Mesoporous NiO nanomagnets as catalysts and separators of chemical agents

Mohamed Khairy [a,b], Sherif A. El-Safty [a,b,*], Mohamed Ismael [a], Hiroshi Kawarada [b]

[a] National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba-shi, Ibaraki-ken 305-0047, Japan
[b] Graduate School for Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

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ABSTRACT

The development of a sustainable catalyst could potentially provide a long-term solution to industrial processes, especial those in the chemical industry, that require the production of a large quantity of raw materials manufactured from renewable resources. Therefore, establishing a proper design for a highly efficient and long-term reusable catalyst is one of the crucial environmental issues facing humanity. In this study, we developed a simple control for hierarchal mesoporous nickel oxide (NiO) nanomagnets (NMs) with flower- and sphere-like morphology and large mesocage cavities. In the fabrication of super-nanostructure NiO, features that were affected by the shape, surface, and size of particles exhibit high catalytic activities of chemical agents, such as o-aminophenol. Our findings shows that the NiO NM with flower-like morphology NFs has higher catalytic activity toward the oxidation of organic contaminates than that of nanospheres NSs or even other magnetic nanoparticles (NPs) such as Fe_3O_4 NPs. Furthermore, the NiO NMs are capable of the high-gradient magnetic separation of organic contaminants from aquatic life with excellent reusability even after several cycles, which may help in wastewater management and supply. To understand the effectiveness of NiO NM functionalities in terms of hierarchical mesocage parameters, as well as in terms of shape- and size-morphologies in such chemical reactions, surface interaction and magnetic separation with chemical agents and theoretical calculations were performed.

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1. Introduction

Hierarchically mesostructured transition metal oxide nanostructures are widely applied in a plethora of technologically important disciplines, ranging from catalysis [1–4], nano-engineering of surfaces [5], energy generation using fuel cells [6] and solar cells [7], optical imaging [8,9], phototherapy [10], and sensor applications [5–11]. Given that the catalytic activity of the transition metal crystals depends on the crystal face used and that different nanoparticles (NPs) with different shapes have different facets and different ratios of the number of atoms on corners and edges to those on the facets, catalysis is expectedly dependent on the NP shape used [12]. Considerable effort has been exerted to control the intrinsic nanostructure and morphology of these materials to achieve tunable properties. However, technical challenges, such as intensive and time-consuming synthetic conditions, remain.

With recent advancements in mesostructured materials and nanotechnology, new synthetic methods for effective nanocatalyst design have emerged. Template synthetic methods have been established as convenient approaches for the synthesis of mesoporous metal oxides. In these methods, either organic or inorganic particles could be used as sacrificial templates. However, the mesoporous structures tend to collapse during the removal of these templates at high temperature [13].

To date, nanoscale magnetic materials are considered to be potential adsorbents because of their large surface area and unique features of easy separation when subjected to external magnetic fields. These properties facilitate a wider range of applications, such as the purification of bio-molecules, magnetic refrigeration, magnetic resonance imaging enhancement, information storage, magneto-optical devices, solid devices, targeted drug delivery, cell separation, and environmental capture [14–17]. Magnetic NP features enable the easy recovery of catalysts in a liquid-phase reaction compared with cross-flow filtration and centrifugation, particularly when the catalysts are in the nanometer-size range and have high surface area that enables the creation of numerous catalytic sites for high activity levels.

Among the different magnetic NPs, nickel oxide (NiO) has received considerable attention for its unique magnetic properties, stability, and feasibility of preparation. NiO is a well-known wide band gap p-type semiconductor and antiferromagnetic material. The synthesis of NiO nanocrystals (NCs) with controlled but large-scale morphology are highly promising candidates because of their extensive applications as catalysts [1–4,18], lithium ion

* Corresponding author at: National institute for Materials Science, 1-2-1 Sengen, Tsukuba, 305-0047 Japan; Graduate School for Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.
Tel.: +81 298592135; fax: +81 298592025.
E-mail addresses: sherif@aoni.waseda.jp, sherif.elsafty@nims.go.jp
(S.A. El-Safty).

Scheme 1. Catalytic transformation and removal of organic pollutants (3-APZ) using mesoporous NiO NM.

batteries and fuel cells [19], electrochromic display devices [20], optical gas sensors [21], magnetic materials [22], dye-sensitized photo-cathodes [23], and solar thermal absorbers [24]. Several NiO nanostructures with unique properties that are mainly affected by their size and morphology have recently been synthesized successfully, such as NiO nanoslices [25], nanoplates [25,27] and nanocolumns [25], nanorods [26–28], nanorings [28], nanosheets or nanoribbons [29], nanowires [30], nanotubes [31], and hollow nanospheres [32,33]. However, these synthetic strategies produce NiO with low porosity and magnetism. Thus, the development of a simple and feasible method for designing magnetic mesostructure NiO with controlled morphology is highly desirable and remains a great challenge to material scientists.

