-1</sup>) was prepared by dispersing raw Ni–Al LDHs or Au/Ni–Al LDHs in ultra-pure water with sonication for 30 min. 15  $\mu$ L of the as-prepared suspension was carefully dropped on the surface of the pretreated GCE. The coating was dried in air at room temperature. In this way, modified GCEs (denoted as LDHs/GCE or Au-LDHs/GCE) were fabricated.

### 2.4. General characterization and electrochemical measurements

Transmission electron microscopy (TEM) observations of the size and morphology of the synthesized LDHs were performed with a Tecnai F30 (FEI). For TEM imaging, a drop of the aqueous solution was placed on a copper grid and allowed to dry. X-ray diffraction (XRD) data

were recorded by an X'Pert-PRO MPD (PANalytical) X-ray diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) under a voltage of 40 kV and a current of 40 mA. The  $2\theta$  angle of the diffractometer was stepped from 5° to 80° at a scan rate of 0.1° min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI QUANTERA-II SXM (Ulvac-Phi) system and Al K $\alpha$  ( $h\nu = 1486.6$  eV) as X-ray source. The binding energies were referred to the C–C peak at 284.6 eV. Metallic elemental analysis was performed using inductive coupled plasma atomic emission spectrometry (SPECTRO ARCOS EOP, SPECTRO) (ICP-AES). Elemental analysis for non-metallic elements was carried out on EA3000 (EuroVector). Thermogravimetric analysis (TGA) was conducted on a DTG-60AH (Shimadzu) thermal analyzer to estimate the interlayer water content. Samples were heated under nitrogen flow from ambient temperature to 800 °C with a constant heating rate of 10 °C min<sup>-1</sup>. For surface area measurements, N<sub>2</sub> adsorption-desorption was performed at 77 K with a BELSORP-MAX (Ankersmid) system utilizing Barrett-Emmett-Teller (BET) calculations.

The electrochemical measurements, including electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and amperometric *i*-*t* curve were carried out with a CHI660C electrochemical workstation (Chenhua Instruments, Shanghai, China) at room temperature. A conventional three-electrode system consisted of a modified glassy carbon working electrode (GCE, 3 mm diameter), an aqueous saturated calomel reference electrode (SCE), and a Pt counter electrode was employed. EIS was measured in the frequency ranging from 10<sup>5</sup> Hz to 0.01 Hz at open circuit potential of -0.05 V in support electrolyte of 0.1 M KCl with 5.0 mM Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> as probe. Amperometric *i*-*t* curve was carried out at the potential of +0.20 V in a 0.05 M pH 7.0 Tris–HCl electrolyte for AA detection. All of the solutions were deaerated by ultrahigh-purity nitrogen for 10 min before electrochemical measurements and maintained under nitrogen atmosphere during the measurements.

## 3. Results and discussion

### 3.1. Structure characteristics of Au-LDHs film

The structures and morphologies of raw Ni–Al LDHs and Au/Ni–Al LDHs were characterized by TEM, XRD and XPS. From TEM images (Fig. 1A, B), large numbers of high crystallinity and hexagonal platelet-like LDH sheets, which was the typical morphology of layered double hydroxide (Du and Fang, 2010), were formed. Fig. 1A', B' depicted the high-resolution transmission electron microscopy (HR-TEM) images of the synthesized LDHs. The electron diffraction pattern of Au/Ni–Al LDHs (inset in Fig. 1B') was consistent with LDHs and Au nanoparticles, while of raw Ni–Al LDHs (inset in Fig. 1A'') consistent with LDHs (Goh et al., 2009; Paul et al., 2015), thus the idea of the synthesis scheme was confirmed. Moreover, the average lateral size of Au/Ni–Al LDHs, which confirmed as  $10 \pm 0.2$  nm, is much smaller than that of raw Ni–Al LDHs with  $20 \pm 0.2$  nm. And even more, from the results of Table 1, it can be confirmed that the size of Au/Ni–Al LDHs was smaller than that of LDHs obtained by literature methods. The XRD patterns were shown in Fig. 2. Characteristic reflection peaks of LDH materials with a series of (*00l*) peaks at low angle were observed for both raw Ni–Al LDHs and Au/Ni–Al LDHs, and all the diffraction peaks could be indexed to a typical hexagonal phase Ni–Al hydroxide (JCPDS no. 15-0087) (Velu et al., 2000; J. Wang et al., 2010), which was in accordance with the TEM results. The sharp diffraction peaks revealed high crystallinity and excellent layered feature of the LDHs. Compared to the raw Ni–Al LDHs, the XRD pattern of Au/Ni–Al LDHs showed one new peak at  $2\theta = 38.2^\circ$ , corresponding to the (111) plane of Au crystal (Belova et al., 2008). Thus it can be confirmed that Au colloidal particles have been doped into Ni–Al LDHs successfully. Further chemical composition information of the materials was analyzed by XPS spectra. As shown in Fig. 3A, there were four predominant peaks corresponding to the Ni, Al, C, O elements in both spectra. However, compared to the

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