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Morphology dependent electrocatalytic properties of hydrothermally synthesized cobalt oxide nanostructures

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Abstract

Cobalt oxide (Co_3O_4) nanostructures with different morphologies (nanocubes, nanowires, nanobundles, nanoplates, and nanoflowers) were synthesized using a simple hydrothermal process and the electrochemical reduction of 4-nitrophenol (4-NP) was chosen as a model system to study the electrocatalytic properties of the Co_3O_4 nanostructures. The nanostructures were successfully characterized using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman analysis. Further, glassy carbon (GC) electrodes modified with Co_3O_4 nanostructures with different morphologies were characterized using electrochemical impedance spectroscopy (EIS), and the results showed the lowest charge transfer resistance (R_{ct}) value for the Co_3O_4 nanocubes toward the $[Fe(CN)_6]^{3-/4-}$ redox couple among all the modified electrodes. The electrochemical reduction of 4-nitrophenol (4-NP) was performed using the different Co_3O_4 nanostructure modified electrodes with phosphate buffer solution (PBS) (pH 7), and it was found that the Co_3O_4 nanocube modified electrode displayed a better catalytic current response. Moreover, the electrochemical detection of 4-NP at the lowest concentration levels was studied with the nanocube modified electrode using square wave voltammetry (SWV). A linear relationship was observed between the current response and the concentration ($R^2=0.997$), and the limit of detection was found to be 0.93 μM. The Co_3O_4 nanocubes could reproduce the current responses in repeated experiments for the detection of 4-NP.

Keywords: Cobalt oxide nanostructures; Hydrothermal synthesis; 4-nitrophenol; Electrochemical sensor

1. Introduction

The introduction of nanoscience and nanotechnology and the ability to synthesize various nanomaterials have breathed new life into catalysis science. In recent years, nanostructured metal oxides have attracted considerable attention because of their envisioned applications in electronics, optics, magnetic storage devices, and electrochemical sensors for environmental analyses [1–3]. The nanostructures of metal oxides like TiO_2, Fe_3O_4, NiO, MnO_2 and Co_3O_4 have been used as catalysts in various applications, including lithium ion batteries, supercapacitors, solar cells, fuel cells and catalysis in order to overcome the high cost of metals [4–6]. Recently, electrodes modified with metal oxide nanostructures have been thoroughly investigated for the electrochemical determination of several biologically important analytes because of their interesting electrocatalytic properties [7,8]. Among the various metal oxides, the Co_3O_4 nanostructure shows some interesting magnetic, optical, and transport properties [9,10], and it is considered to be one of the more promising materials for electrochemical applications because of its well-defined electrochemical redox activity, high theoretical capacity (890 mA h g^{-1}), low cost, and stable chemical state [11]. Further, Co_3O_4 nanoparticles have shown their potential utility in anode materials for rechargeable Li ion batteries [3], electronic devices [12], gas sensors [13], electrochromic devices [14], and high-temperature selective solar-radiation absorbers [15]. With the goal of profitable utilization, much effort has been made to develop synthetic techniques for growing Co_3O_4

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nanostructures, including hydrothermal [3], pulsed laser deposition [10], chemical vapor deposition [12], and radiolysis [16]. Generally, hydrothermal synthesis is highly preferred for the synthesis of metal oxide nanostructures because of its simplicity. An appropriate amount of powdered reagents and water are placed in a Teflon-lined autoclave and heated without stirring from moderate to high temperatures and pressures for the desired time. Further, it is possible to predict the optimum reaction conditions using the electrolyte thermodynamics, and the problem of impurities can be overcome by varying the ratios of the precursors in the hydrothermal synthesis [17]. Recently, more attention has been given to controlling the morphology of the metal oxide nanostructures in the synthesis because the novel functionalities of nanostructures depend not only on their compositions but also on their shapes and sizes.

