Green Chemical Transformation of phenolic pollutants using mesoporous NiO nanocrystals with sheet-like morphology

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Abstract: - We report the fabrication of hierarchical mesoporous NiO nanocrystals (NCs) with sheet-like morphology via a simple, and eco-friendly hydrothermal method. Mesoporous NiO particles were characterized by small- and wide-angle X-ray diffraction, nitrogen adsorption/desorption, Scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results demonstrated that the as-prepared Ni(OH)₂ sheet converted to disordered mesoporous NiO NCs with retention their hexagonal morphology during controlled thermal treatment. The physical characteristics of NiO NCs such as porosity, surface area, and pore volume enabled the phenolic pollutants such o-aminophenol (o-ATP) to access the active site of the nanosheets. The features of NiO NCs with sheet-like morphology induced high catalytic activity and excellent reusability even after extended recycle uses. Moreover, the mechanistic pathway of the phenolic pollutants transformation was demonstrated theoretically using density functional theory (DFT).

Key-Words: -mesoporous NiO, nanocatalysts, pollutants, chemical transformation.

1 Introduction

To date, mesoporous metal oxides have attracted extensive attention because such materials are promising candidates in a plethora of technologically important disciplines including catalysis [1], nanofiltration [2], energy generation using fuel cells [3] and solar cells [4], optical imaging [5], phototheraphy [6], environmental capture [7], and sensor applications [8]. To satisfy these application requirements, large-scale production, low-cost manufacturing, and fast transformation reaction rate are demanded. With recent advancements in mesostructured materials and nanotechnology, new synthetic methods have been developed to design a controlled shape mesoporous metal oxide nanomaterials with high surface area, tunable pores, and pore volumes. Since, there has been an increase in interest in mesoporous materials, particularly the semiconducting metal oxides such as SnO₂, TiO₂, and WO₃[9]. Generally, these mesoporous metal oxides are usually synthesized by using organic templates as template-guided synthesis. During the removal of the organic moieties at high temperature treatments, the mesostructure pores tend to collapse. In addition, the formation of amorphous and/or semi-crystalline walls leads to poor thermal stability of these metal oxide mesostructures.[9,10]. Great efforts have been exerted to control the intrinsic mesostructure and morphology of these materials for tunable properties, yet technical challenges in terms of intensive and time-consuming synthetic conditions remain. Among the varieties of the mesoporous nanomaterials, NiO has received intensive attention because of its unique properties, stability, and feasibility of preparation. Mesoporous NiO with morphology-controlled and large scale are highly promising candidates and have attracted attention as p-type wide-band-gap semiconductors, because of its extensive applications as catalyst and as components of lithium ion batteries and fuel cells, electrochromic display devices, optical gas sensors, dye-sensitized photo-cathodes, and solar thermal absorbers [11]. Recently, a series of novel mesoporous NiO nanostructured have been developed with different morphologies, such as nanoslices, nanoplates and nanocolumns, nanorods and nanorings, nanosheets, nanowires, nanotubes, and hollow nanospheres [12]. However, these synthetic strategies produce NiO with low porosity and magnetism. Thus, the development a simple and feasible method for designing mesoporous NiO nanostructures with controlled morphology is highly desirable.

Generally, with increasing concern for public health and environmental quality, the complete removal and/or conversion of organic pollutants is imperative. The petrochemical, chemical, and
pharmaceutical industries was produce wastewater containing high concentrations of organic materials, which may be difficult to oxidize biologically and are extremely toxic to aquatic life. There are different strategies to remove organic pollutants from water, including adsorption, ion-exchange, membrane filtration, and chemical oxidation [13], but these methods have several distinct problems that can render them ineffective, so more efficient and cost-effective method of removing organic pollutants from water is needed.

2.1 Chemicals

All materials were of analytical grade and used without further purification. Nickel chloride anhydrous (NiCl$_2$), ammonium hydroxide (NH$_4$OH), and $o$-aminothiophenol ($o$-ATP) were purchased from Japan Tokyo Chemical Industry Company Ltd (Japan). $o$-ATP solution (0.015 mol/L) was prepared in water with 3% ethanol content at a concentration of $5 \times 10^{-4}$ mol/L during the oxidation process.

