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# Synthesis and assembly of ultrathin film of $Ni(OH)_2$ nanoparticles at gas/liquid interface, its high electrocatalytical oxidation toward bio-thiols and selective determination of cysteine

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ABSTRACT

A facile strategy was reported to synthesize and assemble a stable ultrathin film of $Ni(OH)_2$ nanoparticles at gas/liquid interface where the aqueous phase contained $Ni^{2+}$ and the organic phase was composed of triethylamine toluene solution. The ultrathin film of $Ni(OH)_2$ nanoparticles that precipitated at the interface was transferred onto the electrode surface for the electrocatalysis of bio-thiols and selective electroanalysis of cysteine. The preparation of $Ni(OH)_2$ ultrathin film and its transfer to an electrode substrate is very simple. The obtained $Ni(OH)_2$ ultrathin film modified electrodes are stable, showing high electrochemical oxidation toward bio-thiols and good selectivity toward cysteine in phosphate buffered solution of pH 7.5.



## 1. Introduction

Electrocatalysis of nickel based materials toward small organic molecules have been the focus of intense study in the areas of fuel cell, organic synthesis and electrochemical sensors. Ni, NiO and $Ni(OH)_2$ exhibit good electrocatalysis for glucose, glycine, methanol, ethanol, cyclohexanol, insulin, ammonia, acetylcholine etc. that are oxidized by NiOOH from the redox couple of $Ni(OH)_2$/NiOOH [1–9]. Various morphologies of $Ni(OH)_2$ such as nanorod, nanowire, nanotube, nanosheet, mesoporous structure, and hollow sphere have been synthesized via a variety of chemical routes [10–14]. They are immobilized onto the electrode surface for electrocatalytical or electroanalytical applications by the techniques of assembly or electrodeposition etc.[15].

The determination of cysteine (CySH), homocysteine (HCy) and glutathione (GTh) is very important in many biological and medical systems. Electrochemical methods have been developed for the detection of these bio-thiols. Although their electrochemical oxidation is thermodynamically favorable, the slow reaction kinetics at conventional electrodes hampers its utilization for analytical purposes. The large overpotential also results in the increased interference. Many nanomaterials, such as Au, $MnO_2$, $Cu(OH)_2$, $TiO_2$, carbon nanotube etc., have been explored for their electrocatalytic determination [16–20].

Herein, an ultrathin film of $Ni(OH)_2$ nanoparticles was prepared by synthesizing and assembling at gas/liquid interface where the aqueous phase contained $Ni^{2+}$ and the organic phase was composed of triethylamine toluene solution. The ultrathin film of $Ni(OH)_2$ nanoparticles precipitated at interface was easily transferred onto the glass carbon electrode (GCE) surface for the electrocatalysis of bio-thiols and selective electroanalysis of CySH.

## 2. Experimental

### 2.1. Reagent and materials

Triethylamine, GTh, L-CySH and DL-HCy were from Aladdin (Shanghai, China), SCRC (Shanghai, China), BBI and Fluka respectively. All other chemicals were of analytical grade and were used without further purification. All solutions were prepared using ultra-pure water from Milli-Q.

### 2.2. Synthesis and assembly of ultrathin film of $Ni(OH)_2$ nanoparticles at gas/liquid interface

In a typical synthesis and assembly experiment, 30 μL of 1% triethylamine toluene solution was carefully dropped and spread onto the surface of 0.7 mL 10 mM $Ni(NO_3)_2$ aqueous solution, forming an organic/aqueous interface where an ultrathin film of $Ni(OH)_2$ nanoparticles appeared. The reaction was allowed to last for 1 h. The formula is applicable to the whole paper except that for the electrochemical study in 0.1 M NaOH where 10 μL of 0.5%

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triethylamine toluene solution and 0.7 mL 5 mM $Ni(NO_3)_2$ aqueous solution was used to avoid the over-high redox signal.

### 2.3. Preparation of $Ni(OH)_2$ ultrathin film modified GCE

The formed $Ni(OH)_2$ ultrathin film was transferred onto the cleaned GCE surface by using GCE to touch vertically the film from the above. The modified electrode was rinsed with ultra-pure water and then dried at room temperature for use.

### 2.4. Apparatus

The $Ni(OH)_2$ ultrathin film was carefully transferred onto the carbon plate surface and studied by scanning electron microscopy (SEM, S-4800 UHR FE-SEM). Electrochemical measurements were conducted using CHI 842B electrochemical workstation (CHI, Shanghai) with three-electrode setup. A $Ni(OH)_2$ ultrathin film modified GCE ($Ni(OH)_2$–GCE) was employed as working electrode, a saturated $Hg/HgCl_2$ electrode (SCE) as reference electrode and a platinum wire as counter electrode.

