



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: [www.elsevier.com/locate/cattod](http://www.elsevier.com/locate/cattod)



## Deep eutectic solvent approach towards nickel/nickel nitride nanocomposites

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### ARTICLE INFO

#### Article history:

Received 3 October 2016  
Received in revised form 2 December 2016  
Accepted 8 December 2016  
Available online xxx

#### Keywords:

Nickel nitride  
Nickel  
Deep eutectic solvents  
X-ray photoelectron spectroscopy  
Nitrogen-doped carbon supports  
Nanocomposites

### ABSTRACT

Nickel nitride is an attractive material for a broad range of applications including catalysis. However preparations and especially those targeting nanoscale particles remain a major challenge. Herein, we report a wet-chemical approach to produce nickel/nickel nitride nanocomposites using deep eutectic solvents. A choline chloride/urea deep eutectic solvent was used as a reaction medium to form gels containing nickel acetate tetrahydrate. Heat treatment of the gel in inert atmosphere forms nanoparticles embedded within a nitrogen-doped carbon matrix. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to understand the decomposition profile of the precursors and to select pyrolysis temperatures located in regions of thermal stability. X-ray diffraction (XRD) confirmed the presence of metallic nickel, whereas X-ray photoelectron spectroscopy (XPS) suggested the existence of a nickel nitride surface layer. According to transmission electron microscopy (TEM) analysis these mixed phase, possibly core-shell type nanoparticles, have very defined facets. These materials represent a unique opportunity to tune catalytic properties of nickel-based catalysts through control of their composition, surface structure, and morphology; in addition to employing potential benefits of a nitrogen-doped carbon support.

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### 1. Introduction

Nickel-based catalysts are recognized as viable earth-abundant substitutes to expensive and rare noble metal catalysts [1]. Nickel nitride ( $\text{Ni}_3\text{N}$ ) has gained particular interest due to unique bulk and surface properties. The presence of nitrogen in the  $\text{Ni}_3\text{N}$  structure results in a larger amount of electron density being located at the surface of the material, causing  $\text{Ni}_3\text{N}$  to be more electron-rich than metallic nickel (Ni) [2]. However,  $\text{Ni}_3\text{N}$  is a metastable interstitial metal nitride and is reported to degrade at temperatures ranging from 287 to 440 °C [1]. In the presence of reactive gases such as carbon monoxide, nitric oxide, and hydrogen, this degradation occurs at much lower temperatures [3,4]. The degradation of  $\text{Ni}_3\text{N}$  results in the evolution of molecular nitrogen out of the structure, creating voids in the crystal lattice where nitrogen was previously present [5]. Physically this corresponds to the growth of a cubic nickel phase in  $\text{Ni}_3\text{N}$ , creating a biphasic Ni/ $\text{Ni}_3\text{N}$  composite

material. These Ni/ $\text{Ni}_3\text{N}$  composites often display material properties that bridge both Ni and  $\text{Ni}_3\text{N}$ . In fact, the ability to control the ratio of Ni/ $\text{Ni}_3\text{N}$  enables the creation of catalysts with tuned physical, chemical, and electronic properties. As such, Ni and  $\text{Ni}_3\text{N}$  nanostructures have been used as catalysts in a variety of energy related applications including the hydrogen and oxygen evolution reactions [6,7], hydrogenation reactions [8,9], lithium and sodium ion batteries [10–13], supercapacitors [14], dye-sensitized solar cells [15,16], and microwave absorbing materials [17].

While the production of thin-film  $\text{Ni}_3\text{N}$  through ion-based [18–20] and deposition techniques [21–23] is well understood, the synthesis of nanoscale  $\text{Ni}_3\text{N}$  particles has historically been elusive. Many traditional chemical methods include high temperature decomposition of nickel salt precursors in the presence of supercritical ammonia [24], highly reactive azides, or hydrazine [25]. However in recent years, derivatives of sol-gel chemistry have emerged as popular methods to produce nanoscale  $\text{Ni}_3\text{N}$  and Ni/ $\text{Ni}_3\text{N}$  catalysts. This is in part due to the ease and low cost associated with synthesis and the use of green procedures that do not require hazardous reagents or extreme reaction conditions [1].

