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Synthesis of nickel nanoparticles: Bioreduction method

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ABSTRACT

Synthesis of nickel nanoparticles using bioreduction (*lactobacillus* assisted) method, an eco-friendly nano-biotechnological approach is reported. The synthesis is performed at room temperature. X-ray and transmission electron microscopy analyses are performed to ascertain the formation of Ni nanoparticles. Individual nanoparticles as well as a number of aggregates having the size of 30-50 nm are found. Possible involved mechanism of biosynthesis has also been discussed.

KEYWORDS

Nano nickel;
Nanoparticle;
Nano-biotechnology;
Eco-friendly.

INTRODUCTION

Nanomaterials are more effective than conventional catalysts for two reasons. First, their extremely small size (typically 10-80 nanometers) yields a tremendous surface area-to-volume ratio. Also, when materials are fabricated on the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons account for the versatility and effectiveness of nanocatalysts. Further, the limited quantity of fossil fuels on the planet has led researchers towards finding alternative sources of energy. Fuel cells have the ability to generate large amounts of energy in an environmental friendly way. Combining oxygen and hydrogen gas within a fuel cell creates enough energy to power a vehicle and other large machines, while producing water as the only byproduct. The efficiency of fuel cells is linked to their rate-limiting reaction, or in this case, oxygen reduction. Conventionally, the promotion of the oxidation reaction is accomplished through the use of expensive platinum catalysts. Recently, it has been observed that nano nickel (abbreviated as n-Ni) acts more like platinum than nickel[1]. Also, n-Ni has the potential to replace platinum as the main catalytic material in a variety of hydrogen fuel cells and other electrode assemblies and provide a renewable source of power to supply the world's energy needs. In addition, n-Ni costing four times less than platinum and has large-scale industrial and military applications.

The interaction between inorganic nanoparticles and biological structures are one of the most exciting areas of research now-a-days. Recently, the legislation on waste electrical/electronic equipment (WEEE) and restriction of hazardous substances (RoHS) has been issued by the European Union. To meet the requirement there is a need to develop an eco-friendly approach for nanomaterials synthesis that should not use toxic chemicals in the synthesis protocol. This is now well known that many organisms, can produce inorganic materials either intra- or extracellularly[2]. Bacteria, being prokaryotes have survived the test of time in enriching ions[3], synthesizing magnetite nanoparticles[2-4], reducing Ag-

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ion into metal particles, forming nanoparticles[5-7] and in generation of cermets[8]. The recent discovery of the bio-synthesis of metal nanoparticles points towards new biotechnological methods in materials science[8-10]. Nanocrystals of gold, silver and their alloys have been synthesized by the assistance of lactic acid bacterial cells[11]. Gold nano-clusters have been synthesized using fungus by Mukherjee et. al.[12]. The synthesis of nanoparticles of gold[13,14], bimetallic[15], zinc[16] and even lanthanide clusters[17] have successfully been demonstrated using the tannins of the biomass of *Medicago sativa* (alfalfa). Recently, the *lactobacillus* sp. (microbe) assisted synthesis of titanium[10], selenium[18] and cadmium[19], have been reported. Tian et al.[20] reported the seed mediated method for the synthesis of silver nanoparticles in which tannin was used to reduce silver salt in aqueous solution.

Keeping in view the importance of n-Ni and environmental issues related to the production of nanopowders, the present work reports an eco-friendly biotechnological approach for the synthesis (*lactobacillus* assisted) of n-Ni for possible applications.