2.2 Fabrication of NiO NCs with sheet-like morphology

The mesoporous NiO nanosheets were synthesized by hydrothermal method without the use of surfactants and structure directing agents. In a typical procedure, 10 mmol anhydrous nickel chloride was dissolved in 50 mL distilled water. The solution pH was adjusted to 10 by the dropwise addition of ammonia solution (28%). Next, the solution was loaded into the Teflon liner of a stainless steel autoclave with a volume of 100 mL. The autoclave was sealed and maintained at 160 °C for 6 h and then the solution was allowed to cool to room temperature. Finally, the precipitate was collected and washed several times with distilled water and ethanol to remove the remaining agents, and then collected by filtration, dried at 45 °C overnight and carefully calcined at 300 °C (the heating rate 2°C/min) for 2 h under an oxygen flow. The mesoporous NiO nanosheet was formed through the decomposition of nickel hydroxide. The key finding is that the generation of mesopores within NiO nanosheet samples was due to the calcination of Ni(OH)$_2$ at high-temperature treatments, with retention their morphology in the nanosheet structures. This method of synthesis enables the fabrication of large yields (92 %) of high quality crystalline mesoporous NiO nanosheets. Significantly, the catalysts based on mesoporous NiO nanosheets are easily developed using a simple and scalable fabrication method for environmental applications, in which large surface area, and highly distribution of nanosheet materials are required. Therefore, our NiO catalyst shows a reliable response to phenolic pollutants ($o$-ATP).

2.3 Batch contact time experiments for transformation of pollutants

The catalytic transformation of phenolic compound ($o$-ATP) was carried out using nickel oxide nanosheets as catalysts. The reaction was

Fig. 1 chemical transformation of $o$-ATP over NiO NCs with sheet-like morphology

The chemical transformation or chemical oxidation of these pollutants is one of the most commonly adopted methods in refinery techniques to produce safe compounds. A critical assessment of the potential nanocatalyst design-based NiO nanosheets in the catalytic transformation of phenolic pollutants (such as $o$-aminothiophenol ($o$-ATP)) was given special emphasis in this work. Significant key factors such as the mesoporosity, surface area that crucially affects the heterogeneous reaction rate, reaction temperature, and type of solvent are discussed. Particularly important was the fact that the NiO nanosheet catalysts offered highly stable catalytic activity even after several reuse cycles as shown in Figure 1. The NiO nanosheets lost about 4% of their original efficiency after a single reuse cycle, indicating long-term activity of the mesoporous ordered NiO as a recyclable catalyst.

2 Experimental
performed in water at various temperatures (range 25–40 °C) using a thermostated shaker at a constant shaking rate. In a typical kinetic experiment, the catalyst (0.025 g) was mixed in 28 mL of deionized water and placed in a water shaker thermostat for 10 min at a specific temperature. A 2 mL standard solution of phenol was added to the mixture and quenched quickly using a micropipette; the reaction time was recorded. The concentration of o-ATP in the reaction vessel was $5 \times 10^{-4}$ M. At a finite time, 3 mL of the solution was quenched and transferred to a quartz cell for measurement. No centrifugation or filtration system was used for detection given the NiO features. The heterogeneous catalytic reaction was monitored spectrophotometrically at 322 nm for 3-aminophenothiozine-3-thizone (3-APT). Theoretical Modelling of the cyclization reaction of o-ATP into 3-APT were carried out on the basis of DFT calculations implemented in the Gaussian 03 suite program. All calculations performed using ordinary B3LYP functional theory, which comprises the hybrid Becke+Hartree-Fock exchange and Lee-Yang-Parr functional correlation with nonlocal corrections, were adopted with the basis set 6-311G (d, p). To obtain more reliable data, the solvent effects on the models were achieved using the polarized continuum model [14].

