

Synthesis and Structural Characterization of Nickel Nanoparticles capped Polyvinylpyrrolidone

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Due to its unique properties such as solubility in water and other organic solvents, adhesion, non-toxicity and biocompatibility, poly-N-vinylpyrrolidone (PVP) is widely used in various industrial processes and scientific applications, including pharmaceuticals and cosmetics. Nickel-based catalysts, on the other hand, are important in many catalytic processes due to their efficiency and economy. The current study involved the fabrication of nickel nanoparticles capped polyvinylpyrrolidone as nanocatalysts, revealing that metal nanoparticles are integrated into both the surface and core of the polymer.

Keywords: Poly-N-vinylpyrrolidone, Nickel nanoparticles, Immobilized, Nanocatalyst.

INTRODUCTION

Recent achievements in the synthesis of polymer immobilized clusters and metal nanoparticles, their use in many organic catalytic reactions are presented. The main types of polymer-immobilized catalysts are reviewed, including cluster containing polymers, polymer-protected metal nanoparticles attached to inorganic modifiers and gel-immobilized catalysts [1-3]. The polymer matrix functions as a stabilizing agent that inhibits nanoparticle aggregation and leakage into the reaction medium, while simultaneously serving as a ligand within the metal coordination sphere, so integrating the advantages of both homogeneous and heterogeneous catalysts [1]. However, as a function of metal ions in the particle of polymer-metal complexes, the heterogeneity of their molecular properties like molecular weight, particle size, composition, *etc.* creates new problems for researchers [4].

The fabrication and incorporation of metal nanoparticles stabilized in the polymer matrix and their applications in medicine, catalysis and various other field provide a substantial foundation for the scaling of research efforts by experts [5-7]. The development of hybrid materials based on the metal-polymers creates the basis for the development of new directions in many areas of the chemical industries [8,9]. In this regard, polyvinylpyrrolidone (PVP), a synthetic polymer, is of great

interest and widely used among synthetic polymers due to its non-toxicity and solubility in water and other organic solvents. Its complex compounds formed with metals and non-metals are used in various fields of industry and medicines [10]. Since nickel(II) based catalysts are more selective and adaptable than other transition metal catalysts owing to their unique reactivity and catalytic behaviour [11], this study aims to construct Ni(II)-polymeric complex as a nanocatalyst. PVP is widely utilized to prevent the aggregation of particles and regulate the average size and shape of nanoparticles. Incorporation of transition metal oxides into a PVP matrix can enhance the chemical and physical properties of the composite [12]. The main advantage of metal polymer nanocatalysts is that it is possible to carry out certain reactions under milder conditions (low temperature and pressure) [13-17].

EXPERIMENTAL

Chemicals *viz.* polyvinylpyrrolidone (Mw 1,300,000), nickel(II) chloride, sodium tetrahydroborate (NaBH₄), N,N-methylenebisacrylamide as crosslinking agent were purchased from Sigma-Aldrich, USA.

Synthesis: The PVP polymer underwent dissolution in 50 mL of water using a magnetic stirrer for 6 h at 70 °C to ensure thorough dissolution. Subsequently, NiCl₂·6H₂O (10%) was introduced to the aforementioned solution and stirred for an

additional 3 h followed by the incorporation of a reducing agent (NaBH_4) to convert Ni^{2+} ions to Ni^0 resulting in a colour change of the solution from green to black and the formation of a precipitate. The resulting precipitate was washed with diethyl ether followed by distilled water to remove Cl^- ions and salt residues. In next step, in order to increase the sustainability of the obtained nanocomposite, 0.15 g of *N,N'*-methylenebisacrylamide was added to the complex and mixed vigorously at 70°C for 4 h. The resulting solution was dried in a drying chamber at 50°C and the obtained films were irradiated under ultraviolet light at $30\text{--}40^\circ\text{C}$ for 6 h.

Structural characterization: The FT-IR spectra were obtained using a FTIR Nicolat iS10 spectrophotometer in the range of $4000\text{--}500\text{ cm}^{-1}$ using KBr pellets method. The X-ray diffraction patterns were recorded at room temperature (25°C) using EMPYREAN diffractometer with $\text{CuK}\alpha$ radiation and operating at 40 kV and 30 mA. The morphology was investigated by capturing the SEM images using a SEM S-3400 N (Hitachi, Japan) instrument.

RESULTS AND DISCUSSION

The structure of the resulting nickel nanoparticles capped polymer complex is hypothesized to resemble the Scheme illus-

trated in Fig. 1. In this complex, nickel metal interacts primarily with the carbonyl ($\text{C}=\text{O}$) functional group present on the PVP polymer chains. This interaction likely occurs through the coordination bonding, where the lone electron pairs on the oxygen atom of the carbonyl group coordinate with the nickel ions, stabilizing the metal within the polymer matrix [18]. In addition to preventing nickel nanoparticles from aggregating, forming such a coordination complex allows for improved control over the dispersion and size distribution of these particles within the polymer. This stabilization mechanism is key to improving the chemical and physical properties of the prepared nanocomposite.

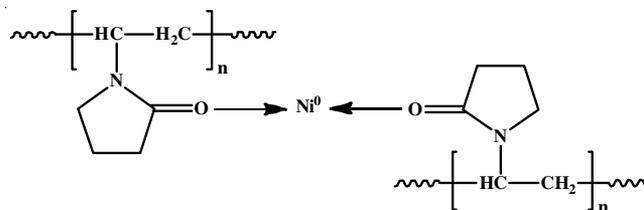


Fig. 1. Possible structure of nickel nanoparticles capped PVP

FTIR spectral studies: The absorption peaks of PVP exhibit at 2922 , 1659 and 1569 cm^{-1} correspond to the C-H, $\text{C}=\text{O}$ and C-N vibrational groups, characteristic of the pyrrolidone ring

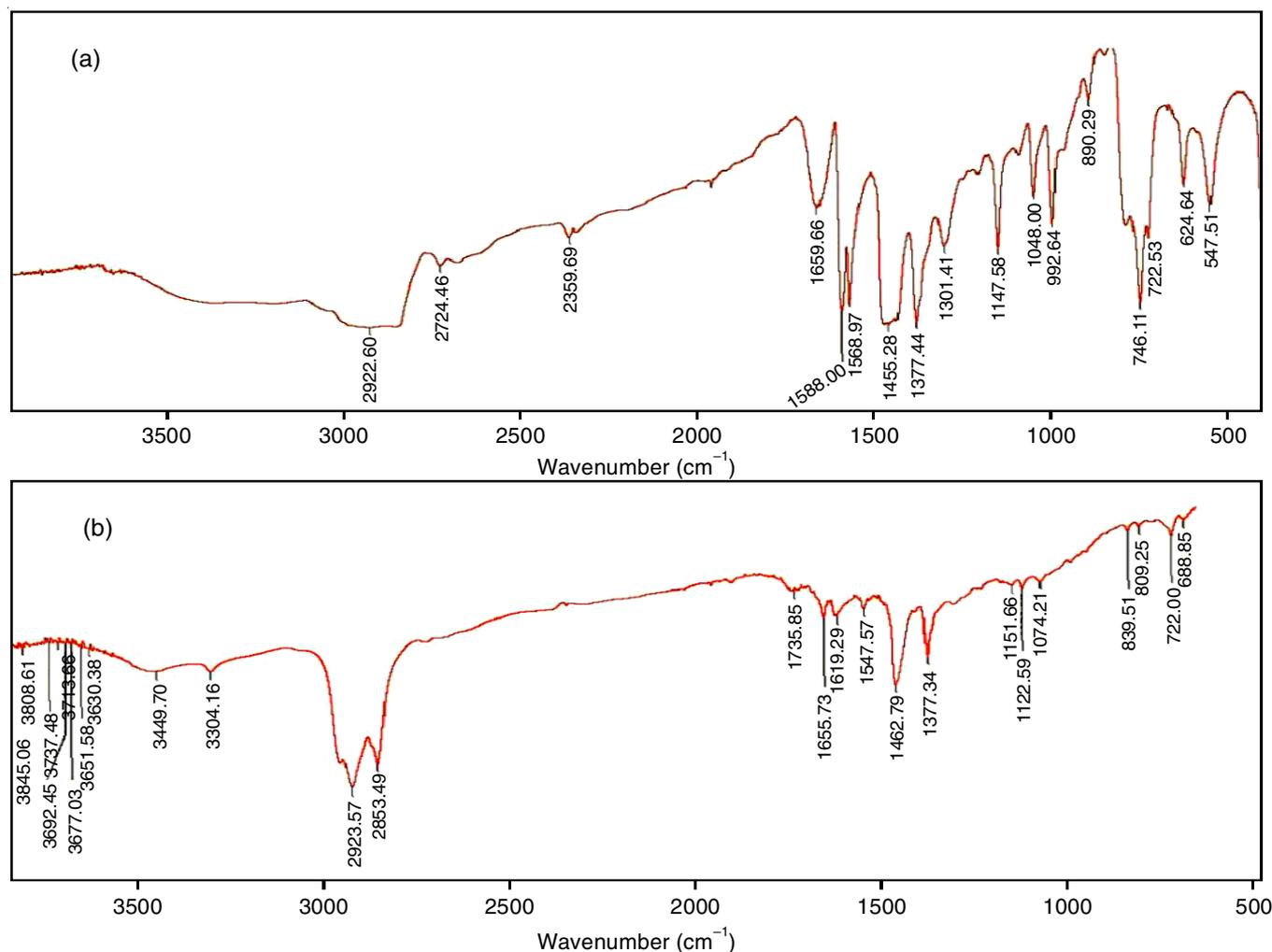


Fig. 2. FTIR spectra of PVP (a) and nickel nanoparticles capped polyvinylpyrrolidone (b)

and the polymer backbone. Comparing the FTIR spectra of PVP and PVP/Ni (Fig. 2b) provides important insights into the molecular interactions and structural changes upon addition of nickel nanoparticles to PVP.

The distinctive peaks of PVP remain in the composite, exhibiting some shifts and changes in the absorption bands intensity after the addition of nickel nanoparticles to PVP particularly around 1588 cm^{-1} and 1619 cm^{-1} . These changes are thought to reflect the interactions occurring between nickel NPs and carbonyl or amide groups in PVP. The emergence of a new absorption band at 1735.85 cm^{-1} in the Ni NPs capped PVP spectrum suggests the potential development of new functional groups due to enhanced interactions or the presence of nickel.

XRD studies: Initially, the PVP polymer was analyzed and found to have an amorphous structure with no long-range crystal order (Fig. 3). A different pattern is observed in the diffractogram of the sample obtained after the addition of nickel ions to the polymer followed by reduction. When nickel NPs is incorporated into PVP, the XRD pattern changes, depending on the shape and dispersion of nickel NPs in the polymer matrix

and the specific peaks corresponding to the crystalline structure of nickel metal are observed.

SEM-EDS analysis is employed to investigate the surface morphology (texture), elemental composition and crystalline structure of solid samples. Initially, PVP was analyzed in an SEM (Fig. 4) and its surface structure appears to be irregular. After the addition of nickel nanoparticles to PVP, the structure becomes regular and the size of spherical shape varies from 3 to $5\ \mu$. The size of nickel nanoparticles capped PVP was determined to be 10-50 nm (Fig. 5).

Conclusion

The synthesis and characterization of nickel nanoparticles capped polyvinylpyrrolidone (PVP). FT-IR analysis confirmed the presence of Ni^0 species in the framework of the polymer as the transfer of electrons from the C=O group of pyrrolidone ring to Ni^0 ions. The specific structure of the nickel NPs capped PVP depends on factors such as stoichiometry, amount of polymer and geometric structure around the nickel center. The materials possess a regular structure that enables the production of immobilized small-sized nanoparticles (10-50 nm).

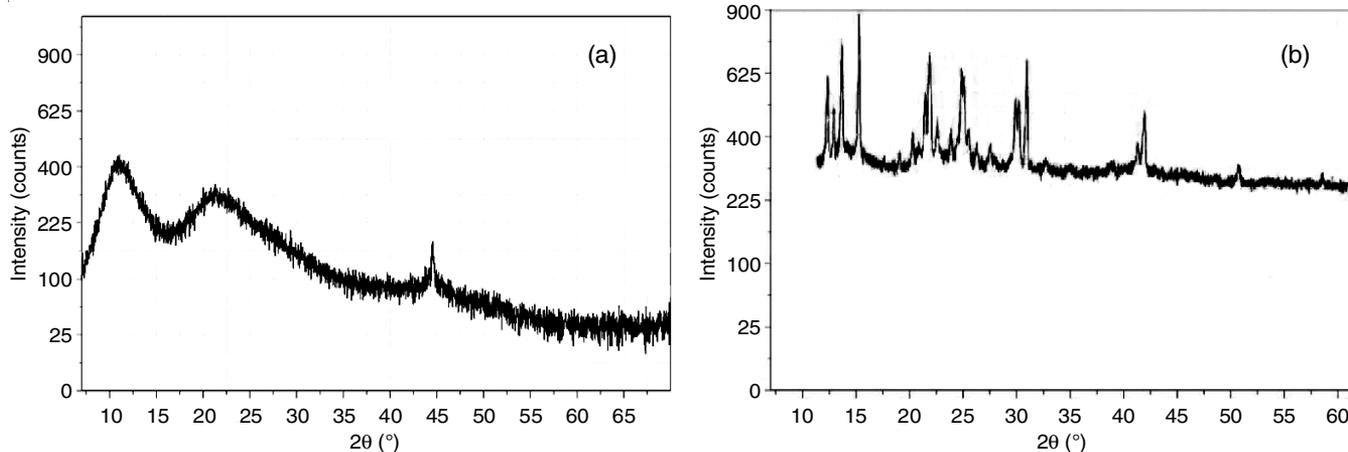


Fig. 3. XRD spectra of PVP (a) and nickel nanoparticles capped polyvinylpyrrolidone (b)