EXPERIMENTAL

Nanoparticles of Ni were prepared using the bioreduction procedure adopted by Canizal et al.[16] and Nair and Pradeep[11] with slight modifications. The finely homogenized full cream yoghurt was filtered through pre-sterilized (autoclaved) serene cloth under laminar flow. The filtrate was now diluted five times with sterile de-ionized water and pH was adjusted in the range of 6.5-8.5 depending upon the strength of the requisite culture solution. Now suitable sugar solution of known strength (10%) prepared in de-ionized and autoclaved water was now added to the filtrate solution and the culture was allowed to grow overnight in laboratory ambience on an orbital shaker. Next morning, each culture solution inoculated with 20 ml of 0.03(M) autoclaved nickel sulphate solution. This inoculated culture solution was stirred thoroughly on a magnetic stirrer for 0.5 h and then allowed to incubate in laboratory ambience on a laminar flow. Deposits of n-Ni become apparent after 2-3 days of continued incubation at the bottom of the conical flask (Figure 1). An interesting change in pH was observed at this stage, which requires further standardization culture solution was filtered after gentle shaking through whatman filter paper, dried under blow of hot air and was subsequently taken into use for physical characterizations. The remaining culture solution containing n-Ni of lower dimension was found to be still active to undertake further transformations and the precipitation of finer particles was observed after addition of suitable sugar solution after 2-3 days. This indicated that the nickel is not causing any toxicity to the *lactobacilli* rather the bacterial cells are well adapted to the metallic ambience. However, we do not completely rule out the partial oxidation and/or hydroxide formation of the Ni-nanoparticles while in media or during the course of filtration. The formation of single-phase compound was checked by X-ray diffraction (XRD) technique using a X-ray diffractometer (Phillips PW1710, Holland) with CuKα radiation λ= 1.5405Å over a wide range of Bragg angles($40° \le 2\theta \le 80°$). TEM micrograph of n-Ni was obtained using Philips CM200 transmission electron microscope at 100 nm.

Figure 1: Photograph showing deposition of n-Ni

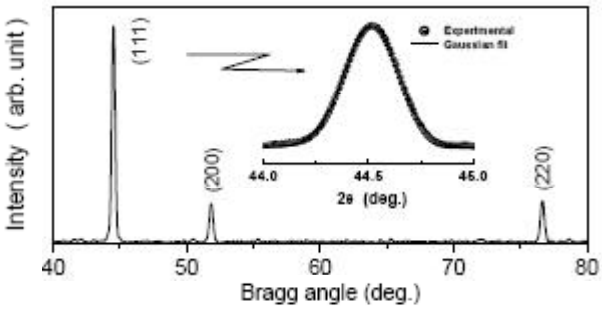

Figure 2: X-ray diffraction pattern of n-Ni at room temperature. Inset: Enlarged (111) peak with Gaussian fit

RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction profile of nickel. The peaks of the XRD-pattern were indexed and cell