## 3. Results and discussion

Current trends in nanoscience and nanotechnology are pointing toward the fabrication of 2D and 3D assemblies of ordered nanostructures, for which a variety of protocols have been developed [21–23]. A liquid/liquid or air/liquid interface offers potential for such assembly with the advantage of easy manipulation of the obtained films. For the synthesis and assembly of ultrathin film of $Ni(OH)_2$ nanoparticles, a small volume of triethylamine toluene solution was carefully dropped onto the surface of $Ni(NO_3)_3$ aqueous solution, schemed in Fig. 1A. With the evaporation of toluene and the chemical reaction, a round film shown in Fig. 1B was observed spreading on the water surface, which is due to the precipitation reaction of $Ni^{2+}$ with $OH^-$ from triethylamine hydrolysis [24]. As can be seen from the SEM images in Fig. 1C, the as-prepared film consists of nanoparticles with diameter about 20 nm. The nanoparticles are present in a close-packed multilayer arrangement. Observed from film brim in Fig. 1D, the film thickness is roughly estimated to be small than 100 nm.

The $Ni(OH)_2$–GCE could be prepared easily by using a GCE to touch the film vertically from above. Cyclic voltammograms (CVs) of a $Ni(OH)_2$–GCE in alkali solution is shown in Fig. 2A (a) with an anodic peak at 0.40 V and an cathodic peak at 0.33 V attributed to the redox of $Ni(OH)_2$/NiOOH. Observed from Fig. 2A (b), an increase of the oxidative current and a decrease of reductive current in the presence of CySH indicate the excellent electrocatalytical activity of $Ni(OH)_2$ ultrathin film toward the oxidation of CySH in alkali solution. The small oxidation peak at about 0.21 V could be contributed to the direct oxidation of CySH catalyzed by $Ni(OH)_2$ ultrathin film [25]:

$$2CySH \Rightarrow CyS{-}SyC + 2e^- + 2H^+.$$

Another more positive peak after 0.40 V exhibits the indirect oxidation of CySH, where the increase of oxidation current is attributed to the production of $Ni(OH)_2$ through the reaction between NiOOH and CySH. The produced $Ni(OH)_2$ is further oxidized to NiOOH at electrode surface.

Although the $Ni(OH)_2$ ultrathin film exhibits excellent electrocatalytical oxidation toward CySH in alkali solution, the development of new techniques for the determination of CySH in nearly neutral buffer solution has been highly sought since CySH are usually unstable in alkali solution. Also, the real sample of CySH often shows a pH close to neutral. Seen from Fig. 2B (a), the $Ni(OH)_2$–GCE in PBS of pH 7.5 exhibits extremely different electrochemical behavior from that in alkali solution. Both oxidation and reduction peaks of $Ni(OH)_2$/NiOOH are more positive and less sharp, located at around 1.1 V. Similar with

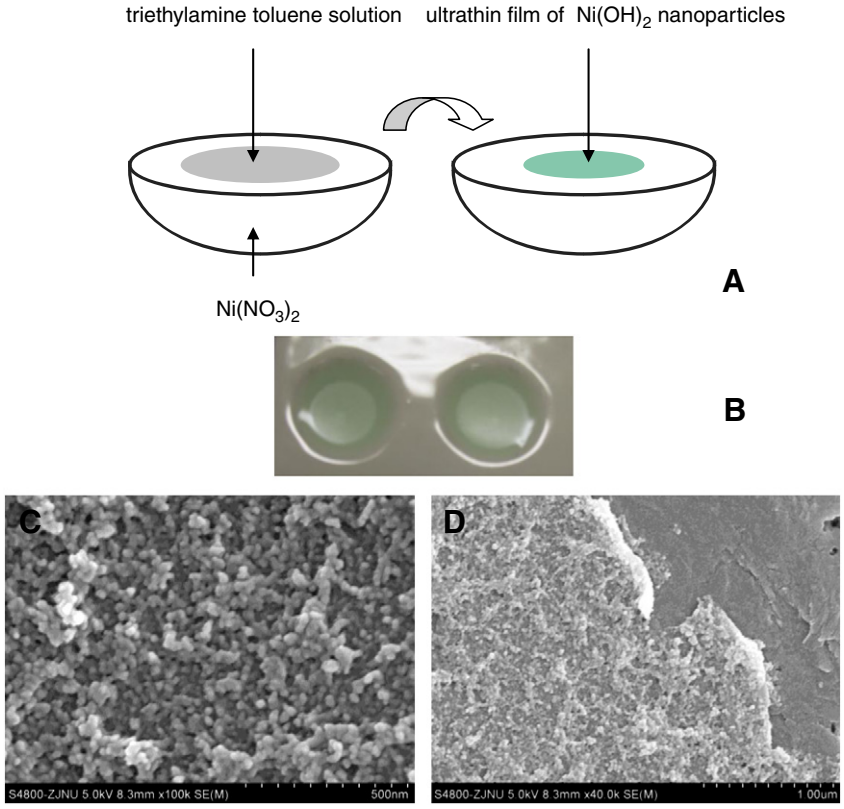


**Fig. 1.** (A) Scheme for the one-step synthesis and assembly of ultrathin film of $Ni(OH)_2$ nanoparticles at gas/liquid interface. (B) Photo of the formed ultrathin film of $Ni(OH)_2$ nanoparticles at gas/liquid interface. (C, D) SEM images of the obtained ultrathin film of $Ni(OH)_2$ nanoparticles.