Phenol-based nitro-compounds are extensively used in the pharmaceutical and chemical industries and are considered to be toxicants, which cause damage to organisms and plants even at a very low concentration and can create various health problems in human beings [18,19]. As an example, 4-nitrophenol (4-NP) is considered to be one of the important toxic phenol-based nitro-compounds that can be found in the waste-water released by the chemical and pharmaceutical industries, and it is a common intermediate in the production of analgesics, leather products, dyes, and pharmaceuticals. Acute exposure to 4-NP can cause headache, fever, breathing problems, and even death at a high level of exposure. It also tends to remain in agricultural crops, vegetables, fruits and water sources when used as an ingredient in a fertilizer or pesticide [18,20]. Because of its high stability in water, low biodegradation, high toxicity, and persistence, 4-NP is on the priority list of the US Environment Protection Agency (EPA) [18,21–23]. Based on the facts described above, it is vitally important to develop simple and reliable techniques for the detection of trace amounts of 4-NP in environmental water samples. Out of the various available techniques, electrochemical techniques have drawn considerable attention because of their potential advantages, which include simplicity, excellent selectivity and sensitivity, easy operation with a rapid response, and cost effectiveness [18,22]. In addition, it is well known that nitro groups can easily be reduced electrochemically in aromatic or heterocyclic compounds and permit the sensitive determination of 4-NP through electrochemical methods under the condition of a very good electrode material [24,25]. Metal oxides such as TiO_2 [26,27], Fe_3O_4 [28], NiO [29], MnO_2 [30], and Co_3O_4 [31] were previously exploited for the detection of 4-NP.

In this study, we synthesized Co_3O_4 nanostructures with different morphologies (nanocubes, nanowires, nanobundles, nanoplates and nanoflowers) using a hydrothermal process and studied their electrochemical properties in the electrochemical reduction of 4-NP. The nanostructures were characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Raman analysis. EIS measurements showed the lowest charge transfer resistance (R_{ct}) value for Co_3O_4 nanocubes toward the $[Fe(CN)_6]^{3-/4-}$ redox couple among all the modified electrodes. The better electrocatalytic activity was observed at a Co_3O_4 nanocube modified electrode toward the electrochemical reduction of 4-NP, and the detection of 4-NP was performed at the same modified electrode using square wave voltammetry (SWV). A linear relationship was observed between the current response and the concentration ($R^2=0.997$), and the limit of detection (LOD) was found to be 0.93 μM.

2. Experimental section

2.1. Materials

Cobalt acetate ($Co(CH_3COO)_2.4H_2O$) was purchased from Sigma-Aldrich. Ethanol (99.8%) and urea (99%) were received from Systerm Malaysia. NaOH (99%), ammonia (25%) and 4-NP (> 98%) were purchased from R & M chemicals. Distilled water was used throughout the experiments unless otherwise stated.

2.2. Synthesis of Co_3O_4 nanostructures with different morphologies

Co_3O_4 nanostructures with different morphological were synthesized using a simple one-step hydrothermal process with the aid of a Teflon-lined stainless steel autoclave with a total capacity of 100 ml filled to 75% with the solution. Co_3O_4 nanocubes were synthesized using the same procedure as previously reported by our group [32]. During the synthesis of the different morphologies, the cobalt precursor was dissolved in deionized water, and structure-directing agents like ethanol, ammonia, NaOH, and urea were added drop-wise under stirring. After the formation of a homogeneous slurry, it was transferred to the autoclave for the hydrothermal treatment process at different temperatures. The total reaction volume was maintained as 75 mL using distilled water for the synthesis of all the Co_3O_4 nanostructures. After the hydrothermal treatment, the solid Co_3O_4 product was collected, washed with distilled water and ethanol and dried in a hot air oven at 60 °C for 24 h to

Table 1
Experimental parameters for the synthesis of different morphologies of Co_3O_4 nanostructures.

Morphology of Co_3O_4	**Cobalt salt** (mM)	**Temperature** (°C)	**Reaction time** (h)	**Structure directing agents**
Nanocubes	2	180	12	15 mL ammonia (6 %)
Nanowires	2	150	5	30 mL ethanol (99.9%) and 3 mmol urea
Nanobundles	2	120	12	2 mmol urea
Nanoplates	2	150	15	13 mL NaOH solution (3.25 mM) with 2 mL ammonia (25%)
Nanoflowers	2	180	12	30 mL ethanol and 15 mL ammonia (6%)