2.4 Analysis

FESEM images were recorded by a field-emission scanning electron microscopy (Hitachi S-4300) at 20 keV. High resolution transmission electron microscopy (HRTEM) was performed using a JEOL JEM model 2100F microscope. HRTEM was conducted at an acceleration voltage of 200 kV to obtain a lattice resolution of 0.1 nm. Small angle x-ray diffraction (SAXRD) experiments were performed with two dimensional (2D) confocal mirror (Rigaku Nanoviewer) and a pinhole collimator, and monochromatic x-ray beam of Cu-Kα radiation ($\lambda = 1.54$ Å). Wide angle powder x-ray diffraction (WAXRD) patterns were measured using an 18 kW diffractometer (Bruker D8 Advance). N₂ adsorption-desorption isotherms were measured using a BELSORP MIN-II analyzer (JP. BEL Co. Ltd) at 77 K. The absorbance spectrum of the heterogeneous catalytic reactions was recorded using a UV-Vis spectrophotometer (Shimadzu 3150, Japan).

3 Results and discussion

3.1 Characterization of mesoporous NiO nanosheet-like morphology

FE-SEM micrographs (Fig. 2A, B) revealed that the NiO had nanosized particle sizes (150–250 nm in diameter and ~20 nm in thickness). The crystal particles of NiO were hexagonal sheet-like with smooth fine surfaces. These results indicate the retention of hexagonal nano-sheet particles during the formation of NiO under gradually thermal treatment at 300 °C.

![FE-SEM and HRTEM Images](image)

Fig. 2 FE-SEM (A, B) and HRTEM of mesoporous NiO NCs. Sheet-like morphology

The HRTEM images of the NiO samples clearly reveal the formation of irregular hexagonal nanosheets with an average size of 250 nm, thickness is less than 20 nm and the adjacent edge angle of approximately 120° [Fig. 2(C)]. Moreover, the TEM micrograph showed the formation of disordered (wormlike) mesopores as evidenced from the SAXS, and N₂ isothermal profiles (see below). The ED pattern recorded on a single nanosheet exhibits the bright spots (Fig. 2D, inset), indicating the crystallinity of the NiO nanosheet. The ED pattern is indexed to cubic NiO, consistent with the XRD result. The high resolution HRTEM image of the nanosheets shows clear lattice fringe s (Figure 2B). The distance between two lattice fringes is 0.24 nm, which belongs to the interplanar space of the $(111)$ planes of cubic (Fm̅3m) NiO corresponding to ED pattern.

The Small angle x-ray pattern of the Ni(OH)₂ sample did not show any diffraction peaks [Fig. 3A(b)] because of the amorphous pore networks
within the Ni(OH)$_2$ nanosheets. After mild thermal treatment at 300 °C, the Ni(OH)$_2$ decomposed to the mesoporous NiO nanosheets [Fig. 3A(a)]. The SAXRD pattern of the NiO nanosheet showed a broadly resolved diffraction peak at approximately 2θ = 1.12°, corresponding to d-spacing = 4.2 nm. Despite the broadening and low resolution in the intense scattering peak, the formation of mesostructures and retention of the mesopore architectures inside the NiO nanosheets were evident. The WAXRD pattern of the hydrothermal product [inset of Fig. 3A(b)] showed well-resolved and distinctive diffraction peaks, indicating the formation of single-phase β-Ni(OH)$_2$ nanosheets with crystalline structures, consistent with the JCPDS No. 14-0117, a = 3.126 Å. The WAXRD pattern of the NiO [Fig. 3A(a)] showed typical strong diffraction peaks. These diffraction peaks are consistent with face-centered cubic Fm3m symmetry with a lattice constant of a = 4.17 Å (JCPDS, No. 04-0835), as evidenced from TEM profiles.

Further evidence for formation of mesoporous NiO NCs with sheet-like morphology, N$_2$ adsorption isotherm of mesoporous NiO nanosheets

Fig. 3 (A) Small angle X-Ray diffraction (inset- wide angle X-Ray diffraction of NiO NCs) (B) and N$_2$ adsorption isotherm of mesoporous NiO nanosheets

3.2 Catalytic performance of the mesoporous NiO NCs.

o-aminothiophenols (o-ATP) were used as a model of organic pollutants for testing the chemical reactivity of NiO NCs. The physical characteristics of NiO NCs such as porosity, surface area, and pore volume (Fig. 4) enabled the organic pollutants to access the active site of the nanosheets.