For example the urea-glass method, which has been demonstrated to be an effective synthetic method to produce a wide range of early transition metal carbides and nitrides [26,27], has

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recently been extended to Ni<sub>3</sub>N and Ni/Ni<sub>3</sub>N nanocomposites. The pyrolysis of an ethanolic solution of nickel acetate tetrahydrate and urea forms carbon-encapsulated Ni<sub>3</sub>N nanoparticles [8]. In this particular case, both a specific molar ratio of metal:urea and precise control of pyrolysis temperature are required to successfully form the Ni<sub>3</sub>N phase. Increasing the pyrolysis temperature above 350 °C introduces a Ni phase into the product and leads to growth of nanoparticle size. Another intriguing technique is the use of high temperature nickel-containing eutectic salt solutions. By carefully tuning the mixture of the eutectic salt and nickel precursor, along with pyrolysis temperature, both Ni<sub>3</sub>N and Ni/Ni<sub>3</sub>N “sponges” can be obtained [9]. However, the high melting point of the eutectic salt mixture necessitates pyrolysis temperatures above 600 °C. As a result, these Ni/Ni<sub>3</sub>N composite materials are large bulk-like structures with a high porosity. Nevertheless, both techniques involve the formation of nitrogen-rich, nickel-containing gels; whereupon precise thermal degradation form the desired Ni<sub>3</sub>N or Ni/Ni<sub>3</sub>N phase.

Deep eutectic solvents (DES's) are yet another promising reaction medium for metal nanoparticle synthesis. DES's are a type of ionic liquid (IL), typically composed of quaternary ammonium salts and a metal salt or hydrogen bond donor. The charge delocalization between the halide ion and the hydrogen donor is responsible for the drop in melting point temperature [28]. Generally, DES's form viscous liquids at temperatures below 100 °C. Due to their low cost, low toxicity, and biodegradability [29]; DES's have grown in popularity as green solvent systems for metal processing [30]. Moreover, DES's have demonstrated the ability to act as templating agents for porous structures [31] and promoters of faceted nanoparticles [32,33]. The unifying advantage of the DES's is the gel-like consistency, which can be synthesized in large scale quantities and processed to produce a multitude of catalytic materials.

Herein we report the use of a DES, composed of choline chloride and urea, for the synthesis of faceted Ni/Ni<sub>3</sub>N nanostructures. This particular DES forms a liquid at room temperature when prepared at a 1:2 molar ratio of choline chloride:urea [30]. By adding nickel acetate tetrahydrate (Ni(Ac)<sub>2</sub>) to this DES, followed by pyrolysis at 320–600 °C, we observe the formation of faceted Ni/Ni<sub>3</sub>N nanocomposites comprised of a bulk metallic Ni and a surface layer of Ni<sub>3</sub>N. These faceted nanoparticles are stabilized by a nitrogen-doped carbon matrix, which is formed during synthesis. The relative amount of Ni to Ni<sub>3</sub>N, along with the degree of nitrogen incorporation into the carbon matrix, is dependent on the pyrolysis temperature. We report a scalable, wet-chemical route to produce supported Ni/Ni<sub>3</sub>N nanocomposites with varying composition and morphology. As such the physical, chemical, and electronic properties of these supported nanocomposites can be tuned to target specific catalytic applications.

## 2. Experimental

### 2.1. Preparation of Ni/Ni<sub>3</sub>N nanocomposite

A deep eutectic solvent of choline chloride and urea (molar ratio = 1:2) was first prepared in a 20 mL scintillation vial. The contents were stirred and heated to approximately 50 °C on a hot/stir plate. Once the clear viscous liquid had formed, an amount of nickel acetate tetrahydrate was added in order to yield a 0.5:1.0:2.0 molar ratio of Ni(Ac)<sub>2</sub>:choline chloride:urea. The deep eutectic solvent/nickel acetate tetrahydrate (DES/Ni(Ac)<sub>2</sub>) gels were stirred until the nickel acetate tetrahydrate was dispersed in the DES.

