Superparamagnetic NiO-doped mesoporous silica flower-like microspheres with high nickel content

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\begin{abstract}
Morphology oriented synthesis of metal oxide doped silica structures have fascinating properties which needed to be explored extensively. In this work, NiO doped silica microsphere with beautiful flower-like morphology has been achieved by adopting a facile surfactant-assisted synthetic route using CTAB-ammonia in H\textsubscript{2}O–ethanol mixed solvent media. The sol–gel synthesis with effective variations of Ni/Si ratios up to 7.0, followed by a simple hydrothermal treatment and subsequent calcination leads to the formation of NiO–silica mesostructures with high nickel content. Detailed structural and elemental characterizations by powder X-ray analysis (XRD), scanning electron (SEM) and transmission electron microscopy (TEM), N\textsubscript{2} adsorption–desorption, X-ray photoelectron spectroscopy (XPS) revealed that single cubic phase NiO doped mesoporous silica microspheres (for Ni/Si = 5:1 and 7:1) with good surface area (169 and 205 m\textsuperscript{2} g\textsuperscript{-1} for sample with Ni/Si = 7:1 and 5:1, respectively) and pore width 3–5 nm, have been formed with 3D flower-like shape and 500–600 nm particle size. These NiO–silica microspheres containing high Ni content up to 76 wt% have shown excellent paramagnetic properties at room temperature.
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\end{abstract}

Introduction

Since the last few decades, metal doped silica porous hybrid nanostructures have been explored extensively in miscellaneous fields of studies like sensing [1], catalysis [2], adsorption [3], energy storage [4], biomedical [5] etc. owing to the high physical and chemical stability as well as tunable pore structures and inertness of silica support, combined with unique properties of the present metal species [6]. Ni-doped silica mesoporous materials are quite popular in this respect, because of the good stability, superior magnetic and chemical properties of Ni-silica suggesting enormous applications in catalytic transformations, biosensing, lithium-storage batteries, and magnetic devices [7–10] and so on. Numerous synthetic methodologies have been adopted so far for the successful syntheses of NiO, Ni(OH)\textsubscript{2} based porous silica or nickel hydroxilicate nanostructures [11–13]. Surfactant-mediated self-assembly is one of those, demonstrating a facile pathway for the formation of uniform mesopores with homogeneous distribution of both Ni and silica species in the framework structure [14]. Moreover, continuous effort is also in progress by the scientists throughout the world to fabricate morphology-controlled Ni-doped silica nanostructures, which have significant role in various potential applications [14–16]. Core-shell, yolk–shell, microsphere, hollow structures, nano-sheets etc. are some interesting morphologies of Ni-based materials which possess crucial role in catalysis, drug delivery, sensing, energy storage, optical and electronic applications [17–20]. Flower-like Ni-silica microspheres, which can be obtained by proper tuning of the synthesis conditions like temperature, pH or precursor concentration, are also reported in literature [18]. Cui et al. proposed a synthetic route for NiO flower-like microsphere which was achieved by careful monitoring of the pH value of precursor solution [18]. Simple hydrothermal route has also been suggested for synthesis of \(\alpha\)-Ni(OH)\textsubscript{2} flower-like nanostructures by Salavati-Niasari et al. [21]. On the other hand, by optimizing the Ni salt precursor, Pan et al. have proposed a successful synthesis of flower-like hierarchical NiO microspheres [22]. Nevertheless, flower-like NiO doped porous silica microstructures synthesized by a facile one-pot surfactant-mediated hydrothermal routes is rarely reported in literature.

Synthesis of mesoporous silica with high loading of transition metal ions is a hot topic of research for modern scientists, because of the exceptional role of these materials in supercapacitor, catalysis, sensing, magnetic devices etc. [14,23]. However, the work is challenging due to the lack of stability and porosity loss in the
resulting materials. Here, we report a simple pathway for synthesis of Ni doped silica porous microsphere using CTAB surfactant and ammonia in water–ethanol media. The synthesized Ni–silica possesses beautiful flower-like microspherical morphology which shows Ni percentage up to 75% with formation of typical NiO cubic phase having good surface area (169 m²/g) as well as pore diameter in small mesoporous range. Additionally, viewing the behavior of other NiO nanostructures towards magnetic response [24–26], our sample has been investigated for magnetic measurement and the material exhibits an excellent superparamagnetism property at room temperature.

