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Synthesis, characterization and optical band gap of NiO nanoparticles derived from anthranilic acid precursors via a thermal decomposition route

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1. Introduction

Nanometer-sized particles have attracted extensive research interest, mainly due to their size-dependent properties and great potential for many applications such as non-linear optics, photo-electrochemical cells, heterogeneous photo-catalysis, optical switching and single electron transistors [1–7]. The morphology of the particles, either spherical, rod, tetra-pod or hexagonal-shaped, will have an effect on the properties and also influence the self-assembly process [8–13]. The use of single-molecule precursors in which a metal-chalcogenide bond is available has proven to be a very efficient route to high-quality nanoparticles [14–16]. One of the advantages of this technique is the shape control of the nanoparticles through variation of the experimental conditions. The thermal decomposition approach to inorganic precursors is considered a very important method in preparing metal oxides nanoparticles [17,18].

Nanostructured NiO has a wide range of applications as a p-type semiconductor with a stable wide band gap (3.6–4.0 eV) [19], although bulk NiO is an antiferromagnetic insulator [20]. Nanosized NiO is also used in alkaline batteries [21], electrochemical capacitors [22], smart windows [23] and as an active layer for gas sensors [24].

High surface area metal oxides with a size of 1–100 nm are desirable absorbents, carriers and catalysts. The catalytic activity of NiO nanoparticles in pyrolyzing biomass components are attrib-

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ABSTRACT

This study focuses on the preparation and characterization of single phase NiO nano particles. Four nickel anthranilic acid complexes were synthesized by the semi-solid phase reaction method as precursors for the preparation of NiO nanoparticles via a solid-state decomposition procedure at 700 °C. Thermogravimetric analysis (TGA) was applied to determine the thermal behavior of the precursors and the temperature at which the precursors decompose leaving the oxide. The crystalline structures of the products were investigated by X-ray diffraction (XRD), the morphology of particles by SEM and TEM. The particles size was determined by STM, and the average particle size was found to be 8 nm. Electronic spectra were used to clarify qualitatively the change in absorption band positions on changing the particle size of NiO. The optical band gap of the NiO nanoparticles increase as the particle size decreases.

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uted to the different effects in terms of volume, quantum size, surface and macroscopic quantum tunnel. NiO nanoparticles contain many important properties over those of bulk and micro-NiO particles [25]. Niasari et al. have prepared NiO nanoparticles from nickel phthalate complexes using a solid-state thermal decomposition route. They studied the effect of calcination temperature on the particle size, which is found to be 29 nm [26].

In this work we prepared NiO nanoparticles with an average particle size of 8 nm from nickel anthranilic acid semi-solid complexes by solid-state decomposition. We aimed to clarify the effect of changing the metal anion and metal to ligand ratio on the crystal lattice and the particle size of NiO.

There are many advantages in this work as it uses a green chemistry solvent technique, is a simple method, saves time, uses cheap available chemicals, has crystalline products and provides smaller nanoparticles of NiO.

2. Experimental

All the chemicals used were of analytical grade and used without further purification.

2.1. Technique

Carbon and hydrogen contents were determined at the Microanalytical Unit of Mansoura University. The metal analyses were carried out by standard methods [27]. Infrared spectra were measured using KBr discs on a Mattson 5000 FTIR spectrometer. Calibration with the frequency reading was made with polystyrene



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film. Electronic spectra were recorded on UV2 Unicam UV–Vis spectrometer using 1 cm Stoppard silica cells. Thermal analysis measurements (TGA and DTG) were recorded on a Schimadzu model 50 instrument using 20 mg samples. The nitrogen flow rate and heating were 20 cm³/min and 10 °C/min, respectively. XRD patterns were recorded using Philips X'PERT-PRO materials research diffractometer. Scanning electron microscopy and scanning tunneling microscopy (SEM and STM) images of the products were obtained with a JEOL electron microscope, JEM-1230, Japan. Transmission electron microscope (TEM) images of the products were obtained with a JEOL JEM-1200EXII electron microscope.

2.2. Synthesis of the precursors

1:1 and 1:2 M ratios of the hydrated nickel acetate and/or chloride with anthranilic acid ($C_7H_7NO_2$) were mixed and ground in 5 ml distilled water. The mixture was ground for 20 min in a mortar. The resultant semi-solid mixture was dried at 100 °C for 2 h, whereupon a green powder was obtained for all four metal complexes.

Anal. Calc. for [Ni(Anth)Ac·2H₂O] (1): NiC₉H₁₃NO₆: C, 37.27; H, 4.48; N, 4.83; Ni, 20.26. Found: C, 37.40; H, 4.10; N, 5.10; Ni, 20.50%. *Anal.* Calc. for [Ni(Anth)₂·2H₂O] (2): Ni(C₇H₈NO₃)₂: C, 45.81; H, 4.36; N, 7.63; Ni, 16.0. Found: C, 45.72; H, 4.40; N, 8.0; Ni, 16.40%. *Anal.* Calc. for [Ni(Anth)Cl₂·2H₂O]4H₂O (3): NiC₇H₁₇. NO₈Cl₂: C, 22.40; H, 4.53; N, 3.73; Ni, 15.7; Cl, 18.94. Found: C, 22.60; H, 4.90; N, 4.0; Ni, 16.0; Cl, 19.20%. *Anal.* Calc. for [Ni(Anth)₂·2H₂O]Cl₂ (4): Ni(C₇H₉NO₃Cl₂: C, 38.20; H, 4.10; N, 6.63; Ni, 13.4; Cl, 16.14. Found: C, 38.40; H, 3.80; N, 6.30; Ni, 13.80; Cl, 16.50%. Scheme 1 represents the formation of the precursors and NiO nanoparticles.

2.3. Synthesis of NiO nanoparticles

The as-prepared Ni–anthranilic acid complexes were ignited in a muffle furnace at a rate of 50 $^{\circ}$ C/min in air. NiO nanoparticles were synthesized at 700 $^{\circ}$ C.

3. Results and discussion

The most important infrared bands of anthranilic acid and its nickel complexes are collected in Table 1. The IR spectrum of anthranilic acid shows several bands in the region 2564-2709 cm⁻¹, indicating its presence in the zwitter ionic form. The spectrum also shows bands at 1664, 1630 and 1459 cm⁻¹ assigned to $v_{as}(COO^{-})$, $\delta(NH_{3}^{+})$ and $v_{s}(COO^{-})$, respectively [28]. The spectra of all the precursors (Fig. 1) show bands in the region 1685-1693 cm⁻¹, assigned to $v_{as}(COO^{-})$ of a coordinated carboxyl group [28]. This band is shifted to higher wavenumbers in comparison with its position in the free ligand. The spectra also show two bands in the regions 3122–3144 and 3305–3314 cm⁻¹, assigned to $v(NH_2)$. These bands are shifted to lower wavenumbers compared with the position for anthranilic acid, indicating the participation of the amino nitrogen in bonding. The difference between $v_{as}(COO^{-})$ and $v_{s}(COO^{-})$ of all the precursors (Table 1) is greater than 200 cm⁻¹, indicating that the carboxyl group is coordinated in a monodentate manner [28,29]. A shoulder band is observed at 1643 cm^{-1} in the spectrum of precursor (1), which may be assigned to $v_{as}(COO^{-})$ of the acetate group. The spectra of precursors (3) and (4) show bands in the regions 3459-3488 and 1356-1360 cm⁻¹, which could be assigned to v(OH) and $\delta(OH)$ of an unionized carboxyl group, respectively. The IR spectrum of the NiO nanoparticles shows a band at 430 cm⁻¹, characteristic of NiO



Scheme 1. Formation of precursors and NiO nanoparticles.

Table 1

Some IR spectral bands of anthranilic acid (Anth) and its nickel complexes.

Precursors	$v(NH_2)$	$\delta(\mathrm{NH}_2)$	$v_{as}(COO)$	<i>v</i> _s (COO)	v(M-N)	v(M-O)
Anthranilic acid [Ni(Anth)Ac·2H ₂ O] (1) [Ni(Anth) ₂ ·2H ₂ O] (2) [Ni(Anth) _{Cl₂} ·2H ₂ O] (4) ₂ O (3) [Ni(Anth) _{Cl₂} ·2H ₂ O] (4) ₂ O (3)	3324s,3239s 3124m,3305s 3122s,3305s 3144m,3311s	1630m 1615sh 1614sh 1617sh	1664m 1685sh 1693w 1683sh	1483m 1456m 1457m 1463m	470w 467w 490w	411w 418w 420w



Fig. 1. IR spectra of: (a) NiO, (b) [Ni(Anth)Ac·2H₂O] (1), (c) [Ni(Anth)₂·2H₂O] (2), (d) [Ni(Anth)Cl₂·2H₂O]4H₂O (3), (e) [Ni(Anth)₂·2H₂O]Cl₂ (4).

[26]. Also, the spectrum of NiO shows the disappearance of any bands assigned to the organic moiety, indicating the complete decomposition of the precursor at 700 $^{\circ}$ C.

