Full Length Article

# Multiple functionalities of Ni nanoparticles embedded in carboxymethyl guar gum polymer: catalytic activity and superparamagnetism

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### A B S T R A C T

Composites comprising of metallic nanoparticles in polymer matrices have allured significant importance due to multifunctionalities. Here a simple protocol has been described to embed Ni nanoparticles in carboxymethyl guar gum (CMGG) polymer. The composite formation helps in the stabilization of Ni nanoparticles which are otherwise prone towards aerial oxidation. Further the nanoparticles retain their superparamagnetic nature and catalytic capacity. Ni-Polymer composite catalyses the reduction of 4-Nitrophenol to 4-Aminophenol very efficiently in presence of $NaBH_4$, attaining a complete conversion under some experimental conditions. Ni-Polymer composite is well characterized using UV–vis spectroscopy, FTIR, XPS, powder XRD, TGA, SEM and TEM. A detailed magnetic measurement using superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM) reveals superparamagnetic behaviour of the composite.

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## 1. Introduction

In the area of nanotechnology, polymer matrix based nanocomposites [1,2] have generated symbolic amount of attention in contemporary research. Composites/hybrids obtained by adding small amount of metal nanoparticles in polymer matrix, can achieve useful property enhancement for potential applications. In particular, the composites are found to possess improved physical and mechanical properties (e.g. stiffness, strength) due to inclusion of metal nanoparticles without sacrificing lightweight nature of polymer matrices. Use of such composites in the field of catalysis [3], thermal stability [4], mechanical resistance [5], electrical conductivity [6], increased flame retardancy [7] and decreased vapour permeability has attracted researchers to develop them with variable compositions. They are proved to be valuable for even more sophisticated use like hydrogen storage [8] or other energy storage [9], in chemical sensing [10], aerospace and electronic industries. Among assorted metal nanoparticles, magnetic nanoparticles are

particularly noticeable: nontoxicity and biocompatibility of the polymer matrix in conjugation with superparamagnetic behaviour of the magnetic fillers, extends the applications in fields like cell separation and protein separation [11], MRI (magnetic resonance imaging) contrast agents [12], drug delivery [13], catalysis and bio sensors [14]. Thus several routes have been exploited to synthesize various metal-polymer composites where incorporation of nano sized metal particles is favoured over micron size particles. E.g. (i) Direct mixing of nanoparticles in the polymer [15] (ii) Sol-gel methods [16] (iii) in-situ techniques [17] and (iv) deposition method [18] are few to mention here from vast literature available currently. Being a simple physical mixing technique, the first method has inherent defects of agglomeration. The next one needs quite a high temperature which sometimes upsets the polymer matrix and this process may end up with more defects and phase composition. In-situ synthesis cannot rule out independent nucleation of polymer and metal nanoparticles which can be improved to a great extent by the last route. Here direct incorporation of metal-precursor solution on the activated polymer matrix followed by reduction to form suitable metal nanoparticles can overcome drawback as discussed earlier.

In the present work, we have developed Ni-Polymer composites where Ni nanoparticles are synthesized on carboxymethyl guar gum (CMGG) polymer. In fact among several candidates including natural polymers and their derivatives, guar gum (GG) [19,20] isolated from the seed endosperm of the guar plant [19], is of high molecular weight, water-soluble non-ionic natural polysaccharide, versatile biopolymer and it is one of the promising materials for microbial degradation [21]. The modified guar gum possesses remarkable rheological properties [22], high food quality [23] and finds applications in catalysis [24], cartridge explosives, mining, froth flotation, oil recovery, textile printing and biology [25]. Carboxymethyl guar gum (CMGG) [26], a guar gum derivatives, is useful in pharmaceutical industry as binder, disintegrators, potential carriers for targeted oral drug delivery [27] and transdermal release of delivering diclofenac sodium [28]. In this present work, Ni-Polymer composite is investigated for its catalytic property and retention of magnetism within the composite. A well-defined simple model reaction followed by Pal and co-workers [29] i.e. a catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in presence of sodium borohydride is chosen because of its easy monitoring and reduction of nitro compounds to amino compounds is industrially cardinal. Being a manufacturer of paracetamol, phenacetin like analgesic and antipyretic drugs [29,30], *p*-Aminophenol also has great commercial importance. It also has a gigantic use as a photographic developer (under trade names activol and azol and in chemical dye industries), corrosion inhibitor, anticorrosion-lubricant and hair-dyeing agent [31,32]. It is important to note that catalytic conversion by $NaBH_4$ is highly effective in presence of catalysts [33,34] (like metallic Ni, Co nanoparticles etc) for abolishing the kinetic barrier of the reaction by supporting electron relay for the reduction [35].

## 2. Experimental section

### 2.1. Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), Oleic acid (9-octadecenoic acid, mentioned as OA throughout the paper) and polymer were purchased from Merk, SRL. 4-Nitrophenol (4-NP) and sodium borohydride ($NaBH_4$) were obtained from Sigma-Aldrich and were utilized as received without further purifications.