Fig. 4 Time-sequence of the increase in the absorption band of 3-APT at 30°C (A) during the catalytic transformation of [5 × 10^{-3}M] o-ATP over a 0.025 g NiO nanosheets, B) Effect of various reaction temperatures on the time-rate dependence of the formation of 3-APT at 322 nm

Furthermore, the surface composition of NiO nanosheet as shown in XPS analysis (data not shown) enhanced the catalytic activity of o-ATP to form hand-safe chemicals such 3-APT compounds, as
shown in Fig. 1. The heterogeneous catalytic reaction usually depends on the temperature, solvent, and concentration of o-ATP. In this paper, the oxidation products were detected and monitored by UV/vis spectroscopy at $\lambda = 322$ nm for 3-APT (Fig. 4 A). The transformation reaction rate constant was calculated at different temperatures as shown in Figure 5A. Further, the oxidation of $(5 \times 10^{-4}$ M) o-ATP was studied in batch contact time experiments at temperatures ranging from 25 to 40 °C (Fig. 4B). Our finding indicated that, the rate of the transformation increases with increasing the temperature, and the reaction more favourable at high temperature (Spontaneous reaction). A key finding in the this study is that NiO nanosheet have excellent properties as catalysts for chemical transformation of phenolic pollutants, and these NCs can retain their activity even after several reuse cycles [Fig. 5B].

![Graph showing temperature vs. reaction rate constant](image)

**Fig. 5** (A) The Effect of temperature on the heterogeneous Transformation reaction of o-ATP over NiO NCs, (B) The reusability of NiO Nanosheet toward the transformation reaction

The catalytic oxidation of o-ATP over NiO nanocatalyst involved four electrons and four protons to produce 3-APT. The sequence of two oxidation processes ($2e^-$ Oxidation) is a result of the reduction of NiO catalyst. Two equivalents of the metal oxides were initially reduced by one equivalent of the phenol molecule. For o-ATP, the benzothione-imine reacted with another molecule of o-ATP to form dimeric oxidation products; the reaction sequence of the expected oxidation products is shown in Fig.1. In order to confirm the proposed mechanism, DFT calculations were performed [14]. Among all optimized models, Fig. 1 shows the most stable configurations of intermediates and product and their charge distribution. Results indicated that, the highest electronegative charge allocated on the amino group of o-ATP was --0.93, suggesting that the oxidation is initiated through electron loss from the amino group. The produced cationic radical attacked the aromatic ring of another o-ATP molecule in the $p$-position with respect to the --SH group, which is the most electronegative part in the aromatic ring -0.19. The structure of the formed dimer revealed that the aromatic ring rotated around the formed C-N bond to release the steric hindrance. Finally; 3-APT is formed through the cyclization of the phenothiazine ring by the attack of the -SH group (–0.70) to the $p$-position with respect to the –NH$_2$ group (–0.18). The calculated energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for o-ATP and 3-APT were shown in Figure 6. The insignificant HOMO-LUMO differences for both molecules suggested that the phenol molecules have tendency for further polymerization.

![Graph showing HOMO and LUMO energies](image)

**Fig. 6** the HOMO and LUMO structures of o-ATP (a, c) and 3-APT (b, d).

**4 Conclusion**

Our approach featured to fabricate mesoporous NiO NCs in large-scale production, low-cost manufacturing, and efficient transformation reaction, as well as to control the size and shape of NCs in hexagonal nanosheets morphology. The intrinsic properties of NiO NCs with sheet-like morphology enhanced accessibility and interaction affinity of phenolic pollutants into the functional active sites of the NiO surfaces Moreover, the mesoporosity and surface composition of the NiO nanosheet played a key factor in the enhancement of the catalytic conversion of organic pollutants to hand-safe chemicals. Furthermore, A key finding in our study was that the NiO NCs have excellent properties as oxidizer for organic pollutants and retained their activity even after several reuse cycles.
References:


