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Synthesis of Chitosan Stabilised Platinum Nanoparticles and their Characterization

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Abstract

A simplistic green synthesis route for the platinum nanoparticles has been successfully identified by using chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$) as the metal precursor and sodium borohydride ($NaBH_4$) as the reducing agent at room temperature. Chitosan was used in minute quantities as capping and stabilizing agent. The visual observation of a black coloured colloidal suspension, the characteristic XRD peaks and the absorption peak in the range of 200-300nm confirmed the production of Pt nanoparticles. The average crystallite size calculated using Debye-Scherrer equation is about 19 ± 2 nm and a less intense absorption peak was found at 246nm and 281nm. The FTIR spectroscopy was used to confirm the capping with chitosan molecules. Zeta-potential calculation gave a surface charge of -23.8mV, and this high negative value, then validated the stability of the nanoparticle. The synthesis of platinum nanoparticles is very significant for their catalytic activity and biomedical applications in industrial as well as healthcare sector.

Keyword : *Chitosan stabilised platinum, nanoparticles, spectroscopy, x-detraction, biomedical.*

1.0 Introduction

Nano-materials are those substances which are manufactured using various physical, chemical, or biological engineering routes with at least one of its dimensions in the nano- regime, i.e.; 1 to 100nm[24]. The reduced size provides the important features to these materials including large surface area to volume ratio, quantum confinement effects, electronic and optical properties etc[6,26].

Among the noble metals platinum nano-particles have now gained the research interest after gold and silver. These studies at the nano-scale have considerably assisted our efforts to manage energy, implement energy-saving measures, reduce air and water pollution, empower the automotive sector, catalyse the chemical industry, manufacture better consumer products like cosmetics, paints, etc., and, more recently, revolutionise medical diagnosis and treatment[19]. Being a rare as well as precious metal the optimised usage is demanded. Just like the other nano-materials, in the nano-dimensions the surface area to volume ratio is tremendously increasing, hence a large number of surface atoms at their corners and edges which make them highly active in their interactions, hence as an excellent catalyst[8].

Initially the nano-scale production of platinum nano-particles was mainly through the physical or chemical routes. But currently there is an increased demand for greener path for the synthesis of this material. Platinum nano-particles possess multidimensional applications in physical, chemical and biological fields. The first and the foremost field of application of platinum nano-particles is nothing but the catalytic activities in the chemical industry. There are a lot many current research activities intended to beat the supremacy of platinum nano-particles in this field by developing other economic materials for the same purpose,

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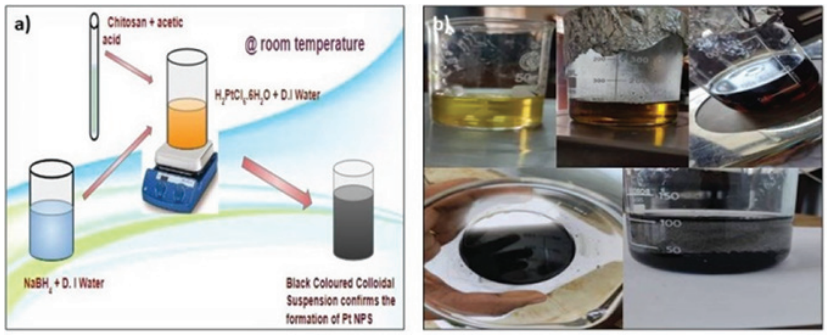

Figure: 1 (a) Schematic representation of synthesis of chitosan stabilised Pt nano-particles (b) Visual observation of colour change of the reaction mixture

but the scope of platinum nano-particles is still unquestionable[7]. According to reports, Pt nano-particles made through more environment friendly processes are less cytotoxic and more biocompatible, as well as haemo-compatible. As a result they are currently being researched for use in drug discovery and development[14,16].

Many researchers have devoted their time and resources for synthesizing platinum nano-materials with variety of shapes and sizes such as quantum dots, nano-wires, nano-sheets and also nano-porous structures. Hence the investigations for intrinsic properties of Pt NPs are significant. Here in this work we have synthesised platinum nano-particles using chitosan as the stabilising agent. Because of its interactions with metal nano-particles via steric and electrostatic effects, chitosan is one of the ecologically benign polymer that is particularly intriguing in the synthesis of metal nano-particles. This is somewhat a greener synthesis approach, as the by-products of the reaction are purely eco-friendly[17].

2. Experimental Section

2.1. Chemicals and Materials

The metal precursor chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$), the reducing agent sodium borohydride ($NaBH_4$) and the capping agent chitosan were bought from Sigma Aldrich. All reagents and chemicals were of good quality and are stored and used with at most care. Deionised water was used as the solvent in the experiment.

2.2. Methods and Characterisation

Here in our experimentation, we have mixed equi-molar solutions of chloroplatinic acid hexahydrate and sodium borohydride in the presence of chitosan. The solution was stirred continuously for one hour. The reaction was found to be instantaneous and spontaneous at room temperature (Figure:1a), and a visual observation of a colour change from deep yellow to black coloured colloidal solution confirmed the formation of platinum nano-particles[19,21]. Chitosan molecules act as the capping or stabilizing agent. The as synthesised chitosan capped platinum nano-particles (Ch-Pt NPs) are centrifuged, filtered and stored under normal room temperature.

Here we have done several characterisation techniques as structural optical and surface morphological analytical tools. The UV-Visible spectroscopy was used for the optical study. X-Ray diffraction (XRD) (Rigaku miniflex X-Rat Diffractometer) and Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu IR Spirit-L) were used for the structural investigations including the nature of bonding between Pt NPs and Chitosan molecules. Using dynamic light scattering, the size and surface charge were calculated (DLS: Zetasizer Malvern Instruments Ltd.)

3. Results and Discussions

3.1 X-Ray Diffraction

The atomic arrangement and position are described by the X-Ray analysis of the crystal structure in relation to the intensity of the diffraction peaks. The formation of prepared platinum nano-particles from chloroplatinic acid solution was confirmed and the crystal structure also the crystalline size of the platinum nano-particles formed were determined by X-ray diffraction measurement, as shown in the Figure 3(a).

All the broad diffraction peaks of the XRD pattern at 2θ = 39.88, 46.34, 67.56, 81.34 and 85.80°, corresponds to the reflections (111), (200), (220), (311) and (222), respectively.[20] The unique pattern of the diffraction beam is compared to the ICDD reference no: 04-0802, thus demonstrating the presence of crystalline Pt nano-particles[10].

The average grain size was calculated using Scherrer equation and is found to be 19±2 nm and the interplanar spacing was found to be 0.16 nm. Williamson-Hall plot is derived from the XRD data. It is possible to use the XRD data to perform the fundamental calculations for the graphs. It provides the strain and crystallite size. The microstrain and crystallite size from the WH Plot are both about -0.0004933 and 22nm, respectively.

3.2. Fourier Transform Infra-Red Spectroscopy

In order to confirm the capping with chitosan molecule on the Pt NP surface, FTIR spectroscopic study was used. The chemical as well as surface morphological properties of the

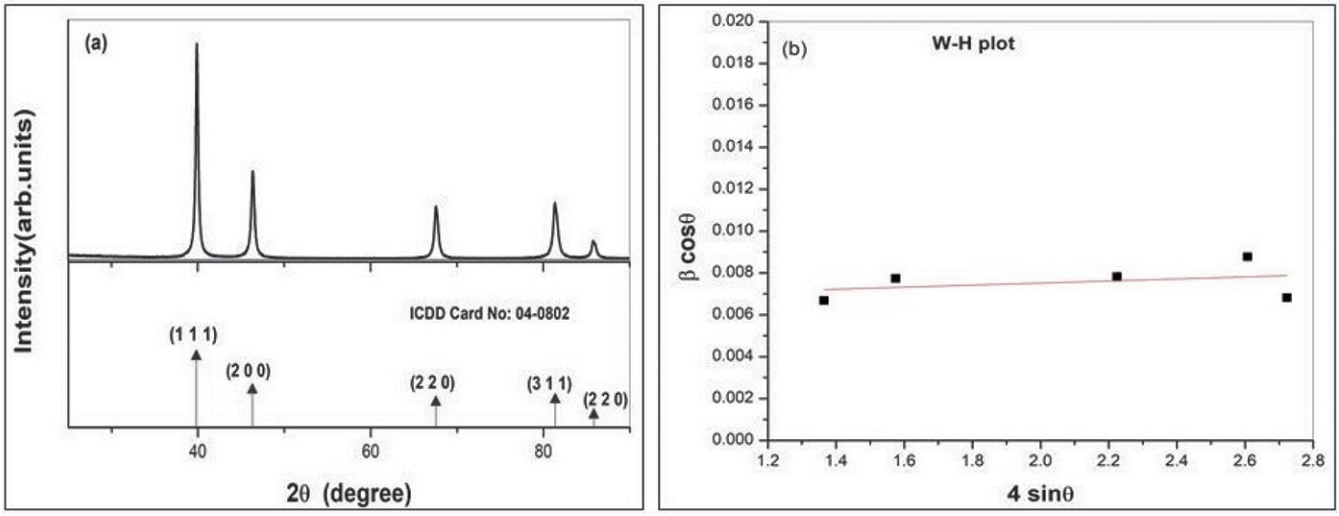

Figure: 2 (a) XRD pattern of chitosan stabilised Pt NPs (b) Williamson-Hall plot

Ch- Pt NPs were revealed by FTIR spectroscopy. Figure 4(a), shows that in the Ch-Pt NP spectra, a peak at 3436 cm^{-1} is identified as the merged peaks of OH and NH_2 groups (symmetric stretching vibrations of chitosan). The vibrations corresponding to the symmetric stretching of C=O in the amide group of the chitosan molecule at 3286 cm^1 is obtained here at 3224cm^{-1} which then confirmed the attachment of chitosan molecule on Pt NPs[12]. The symmetric stretching vibration of C-H bond in the chitosan is observed at 2846 cm^{-1}. The peak at 1622 cm^{-1} determined as due to the C=O secondary amide group[5,22]. and the peak at 1304 cm^{-1} indicates symmetric stretching vibration of $–CH_3$ in the tertiary amide group. The peak at 1025 cm^{-1} was red shifted to 1032 cm^{-1} representing the C_6–O stretching vibration. The peak at the lower wavelength at 700 cm^{-1} corresponds to C-H vibration[9,23]. These important vibrations in the FTIR spectra suggested that the secondary and tertiary amide groups of Chitosan are responsible for interacting with Pt NPs.

3.3 Particle size and Zeta potential

In the solution, the hydrodynamic diameter of the chitosan stabilised PT NPs was well above the expected or

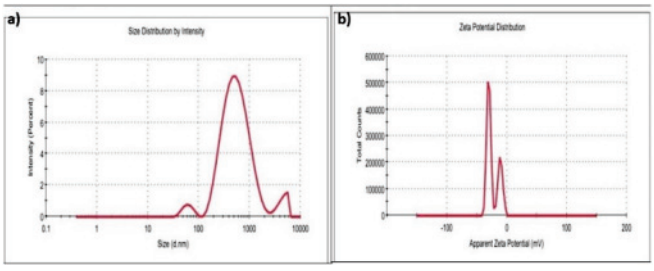

Figure: 3 (a) Dynamic Light Scattering size distribution by intensity of Pt NPs (b) Zeta Potential distribution

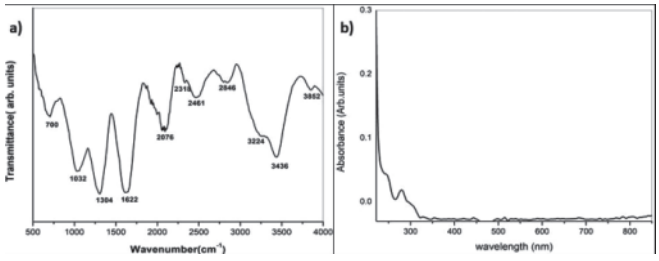

Figure 4: (a) FTIR spectrum (b) UV-Vis absorption spectrum of solution containing chitosan stabilised Pt nano-particles

calculated size, this is because of the presence of the large chitosan molecule capped over the nano-particles and also the dipolar hydration shell formed around the structure. (Figure 3: (a), (b)) The zeta potential value was found to be highly negative of –23.8 ± 9.8 mV, indicating good stability for the Pt NPs[10,3].

3.4 UV Visible Spectroscopy

One of the important optical phenomena exhibited by metallic nano-particles is the strongest absorption of the UV-Visible light due to the coherent intraband oscillations of the conduction electrons, known as surface plasmon resonance (SPR). Pt nano-particles showed a broad absorption spectrum in aqueous solution that included the entire UV-visible spectrum. Other reports claim that Pt nano-particles with single or double unsteady absorption peaks in the UV spectral region also exist, and that these peaks exhibit a blue shift as particle size increases[27].

Here in this investigation, 246 and 281 nm were the locations of two successive peaks. The interaction of UV-Visible light with the conduction band electrons stimulates them, and a potential transition scheme is anticipated as an intraband transition from lower atomic energy levels, such as

5P and 6S, to higher energy levels of the energy band structure[19].

Platinum nano-particles are proved to be a better theranostic agent. The basic challenges in using this material for the biomedical applications are the unavoidable toxic effects. By following a greener synthesis route, use of hazardous chemicals can be avoided and the biocompatibility of the end product can be improved[3]. By carrying out a hierarchical approach for the toxicity study of the material with the animal body starting from the interaction studies the safety profile can be ensured and the material can be used for biomedical applications[1]

4.0 Conclusions

In this work we have reported a simplistic approach for the synthesis of platinum nano-particles using chloroplatinic acid as metal precursor, sodium borohydride reducing the metal ion to zero valent metal atom and chitosan as the stabilizing agent. The characteristic XRD pattern confirmed the formation of platinum nano-particles while FTIR spectrum revealed the surface modifications made by the stabilizing agent. The highly negative zeta potential indicates the superior stability of the nano-particles so formed. The surface functionalization of the material with a green material like chitosan improves the stabilitity and biocompatibility of the platinum nano-particles, and these nano-particles may be investigated for their biomedical applications in future.

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