**Experimental section**

**Materials**

Hexadecyltrimethylammonium bromide (CTAB, 98%, Aldrich) was used as a structure-directing agent. Tetraethyl orthosilicate (TEOS, 98%, Aldrich) and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Aldrich) were used as silica and Ni precursors, respectively. Ammonium hydroxide (NH₄OH, 28–30% NH₄, Aldrich) was used to adjust pH as a basic catalyst and ethanol (EtOH, Aldrich) was used as a co-solvent during sol–gel synthesis. Deionized water was used as a solvent for sol–gel condensation. All the chemicals were obtained from Sigma-Aldrich except for deionized water and used as received without further purification.

**Preparation of mesoporous NiO–silica samples**

Mesoporous nickel–silica samples with high Ni content from Ni/Si = 0.5 to 7.0 were prepared in the presence of a cationic surfactant template CTAB, under basic conditions. In a typical synthesis for MNS51 (i.e. mesoporous nickel–silica with Ni/Si = 5, Table 1), 1.5 g (4.1 mmol) of CTAB was completely dissolved in a mixture of 30.0 mL of deionized water, 45.6 mL of EtOH, and 35.0 mL (0.50 mol) of NH₄OH (28–30%) under vigorous stirring at 298 K for 30 min in a 125 mL glass bottle. Then, 0.50 g (2.23 mmol) of TEOS was added to the solution and it was stirred for another 30 min to form a sol. Next, 3.26 g (11.2 mmol) of Ni(NO₃)₂·6H₂O was added to the ‘sol’ and it was stirred for 24 h more at room temperature, followed by hydrothermal treatment at 373 K for 24 h in a convection oven when the sol was converted to gel. The Ni–silica gel was filtered and washed with deionized water and ethanol. The final solid sample was obtained after calcination at 723 K for 5 h flowing air to remove the surfactant. Analogous synthetic methods were also employed to prepare all the other mesoporous nickel–silica samples used in this study. Nomenclature and chemical components for respective six kinds of mesoporous samples are listed in Table 1.

**Characterization of mesoporous NiO–silica samples**

The weight percentages of Ni in the samples were determined by using an inductively coupled plasma optical emission spectrometer (ICP-AES, JobinYvon Ultima 2C) with the wavelength adjusted to 395.254 nm at the Korea Basic Science Institute (KBSI) Seoul centre. Final data were obtained by averaging data measured by three times.

The wide angle X-ray diffraction (XRD) patterns were obtained using a PANalytical Empyrean multipurpose diffractometer with Cu-Kα radiation (λavg = 1.5418 Å) at 40 K and 30 mA at KBSI Daegu center. The diffraction spectra of powder samples were collected from 10 to 80° of 2θ with a scan rate of 0.04°/s.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Theta Probe AR-XPS System (Thermo Fischer Scientific) using monochromatic Al Kα (1486.6 eV) radiation as X-ray source to KBSI Busan center. The spectra of the samples were calibrated by the binding energy of the adventitious carbon (C 1s) at 284.6 eV. Prior to the measurement, all the samples were degassed in vacuum overnight. The analysis was done under very low pressure of typically less than 10⁻⁶ Pa at room temperature.

Nitrogen adsorption–desorption isotherms were obtained using a Micromeritics 2420 analyzer at 77 K. Before analysis, all the samples were pre-treated at 773 K under a vacuum below 30 µmHg to remove remained gases. The Brunauer–Emmett–Teller (BET) specific surface area (S BET) was calculated from adsorption isotherm data in the range of 0.04–0.2 of relative pressure (P/P0). The total pore volume (Vt) was recorded from the amount adsorbed at a relative pressure of 0.99. The pore size distribution (PSD) curves were obtained from the adsorption branches of the isotherms by using the Kruk–Jaroniec–Sayari (KJS) method [27]. The micropore volume was obtained by t-pplot calculation.