From the above findings it could be concluded that anthranilic acid binds to Ni in a mono-negative bidentate manner through the carboxylate oxygen, after deprotonation, and the amino nitrogen in the case of precursors (1) and (2). While in precursors (3) and (4) it acts as a neutral bidentate ligand, coordinating to Ni through the carboxyl group in the protonated form and the amino nitrogen. The molar conductivities values in DMF (10^{-3} M) at 25 °C are 5.0, 7.0, 10 and 90 Ω^{-1} cm² mol⁻¹ for precursors (1), (2), (3) and (4), respectively. These values suggest that precursors (1), (2) and (3) are non-electrolytic, while precursor (4) has a 1:2 electrolytic nature [30]. Precursor (3) reacts with AgNO₃ in HNO₃ solution, and this fact is taken as evidence that the chloride ions are bonded to nickel in the complex.

The magnetic moment values of all the precursors lie in the range 3.20–3.30 B.M. Also, the electronic spectra of all the precursors in nujol show two bands around 14 000 and 24 000 cm⁻¹, assigned to ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g} (\nu_2)$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P) (\nu_3)$ transitions, respectively. These findings suggest the presence of a six coordinated Ni(II) center [31,32].

3.1. Thermal analyses

The results of thermogravimetric analyses of the precursors (2) and (3) are given in Figs. 2 and 3. The TGA curves serve as a guide in deciding the calcination temperature for the precursors. The thermal analyses (TGA and DTG) curves of the complexes were carried out within a temperature range from room temperature up to 800 °C. The estimated mass loss was computed based on the TGA results and the calculated mass loss is computed using the results of the microanalyses (Table 2). The thermograms indicate that precursors (1), (2) and (4) are stable up to 200 °C. Precursor (3) loses four molecules of water of hydration in the temperature range 25–103 °C, indicating that it has not been dried enough. All the precursors lose coordinated water, followed by acetate or chloride,





then the anthranilic acid decomposes. Precursor (**2**) decomposes completely at 400 °C, while the others completely decompose at *ca* 600 °C, leaving NiO as a residue. From the above findings, the calcination temperature was chosen to be 700 °C for preparing NiO nanoparticles. It is expected that calcination of precursor (**2**) at a lower temperature of *ca* 400 °C may lead to a smaller particle size of the NiO nanoparticles. As precursor (**2**) was calcined above the decomposition temperature, there should be sudden decomposition of the precursor leading to rapid nucleation and growth of the crystals [14,26].

3.2. XRD and electron microscope (SEM, STM and TEM) patterns

Fig 4 shows the XRD pattern of NiO derived from precursors (1)-(4) after calcination at 700 °C. The crystallite size of NiO was



Fig. 3. TGA of [Ni(Anth)Cl₂·2H₂O]4H₂O (3).

 Table 2

 Thermo analytical results (TG) of precursors (1), (2), (3) and (4).

Precursor	T range (°C)	Mass loss estim. (Calcd %)	Assignment of fragment lost
$[Ni(Anth)Ac\cdot 2H_2O] (1)$	355– 470	47.5 (47.9)	$2H_2O$, CO, NH_2 and Ac
	471– 621	31.3 (32.1)	Anthranilic acid without CO and NH ₃
$[Ni(Anth)_2 \cdot 2H_2O] (2)$	200- 360	9.8 (9.2)	2H ₂ O
	361– 400	71.0 (70.5)	2 Anthranilic acid without one O
$[Ni(Anth)Cl_2 \cdot 2H_2O]4H_2O$ (3)	24– 103	20.0 (19.2)	4H ₂ O of hydration
	104– 391	18.1 (18.9)	Cl ₂
	392– 560	37.4 (38.4)	Anthranilic acid
$[Ni(Anth)_2 \cdot 2H_2O]Cl_2~(\textbf{4})$	210– 470	55.0 (55.5)	$2H_2O$, 1 anthranilic acid and Cl_2
	471- 570	31.0 (31.15)	1 Anthranilic acid

calculated from the major diffraction peak of NiO using Debye-Scherrer formula $D = 0.89\lambda/\beta \cos \theta$ [33], where λ is the wavelength of the X-rays (1.5406 Å for Cu K α radiation), β is the full width at half maximum and θ is the peak position. The estimated particle size was found to be 25, 20, 19 and 17 for samples of NiO which resulted from the ignition of the precursors (1), (2), (3) and (4), respectively. All the peaks are well indexed to a rhombohedral lattice for NiO obtained from precursors (1), (2) and (4). The bunsenite syn lattice is well indexed for NiO obtained from precursor (3). This variation in lattice of NiO may result from the effect of the anion, where in the case of NiO derived from precursors (1), (2) and (4) the suggested active sites which coordinate to Ni are O and N of the anthranilic acid only, while in the case of precursor (**3**), the active sites are O, N of the anthranilic acid and Cl donors. Precursors prepared from a 1:2 Ni:anthranilic acid ratio provide a good coating of the central Ni atom. So, a smaller particle size of NiO was obtained after the removal of the organic moieties by calcination.