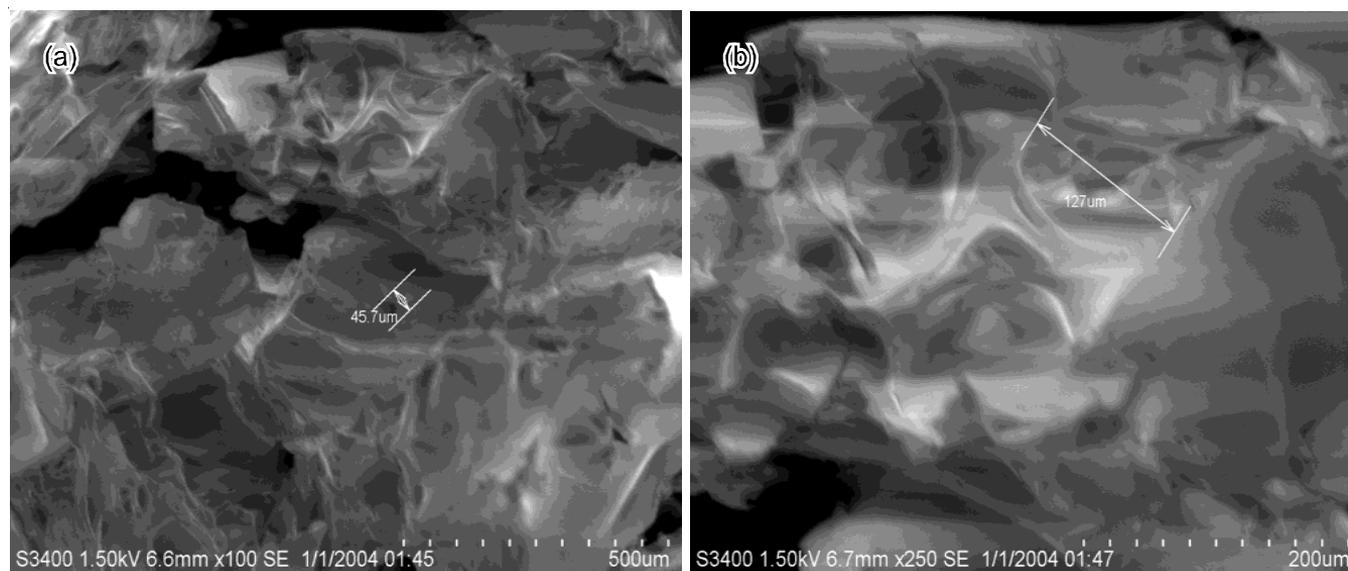


Fig. 4. SEM images of PVP 100X (a) and 250X (b) magnifications

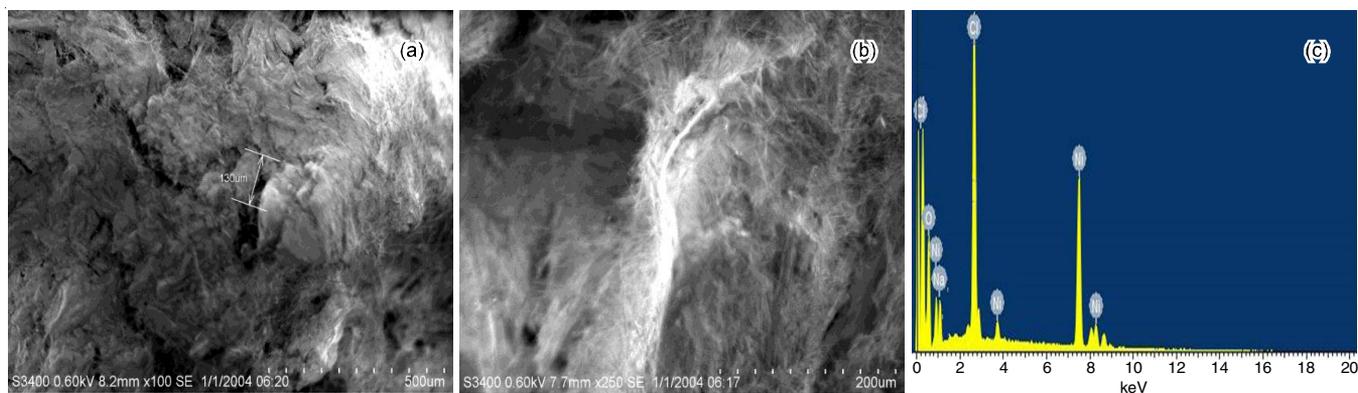


Fig. 5. SEM images of nickel nanoparticles capped polyvinylpyrrolidone at 100X (a), 250X (b) magnifications and EDS spectrum (c)

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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