Field emission scanning electron microscopy (FE-SEM) and elemental mapping images for Si and Ni were obtained using a JEOL JSM-4300F microscope equipped with an embedded energy dispersive system (EDS) and operated at an accelerating voltage of 15 kV.

Transmission electron microscopy (TEM) image was acquired using a JEOL JEM-2010 microscope operated at an accelerating voltage of 200 kV. The specimens were prepared by adsorbing sample powder onto a meshed copper grid covered with porous carbon film after 2 h treatment in an ultra-sonicator.

Magnetic properties (M–H hysteresis loops) of the samples were measured at 2, 10, 50, and 300 K using a Quantum Design superconducting quantum interference device magnetometer (Quantum Design SQUID-VSM). SQUID was conducted in a MPMS system between ±10 kOe. ZFC/FC measurements were employed in the temperature range of 2–300 K with an applied field of 100 Oe.

**Results and discussion**

A schematic representation of the fabrication of NiO doped flower-like silica microsphere in CTAB-assisted sol–gel hydrothermal route has been illustrated in Scheme 1. Ammonia alkaline conditions as well as the slow hydrolysis of silica and Ni precursors form a sol in the reaction mixture, which was further condensed to form gel during ageing at room temperature followed by

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**Table 1**

Physicochemical analysis of mesoporous NiO–silica samples prepared in this study.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>fNi/si</th>
<th>S BET (m²/g)</th>
<th>Vt (cm³/g)</th>
<th>V mic (cm³/g)</th>
<th>D 2θ (nm)</th>
<th>wNi ICPS (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNS051</td>
<td>0.5</td>
<td>531</td>
<td>0.6452</td>
<td>0.4954</td>
<td>4.02</td>
<td>32.2</td>
</tr>
<tr>
<td>MNS071</td>
<td>0.7</td>
<td>577</td>
<td>0.5660</td>
<td>0.4561</td>
<td>3.85</td>
<td>37.1</td>
</tr>
<tr>
<td>MNS11</td>
<td>1</td>
<td>530</td>
<td>0.4446</td>
<td>0.3529</td>
<td>3.67</td>
<td>46.5</td>
</tr>
<tr>
<td>MNS31</td>
<td>3</td>
<td>321</td>
<td>0.2863</td>
<td>0.1940</td>
<td>3.52</td>
<td>61.6</td>
</tr>
<tr>
<td>MNS51</td>
<td>5</td>
<td>205</td>
<td>0.2268</td>
<td>0.1138</td>
<td>3.42</td>
<td>71.7</td>
</tr>
<tr>
<td>MNS71</td>
<td>7</td>
<td>169</td>
<td>0.2100</td>
<td>0.0850</td>
<td>3.33</td>
<td>75.7</td>
</tr>
</tbody>
</table>

fNi/si = molar ratio of Ni to silica precursor (Ni/Si) in the synthesis gel; SBET = specific surface area; Vt = total pore volume obtained at P/P0 of 0.99; V micropore volume estimated by t-pplot; D 2θ = pore width calculated at the maximum of PSD using the KJS method; wNi ICPS = weight percentage of Ni in the solid product obtained by ICP-AES analysis.
hydrothermal at 373 K [28]. During the conversion of sol to gel, metal–oxo–Si bond formation facilitates the growth of the material into sheet-like nanosphere [18,28]. Finally, the calcination results in the formation of NiO–silica flower-like microsphere.