The SEM image (Fig. 5) shows the NiO nanoparticles are spherical in shape. The STM image (Fig. 6) shows the average diameter of the spherical NiO nanoparticles is 8 nm. This value is relatively smaller than that calculated from XRD data. In Table 3, the size of the NiO nanoparticle is compared with results of several previous reports. According to these results, it is clear that the NiO obtained from [Ni(Anth)₂·2H₂O]Cl₂ is the smallest in size, compared to the other precursors [26,34,35]. The TEM image (Fig. 7) indicates that uniform spherical particles were prepared from [Ni(Anth)₂·2H₂O].

3.3. Electronic spectra and optical band gap

The variation of absorbance of NiO nanoparticles resulting from precursors (1), (2), (3) and (4) with wavelength is shown in (Fig. 8). The absorption edges are seen to be shifted slightly towards lower wavenumber (blue shift). This shift indicates an increase in the band gap, which can be attributed to a decrease in particle size [36].

The optical band gap was estimated using Tuac's equations [37,38]: $\alpha hv = A(hy - E_g)^n$, where *n* is equal to 1/2 and 2 for direct and indirect transitions respectively, α is the absorption coefficient. *A* is an energy independent constant. The plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ versus *hv* have been produced, from which a direct band gap was



 $\label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (1), (b) [Ni(Anth)_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)_2·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (2), (b) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)Ac·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (2), (b) [Ni(Anth)Cl_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·2H_2O] 4H_2O (3), and (d) [Ni(Anth)Ac·2H_2O] Cl_2 (4). \\ \label{eq:Fig. 4. XRD patterns of: (a) [Ni(Anth)Ac·2H_2O] (2), (b) [Ni(Anth)Cl_2·2H_2O] (2), (c) [Ni(Anth)Cl_2·$



Fig. 5. SEM image of NiO derived from precursor (2).



Fig. 6. STM image of NiO derived from precursor (2).

Table 3Comparison of NiO particle size using different methods.

Precursor	Method	Calcination temp. (°C)	Calcination time (h)	Particle size ^a
Nickel citrate [34]	ultrasonic spray pyrolysis	700	2	54
Nickel dimethylglyoximate [35]	thermal decomposition	700	2	70
Nickel phthalate [Ni(pht)2] [26]	solid-state decomposition	700	2	29
Nickel anthranalate [Ni(Anth) ₂ ·2H ₂ O]Cl ₂	solid-state decomposition	700	2	17

^a According to XRD.



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Fig. 8. Absorption spectra of NiO nanoparticles A1 = NiO derived from precursor (1), A2 = NiO derived from precursor (2), A3 = NiO derived from precursor (3), and A4 = NiO derived from precursor (4).

found (Fig. 9) by extrapolating the linear portion of the curve to $(\alpha h v)^{1/2} = 0$. The curves indicate that the values of the direct band gap (E_g) are equal to 2.45, 2.82, 2.93 and 3.12 eV for NiO derived from precursors (1), (2), (3) and (4), respectively. The band gap values suggest that NiO nanoparticles are semi-conductors. Also, these values of (E_g) are in the same range as that of highly efficient photovoltaic materials. So, the present compounds could be considered as potential materials for harvesting solar radiation in solar cell applications [39].



Fig. 9. Optical band gap of NiO nanoparticles A1 = NiO derived from precursor (1), A2 = NiO derived from precursor (2), A3 = NiO derived from precursor (3), and A4 = NiO derived from precursor (4).

4. Conclusion

Metal complexes derived from anthranilic acid have been used as new precursors for synthesizing NiO nanoparticles. The NiO nanoparticles are spherical with a nanosize range from 17 to 25 nm, as deduced from the results of XRD data. The particle size and the crystal form of NiO are affected by the anion of the nickel salts and the ratio of Ni to anthranilic acid. The solid-state decomposition method provides a simple method of obtaining nanoparticles. Also, a green chemistry solvent technique and smaller particles of NiO have been obtained in this study.

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