The gels were heated at 5 °C/min to the target temperature and then held for 4 h under a continuously flowing N<sub>2</sub> atmosphere at 200 mL/min. The product after pyrolysis is a black solid which could be ground into a fine powder for characterization and/or catalytic

testing. In addition, the synthesis can be easily scaled to generate large amounts of product. Pyrolysis temperatures, ranging from 320 °C to 600 °C, were probed in order to vary the properties of the resulting Ni/Ni<sub>3</sub>N nanocomposite.

### 2.2. Characterization

#### 2.2.1. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

TGA/DTA were measured using a Setaram Setsys Evolution, simultaneous TGA/DTA/DSC instrument. The sample chamber was purged with nitrogen at 200 mL/min and heated at 5 °C/min from room temperature to 800 °C under a constant nitrogen flow of 40 mL/min.

#### 2.2.2. Brunauer-Emmett-Teller (BET) surface area analysis

Specific surface area and nitrogen adsorption-desorption were determined using an ASAP 2020 surface area and porosity analyzer (Micromeritics) via the Brunauer-Emmett-Teller (BET) method. A gaseous mixture of nitrogen and helium was allowed to flow through the analyzer at a constant rate of 30 mL/min. Nitrogen gas was used to calibrate the analyzer and also used as the adsorbate at liquid nitrogen temperature. The samples were thoroughly outgassed for 2 h at 473 K, prior to exposure to the adsorbent gas.

#### 2.2.3. Transmission electron microscopy (TEM)

A small amount of the nanocomposite powders were sonicated in methanol and drop-cast onto holey carbon supported on copper TEM grids. Bright field images were acquired at 200 kV using a Phillips CM 200.

#### 2.2.4. X-ray diffraction (XRD)

The nanocomposite powders were finely ground using a mortar and pestle. The samples were pressed into the cavity of a zero background XRD plate. The plate was loaded into a PANalytical PW3040 X-ray Diffractometer. The diffractograms were acquired using a Cu K $\alpha$  source, with 45 kV accelerating voltage and 40 mA of current. The scanning ranged from 10 to 150° 2 $\theta$  with a step size of 0.083° and a scan speed of 3.175 s/step.

#### 2.2.5. X-ray photoelectron spectroscopy (XPS)

The samples were prepared for XPS analysis by pressing the catalyst powders onto double-sided tape on a multi-sample plate. XPS analysis was performed on a Kratos Nova spectrometer. X-rays were supplied by a monochromatic Al K source operated at 300 W. High-resolution spectra were collected for carbon (C 1s), oxygen (O 1s), nitrogen (N 1s), and nickel (Ni 2p) at an analyzer pass energy of 20 eV. Data analysis was performed using CasaXPS software. A linear background was applied to C 1s, O 1s, and N 1s. A Shirley background was applied to the Ni 2p spectra. The spectra were calibrated by setting the C 1s peak maximum to 284.8 eV, which is in accordance with XPS studies of nickel compounds in the literature [34,35].

## 3. Results and discussion

### 3.1. Thermal degradation on DES/Ni(Ac)<sub>2</sub> gels

After preparation of a 0.5:1.0:2.0 Ni(Ac)<sub>2</sub>:choline chloride:urea gel, the thermal properties of the DES/Ni(Ac)<sub>2</sub> precursor were measured using TGA/DTA. Fig. 1 shows the wt% loss of the gel from room temperature to 800 °C under a continuous nitrogen flow. At temperatures 320 °C, 425 °C, and 600 °C, plateaus in the wt% loss were observed. These plateaus represent phase changes occurring during the thermal degradation of the DES/Ni(Ac)<sub>2</sub> gel. The thermal decomposition of carbon/nitrogen-rich gels in the presence

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