The petrochemical, chemical, and pharmaceutical industries produce wastewater that contains high concentrations of organic materials, which are extremely toxic to aquatic life. Given the increasing concern for public health and environmental quality, the transformation and complete removal of organic pollutants from the environment is imperative. Both functional processes are promising approaches for the treatment of organic contaminants to produce safe compounds, but present a great challenge to water suppliers. Aminophenols (APs) are widely used as reducing agents, as intermediates in chemical synthesis, bleaching, and hair dyes, and as materials for photography [34]. Therefore, the chemical oxidation and removal of APs from aquatic environments with an effective and sustainable global strategy has become a major public concern in almost all parts of the world. Recently, our group has reported on the fabrication of multidirectional porous mosaic-like NiO nanoplatelets using the hydrothermal strategy [35]. These porous NiO nanoplatelets showed an efficient chemical transformation of phenolic compounds. However, the treatment of organic contaminants is necessary to reduce storage space requirement and to prevent the release of such contaminants to the environment, which may cause long-term problems. To control the catalytic transformation and separation of chemical pollutants from the environment, the designing of nanomagnetic materials is highly desirable.

In this work, the hierarchical mesoporous NiO nanoflower (NF) and nanosphere (NS) magnets were fabricated using a simple and reproducible method. The mesoporous NiO nanomagnets (NMs) featured high mesocage porosity, surface area, and magnetization and can act as nanocatalysts with easy recovery and dynamic working ranges. In this regard, critical assessments for potential nanocatalyst design based NiO NMs in the chemical oxidation of phenolic pollutants are emphasized in this work. Our experimental findings showed that the NiO NFs offer higher catalytic activity than NSs or even Fe_3O_4 NPs (Scheme 1). To understand the proposed chemical transformation mechanism of pollutants over NiO NMs, the energy profiles and the charge distribution of reactants and intermediates, as well as the magnetization effect on the resultant products, were examined using the density function theory (DFT). A major advantage of NiO NM catalysts is their retained texture, morphology, and magnetic characteristics (i.e., easy recovery) in terms of reactivity with fast chemical oxidation even after multiple cycles.

2. Experimental

All materials were of analytical grade and were used without further purification. Anhydrous nickel chloride, o-aminophenol (o-AP), sodium acetate (NaAc), and ethylene glycol (EG) were purchased from Japan Tokyo Chemical Industry Company Ltd. (Japan). The solutions of o-AP ($0.015\,mol\,L^{-1}$) were prepared in water with 3% ethanol. The phenol concentration was $5 \times 10^{-4}\,mol\,L^{-1}$ during the oxidation process.

2.1. Fabrication of mesoporous NiO NMs with flower-like morphology

The NiO NFs were synthesized using a one-pot hydrothermal method in the presence of EG and NaAc. During typical synthesis, 20 mmol of anhydrous nickel chloride precursor was dissolved in 40 mL of EG, followed by 40 mmol of anhydrous NaAc, which were then combined through sonication. The solution was loaded into a 100 mL Teflon-lined, stainless steel autoclave at 200 °C for 8 h. The solution was then allowed to cool to room temperature. Finally, the precipitate was collected and washed ten times with distilled water and ethanol to remove the remaining agents, after which it was dried at 60 °C.

2.2. Fabrication of magnetic NiO NSs

A combination of 1.47 g nickel chloride precursor and 4.5 g of anhydrous NaAc were dissolved in 25 mL Triethanol amine diluted in a 50 mL deionized H_2O plus 2.0 g polyethyleneimine. The solution was transferred to a 100 mL Teflon-lined, stainless steel autoclave, which was sealed and maintained at 200 °C for 8 h and then cooled to room temperature. The precipitate was collected and washed ten times with distilled water and ethanol to remove the remaining agents and was then dried at 45 °C. Finally, NiO powder was calcined at 270 °C for 30 min with a heating of 2 °C/min.

2.3. Catalytic reaction of mesoporous NiO NMs

The catalytic oxidation of phenolic compounds was conducted using NiO NMs as catalyst. The reaction was performed in water at varying temperatures (25–40 °C) using a thermostatic shaker at a constant shaking rate (150 rpm/min). In a typical kinetic experiment, the catalyst (0.025 g) solution is dissolved in 28 mL deionized water with shaking for 15 min and cleansing of N_2 gas at a specific temperature. (25–40 °C) Subsequently, 2 mL standard o-AP solution was added to the mixture for quick reduction, and the reaction time was recorded. The phenol concentration in the reaction vessel was 5×10^{-4} M. At finite time, 3 mL of the solution was reduced and transferred to a quartz cell for measurement. The catalytic reaction was monitored spectrophotometrically at $\lambda = 430$ nm for 3-aminophenoxazone (3-APZ).

2.4. Materials characterization

N_2 adsorption/desorption isotherms at 77 K were used to investigate the textural surface properties and pore size distribution