### 2.2. Synthesis of Ni-Polymer composites

In a typical experiment, 10 mL aqueous solution of $1 \times 10^{-2}$ M nickel nitrate, 5 mL methanolic solution of $1 \times 10^{-2}$ M oleic acid were taken in total volume of 100 mL aqueous solution. To this solution 0.15 g of CMGG polymer was added and this was designated as Sample-1. The solution turned black immediately after the addition of 0.025 g of sodium borohydride, due to reduction of $Ni^{2+}$ to $Ni^0$. To ensure the complete reduction the solution was kept at ambient conditions for 30 min. Then the synthesized product was separated as pellet by repetitive centrifugation at 8000 rpm for 20 min. After centrifugation, the black coloured pellet of Sample-1 was dried thoroughly for further characterizations.

Sample-2 was prepared following similar steps like Sample-1, but by adding $Ni(NO_3)_2$ solution in four consecutive batches. After addition of first batch of $Ni(NO_3)_2$ solution, it was reduced by $NaBH_4$ to generate Ni nanoparticles. After centrifugation, the filtrate was found to be colourless which indicated scope for further loading of Ni nanoparticles. Thus the 2nd batch of $Ni(NO_3)_2$ solution was added and same steps were repeated. Then successively 3rd and 4th batches of $Ni(NO_3)_2$ solution were added. The filtrate after centrifugation at the end of 4th batch was found to retain fade blackish

tinge, which intimated ample loading of Ni nanoparticles in the above mentioned amount of CMGG polymer.

### 2.3. Catalytic reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) in the presence of Ni-Polymer composite catalyst using $NaBH_4$

An extensive study was made on the catalytic $NaBH_4$ reduction of 4-NP in the presence of Ni-Polymer composite in a well-stoppered standard quartz cuvette with a $45 \times 12.5 \times 12.5$ mm$^3$ path length, 3 cm$^3$ of experimental solution. Typically, to a 15 mL, 0.25 mM solution of 4-NP, $NaBH_4$ solution was added which corresponds to colour change from yellow to yellow-green due to conversion of 4-NP to 4-Nitrophenolate ion. Thus the initial UV–vis peak of 4-NP red shifted from 315 nm to 400 nm due to formation of 4-nitrophenolate ion in alkaline condition caused by sodium borohydride. To this mixture catalyst was added, the colour of the solution faded as reaction (reduction of 4-Nitrophenolate ion to 4-AP) proceeded. The supernatant was taken from solution mixture after 0, 15, 30 and 60 min of addition of catalyst and the reaction was monitored by UV–vis measurement. Blank experiments were also carried out to show that the reactions did not proceed in absence of catalyst. While studying the effect of catalyst dose, the catalyst dose was varied from 10 mg to 30 mg to 50 mg, sodium borohydride concentration was varied from 0.5 mM to 1 mM to 1.5 mM and the temperature had been varied from 353 K to 363 K to 373 K.

### 2.4. Characterizations

#### 2.4.1. UV–vis spectroscopy

UV–vis spectra were recorded by PerkinElmer 25 Lambda UV–vis Spectrometer to monitor the optical properties of Ni-Polymer composite at a resolution of 1 nm.

#### 2.4.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the powdered samples were measured by PerkinElmer Spectrum 100 FTIR spectrometer at a resolution of 4 cm$^{-1}$.

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

TEM investigations were carried out using "JEOL JEM 2100 HR with EELS" microscope operating at 200 kV with LaB$_6$ lamp with point to point resolution of 0.23 nm and resolution of 0.14 nm. The compositional analysis was performed by energy dispersive analysis of X-ray (EDS, EDX Inc.) attachment on the INCA energy TEM 200. Samples for these purposes are prepared by drop casting the solution on carbon coated copper grid and allowing the solutions to dry up thoroughly at ambient condition.

#### 2.4.4. Scanning electron microscopy (SEM)

SEM images were taken on ZEISS EVO-MA 10 microscope with tungsten filament bulb. The liquid samples were drop casted on $0.7 \times 0.7$ cm$^2$ sized glass slide, dried well for several hours.

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

XPS analysis were carried out with custom built ambient pressure photoelectron spectrometer (APPES) (Prevac, Poland), equipped with VG Scienta's R3000HP analyzer and MX650 monochromator [36,37] Monochromatic Al Kα X-ray was generated at 450 W and used for measuring X-ray photoelectron spectrum (XPS) of the above samples. Base pressure in the analysis chamber was maintained in the range of $2 \times 10^{-10}$ T. The energy resolution of the spectrometer was set at 0.7 eV at a pass energy of 50 eV. For peak synthesis, a mixed Gaussian-Lorenzian function with a Shirley type background subtraction was used. Samples were