The crystalline phase and composition of the calcined Ni-doped silica samples have been identified by wide-angle powder XRD analysis. Representative XRD data of MNS samples are shown in Fig. 1(a)–(d). The samples with lower Ni/Si ratios (0.5 and 1.0) have XRD patterns which show broad peaks of moderate intensity at 2θ values near ~20.8, 35.6, and 61.3°, matching to monoclinic phase nickel hydrosilicate Ni$_2$Si$_2$O$_5$(OH)$_4$. The peaks correspond to the diffraction planes (110), (200) and (060), respectively, according to JCPDS file No. 49-1859 [14]. No peak indicating the presence of NiO is observed in the XRD pattern of MNS051 (Fig. 1(a)), although two extra tiny peaks are observed near 2θ~37.0 and 43.0° in the XRD pattern of MNS11 sample (shown by red arrow in the picture) indicating the appearance of cubic NiO phase, the reason may be due to the higher Ni content in the sample. On the other hand, MNS51 and MNS71 samples, with very high Ni percentage exhibit sharp diffraction peaks at 2θ = 37.2, 43.2, 62.7 and 75.3°, revealing a predominant crystalline phase of NiO (Fig. 1(c) and (d)). The peaks refer to the typical reflection planes (111), (200), (220) and (311), respectively (JCPDS file No. 78-0643), characteristic face centered cubic phase of NiO with lattice parameters a = 4.17 Å [29]. The average crystallite sizes calculated using Scherrer equation (i.e. L = Kλ/βcos θ) for MNS51 and MNS71 samples are 20.1 and 20.5 nm, respectively. So, from the XRD analysis it is evident that, CTAB-ammonia assisted sol–gel synthesis followed by hydrothermal treatment and thermal calcination has resulted in the formation of pure nickel hydrosilicate phase for Ni–silica sample when Ni concentration is low (up to Ni/Si = 1:1) [14]. Whereas, for samples with higher Ni content (MNS51 and MNS71) cubic NiO phase has been formed. The reason is the higher percentage of Ni than silica in the materials, for which NiO phase predominates over nickel hydrosilicate Ni$_2$Si$_2$O$_5$(OH)$_4$ phase.

ICP-AES analysis was carried out to find out the exact percentage of Ni in the silica samples. The result (Table 1) clearly indicates that Ni content increases gradually in the samples and the amount varies from ~32.0 to ~76.0 wt%. Although the amount of Ni is somewhat less than that used in the respective synthesis gel, which is due to the leaching of soluble Ni species from the reaction mixture during the whole synthesis process [3].

Further analysis of the electronic states of the elements present in these MNS samples have been confirmed by X-ray photoelectron spectroscopic (XPS) study. XPS analysis results of Si 2p, O 1s and Ni 2p species for different samples have been shown in Fig. 2(a)–(c). A single peak near binding energy (BE) value ca. 102.9 eV for Si 2p core level electron appeared in all the four MNS samples which is attributed to the presence of O–Si–O in the material (Fig. 2(a)) [14]. Though, a small shifting of the peaks towards lower binding energy is observed in the samples with increasing Ni content, which may be due to the transformation of silicate to SiO$_2$ (nickel hydrosilicate to NiO–SiO$_2$ mixed oxide) [30,31]. For O 1s species of MNS051 and MNS11 materials (Fig. 2(c)–A, B), a broad symmetric signal near ~532.2 eV appeared which is due to the oxygen atom present in the sample as SiO$_2$ [14]. Whereas for other two samples MNS51 and MNS71, O 1s spectrum is consist of two peaks, the peak at 532.1 eV along with the other peak at low binding energy (LBE) near ~530.1 eV, which is indicating the presence of lattice oxygen atom of NiO, formed in case of the MNS samples with higher Ni content.

**Fig. 1.** Wide-angle XRD patterns for MNS051 (a), MNS11 (b), MNS51 (c), and MNS71 (d) samples. The peaks are assigned according to JCPDS file.

**Scheme 1.** A schematic representation of the formation of NiO doped flower-like silica microsphere in CTAB-assisted sol–gel hydrothermal route.
(Fig. 2(c)–C, D) [8]. On the other hand, several small and broad peaks referring in the range of 855–882 eV is observed in XPS data of Ni 2p core level electron of all MNS samples (Fig. 2(b)–A–D). The signals at BE values ca. 857.1, 862.5, 874.0 eV and 881.0 eV correspond to the binding energy of Ni 2p$^{3/2}$ and Ni 2p$^{1/2}$ states, respectively, indicating the spin-orbit doublets with the BE separation of $\sim$18.5 eV [8,14,32]. This type of multiplet splitting pattern is unique for NiO species and agrees well with the results reported in literature [32]. So, from the XRD and XPS analyses, it is confirmed that at low concentration of Ni, although nickel hydrosilicate phase, Ni$_2$Si$_2$O$_7$(OH)$_4$ predominates, [14] but subsequently, as the Ni percentage becomes very high in the sample, the cubic phase NiO has been formed.