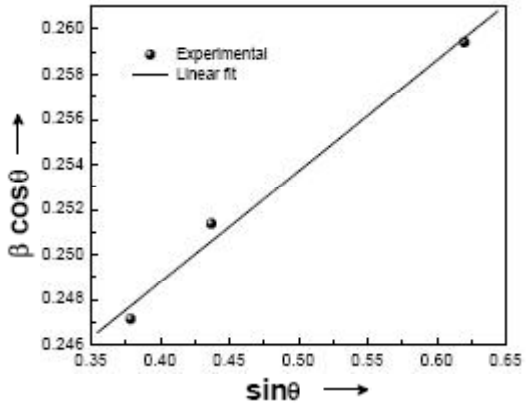

Figure 3: Williamson-Hall plot for n-Ni

Figure 4: TEM photograph of n-Ni at 38 K

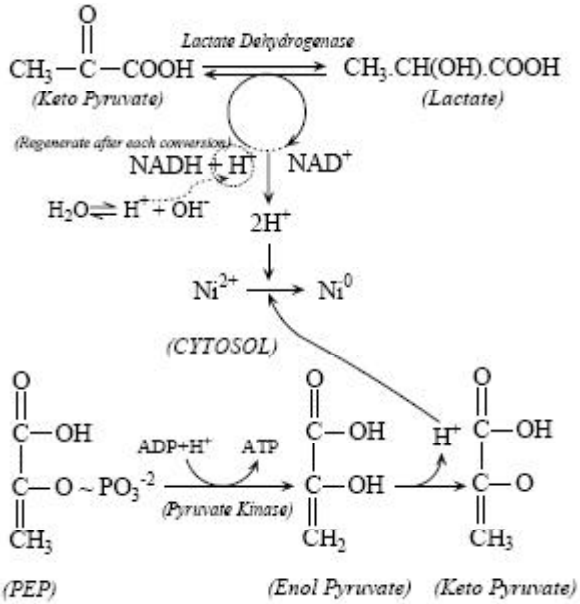

Figure 5: Hypothetical mechanism of n-Ni biosynthesis

parameters were determined with a standard computer program PowdMult[21] using experimental d-values of peaks on different crystal systems. Finally, unit cells of face centred cubic system were selected. The least squares regression fit to diffraction data yielded the lattice parameters. The lattice parameter as obtained for Ni particles is a = 3.523(4) Å with an estimated error of ±0.00018 Å which is in agreement with the literature report (PCPDF No. #04-0850). The unit cell volume was estimated to be 43.76 Å^3. The criterion adopted for evaluating the rightness, reliability of the indexing and the structure of nickel was $\Sigma\Delta d$ [=$\Sigma(d_{obs} - d_{calc})$] found to be a minimum. Inset figure 2 illustrates the enlarged (111) peak. It is important to note that the ratio $I_{\{111\}}/I_{\{200\}}$ comes out to be 5.5. This indicates that the nanoparticles are abundant in {111} plane. Thus, diffraction intensity of {111} plane should be greatly enhanced in comparison to that of other planes. The average particle size of Ni was estimated by analyzing the X-ray diffraction peak broadening, using Williamson and Hall approach[22]:

$$\beta\cos\theta = K\lambda / D + 2\eta\sqrt{<\varepsilon^2>}\sin\theta \qquad (1)$$

where D is the avere particle size, β is diffraction peak width at half intensity and $\sqrt{<\varepsilon^2>}$ is the average strain, K is the Scherrer constant (0.89), η is the coefficient which depends on the distribution of strain. The term Kλ/D represents the Scherrer particle size broadening. The term $2\eta\sqrt{<\varepsilon^2>}\sin\theta$ represents the strain broadening. The strain ε can be estimated from the slope of βcosθ versus sinθ plot and the average particle size can be estimated from the intersection of this line at sinθ = 0. A Gaussian model was applied to analyse the curve.

$$I = I_o + (A / w\sqrt{\pi/2})\exp[-2\{(\theta - \theta_c)/w\}^2] \qquad (2)$$

where A, w and θ_c are respectively the area, width and centre of the curve. The fitting parameters as obtained for the peak (111) are I_o = 33.466, A = 658.153, w = 0.257 and θ_c = 44.514. The value of regression coefficient (r^2) was found to be 0.9991 χ^2/DoF = 346.735. Figure 3 illustrates the Williamson-Hall plot for n-Ni. The apparent particle size and strain broadening are estimated respectively to be of the order of 58 nm and 0.0493.

Figure 4 shows the TEM micrograph of n-Ni being formed using *lactobacillus* strain at 100 nm. The micrograph clearly illustrates individual nanoparticles as well as a number of aggregates having the size of 30-50 nm. The measurement of size was carried along the largest diameter of the particles. It is found that the size of the n-Ni estimated using Williamson-Hall approach to be in fairly good agreement with the size estimated by the TEM analysis. The difference in particle size is possibly be due to the fact that the nanoparticles are being

formed at different times, which may limit the nanoparticle size due to constraints related to the particles nucleating inside the organisms. The possible mechanism for biosynthesis of n-Ni is illustrated in figure 5. Pyruvate formed as product of glycolysis (in culture) undergoes formation of lactate in the cytosol in a reversible reaction involving lactate dehydrogenase and NADH + H^+. The regeneration of NADH + H^+ in the reduction of pyruvate to lactate sustains the continued operation of glycolysis under anaerobic conditions[23]. This conversion involves an obligatory availability of $2H^+$[24]. Along with this, the conversion of unstable enol pyruvate to stereo chemically stable keto pyruvate also remains continuously operative in the cytosol thereby making H^+ available all the time[23]. This availability of hydrogen atoms might facilitate the synthesis of n-Ni particles. The results presented in this paper are at single pH value and is a part of our systematic work.

CONCLUSION

In conclusion, the present biotechnological method is capable of producing Ni-nanoparticles. Also, it is a low cost eco-friendly approach. The synthesis of n-Ni might have resulted due to conversion of pyruvate to lactate and due to tautomeric conversion of enol pyruvate to keto pyruvate.

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