To get information about the porosity and surface area of the Ni-doped silica materials $N_2$ adsorption–desorption analysis was carried out [3]. The isotherms for all the samples are shown in Fig. 3 and the corresponding physicochemical data evaluated from the sorption analysis is given in Table 1. The isotherms are following type IV patterns as per IUPAC classification which is typical for mesoporous materials and the hysteresis with capillary condensation steps are located at $P/P_0$ near about 0.41–0.95. Capillary evaporation also took place at the same pressure which is shown by the reversibility of the adsorption and desorption branches [14]. However, the $P/P_0$ range of capillary condensation–evaporation decreases with increasing Ni content. Similarly, the Brunauer–Emmett–Teller (BET) surface area ($S_{BET}$) evaluated in the range of 169–531 m$^2$/g, and the total pore volumes ($V_t$) from 0.216 to 0.645 cm$^3$/g (Table 1) are also decreasing with increasing Ni content, which is attributed to the gradual decrease in ordering of silica mesostructures on incorporation of Ni species [3]. Although, the isotherm patterns are almost identical even for higher Ni loading, which clearly indicate very high stability of the porous silica framework of upon metal loading [33].

Respective pore size distributions (PSD) plots evaluated by using the Kruk–Jaroniec–Sayari (KJS) method are shown in Fig. 4. All MNS samples show narrow pore size distribution and the pore diameters corresponding to the peak maxima ($D_{pk}$) are obtained in the range of 3.33–4.02 nm (Table 1), indicating the presence of
uniform and small sized mesopores in all the samples [27]. So from 
N₂ sorption analysis, it is quite evident that, in spite of high loading 
of Ni (∼75%), the mesoporosity of the Ni-doped silica is retained 
beautifully as well as the pore diameter is also in the range of 
typical mesoporous material.

FESEM images of these MNS samples have been recorded to 
know the morphology and particle size of the material as well as 
the variation of these characteristics on increasing amount of Ni in 
silica. Figs. 5 and 6 are showing FESEM images of four MNS samples 
in different resolutions. MNS051 and MNS11 samples (Fig. 5) have 
3-dimensional (3D) spherical type microparticle with size varying 
from 500 to 800 nm. The high resolution images of these 
microspheres exhibit flower-like pattern of each particle with a 
number of petals throughout the full body. 3D flower-type 
morphology is still retained at higher concentration of Ni as 
observed in case of MNS51 and MNS71 samples (Fig. 6). Although, 
the shape of the microspheres has become rod type rather than 
spherical in nature. This rod-shaped geometry is more prominent 
in MNS71 sample having particle size 600–750 nm. This observation 
clearly reveals that the geometry of NiO-doped silica 
microsphere is highly dependent on the factor viz. Ni percentage 
in the material, though the flower-morphology of the particle is not 
much affected by it. Also, the difference between crystallite size 
around 20 nm and particle size of these NiO–silica samples clearly 
suggest that the materials are polycrystalline in nature [34]. 

The internal nanostructural features of these MNS samples are 
evaluated from the TEM image analysis. TEM images of the Ni-
doped silica microsphere are displayed in Fig. 7, which clearly 
demonstrate the flower-like nature of the samples with thin petals 
outside it as indicated from the high resolution image of the 
material.

The energy-dispersive spectrometry (EDS) mapping of the two 
representative samples MNS51 and MNS51 are shown in Fig. 8. The 
colored images (Fig. 8(a), (b)) of both samples clearly suggest the 
presence of Si, Ni, and O species in the material as well as confirm 
the uniform distribution of each element in the framework 
structure.

The morphology and nanostructures of NiO are highly 
interconnected with the magnetic properties of the materials 
[18,24]. The magnetic data of mesoporous nickel–silica samples 
MNS have been recorded to find interesting properties of the 
materials. Fig. 9(a)–(d) shows the temperature dependent 
magnetization curves (M–T) measured from 2 K to 300 K with 
an applied field of 100 Oe showing the zero-field-cooled (ZFC) 
magnetic curves. The ZFC curves for all the samples have diverged 
at very low temperature, and blocking temperature (Tₜ) of each

![Fig. 5. SEM images for MNS051 (a-1, a-2, a-3) and MNS11 (b-1, b-2, b-3) samples.](image-url)
Fig. 6. SEM images for MNS51 (a-1, a-2, a-3), and MNS71 (b-1, b-2, b-3) samples.

Fig. 7. TEM images for MNS051 (a), MNS11 (b, c), MNS51 (d, e), and MNS71 (f) samples.
samples were 16.7, 18.9, 16.5 and 15.6 K, respectively. Three samples have almost similar $T_B$ values, and it means analogous size distribution of these Ni-silica crystalline microspheres between the samples [18,35]. In previous literatures, flower-like 2.5 μm sized NiO microspheres and 20 nm sized NiO nanoflowers exhibited $T_B$ with 139 K and 75 K, respectively [18,36]. The difference of $T_B$ is derived from inter-particle interactions which cause an increase in the effective anisotropy energy of the magnetic moments [37]. As the size of the NiO become larger, the inter-particle interactions become stronger and $T_B$ shifts to

Fig. 8. EDS mapping for MNS11 (a) and MNS51 (b) samples.
higher temperature in general \[18\]. MNS051, MNS11, MNS51, and MNS71 samples of this study exhibit lower \( T_B \) values near 16–19 K compared with the NiO microspheres and NiO nanoflowers as reported, which can be explained that the incorporated NiO crystalline domains are not only of considerably smaller size (ca. \( \sim 20 \text{ nm} \)), but are also well dispersed surrounded by amorphous silica networks to further lower inter-particle interaction. The result is consistent with TEM data of some of NiO doped nanoparticles with a diameter of less than 20 nm (Fig. 7). Room temperature M-H measurements of these samples (at 300 K) have displayed a closed hysteresis curves without any remanence and coercive force (Fig. 10(a)–(d)). In case of M-H curve at 50 K, a closed hysteresis was also observed (Fig. 10(a)). The graphs indicate that the samples exhibit paramagnetic properties at the temperature,
because thermal energy is enough to hinder magnetic ordering [38]. Although NiO is an antiferromagnetic material, superparamagnetic properties of our samples may be derived from the presence of Ni^{2+} impurities or non-stoichiometric ratio of Ni/O species [18,39]. Opened hysteresis was shown under \( T_{\text{c}} \) (2 K) in all samples (Fig. 10(b)). Thermal fluctuation was suppressed effectively and typical ferromagnetic behavior was detected at all samples [38]. The saturation magnetization and coercive field at 2 K for MNS051, MNS11, MNS51, and MNS71 are 38, 37, 11, and 14.5 emu/g, 5.4, 2.6, 4.3, and 10.1 kOe, respectively.

Conclusions

In brief, one-pot soft-template mediated hydrothermal route has been employed for synthesis of NiO–silica materials with high Ni content up to 76 wt\%. Water–ethanol mixed solvent media, sol-gel reaction at high pH (using NH\(_4\)OH) followed by heat treatment facilitates the formation of flower-like 3D spherical and rod shaped microspheres which has been confirmed from FESEM study of the material. Template removal by calcinations consequences the development of pure nickel hydroxylate phase (sample with lower Ni content) and pure NiO cubic phase (sample with higher Ni content) having small mesopores which have been established by powder X-ray analysis and \( N_2 \) sorption study, respectively. ICP-AES elemental detection demonstrated a large amount of Ni incorporation in the sample and uniform distribution of Ni as well as Si species is confirmed by EDS elemental mapping. The magnetic measurement of these samples reveals the superparamagnetic behavior of the flower-like microspheres which are visible at low temperature. So, the novelty of the present work is the facile and low cost synthesis method for NiO-doped silica flower-like porous 3D microsphere with very high Ni content using easily available chemicals. Hence, based on this technique, other metal doped silica microspheres can also be prepared in future for potential bio-applications.

Acknowledgments

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