

GREEN SYNTHESIS AND CHARACTERIZATION OF POLYETHYLENE GLYCOL-12000 (PEG12K) SUPPORTED PALLADIUM NANOPARTICLES IN AQUEOUS MEDIUM**Abdul Majeed Ansari¹, Naresh Kumar Sharma^{1*}, Ravi Kant² and Sajid Ali³**¹Department of Chemistry, Government P.G. College Bundi-323001, India²Department of Chemistry, Government Post Graduate College, Noida, G.B. Nagar, UP 201301, India³Department of Chemistry, Krishna Engineering College, Mohan Nagar, Ghaziabad-201007, India**ABSTRACT**

An efficient green synthesis of polyethylene glycol supported palladium nanoparticles in water has been developed using polyethylene glycol-12000 (PEG12K) as capping agent. The stability of the prepared nanoparticles is due to protective polymer PEG molecular weight 12000 employed that fulfils the various requirements.

Keywords: Palladium; PEG12K; nanoparticles; monodisperse; water soluble.

1. INTRODUCTION

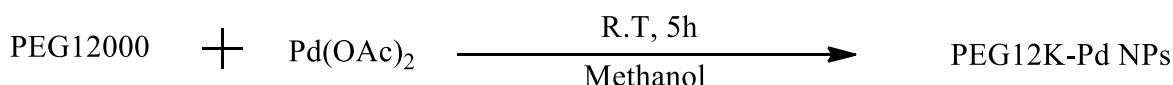
Nanoparticles have garnered significant interest in academic and industrial domains because to their distinctive chemical and physical characteristics, including catalytic, optical, and magnetic capabilities that differ from those of bulk metals or atoms [1–4]. Preparation, structural determination, and uses of transition-metal nanoparticles are fascinating subjects right now, and they've garnered a lot of attention in the past decade [5-18]. Nanoparticles are highly intriguing in catalysis due to the fact that a greater proportion of atoms are located on the surface as the cluster size decreases [10,15,18]. Heterogeneous catalysts employ metal nanoparticles for the purpose of catalyzing the hydrogenation of nitroarenes. Nanoparticles can be formed by generating metal atoms through many methods, including chemical reduction of a metal salt, thermal, photochemical or sonochemical breakdown of a metal(0) complex, hydrogenation of a coordinating olefinic moiety, and vapor phase deposition. In addition to the list suggested by Bradley [6], the electrochemical reduction of higher valent species of the metal should be included [13]. The process of nanoparticle generation involves the following steps: (i) creating individual atoms, (ii) forming a small cluster of atoms through nucleation, (iii) allowing the cluster to grow until it reaches a specific size, and (iv) surrounding the cluster with a protective shell to prevent clumping together. Consequently, it is necessary to create nanoparticles when a safeguarding agent is present. The protectors can be categorized into two main groups: those that offer electrostatic stabilization and those that offer steric stabilization. Electrostatic stabilization occurs when ions of the same charge are adsorbed onto the surface of a nanoparticle, creating a double electric layer. The catalytic characteristics of heterogeneous catalysts are widely recognized to be influenced by the size of the metal particles and the surface structure of the supports [19]. Transition metal nanoparticles have high catalytic activity in chemical reactions owing to their expansive surface area and distinctive amalgamation of reactivity, stability, and selectivity. Controlling the size and polydispersity of nanomaterials is a crucial prerequisite for their widespread deployment. PEG and PEO, which have varying molecular weights, are utilized in diverse applications and exhibit distinct physical features, such as viscosity, as a result of the length of their chains. However, their chemical properties are almost indistinguishable [20]. Transition metals, including noble metals, exhibit high standard reduction potential. For instance, palladium metal has a reduction potential of 0.938 V [21]. Nanoparticles have been fixed onto inorganic solid substrates [22] or incorporated into organic

polymers [23], dendrimers [24], multilayer polyelectrolyte films [25] and ionic liquids for the purpose of separation and subsequent reuse [26].

Nevertheless, immobilization frequently encounters issues such as limited reactivity, degradation, palladium leaching, and complex synthesis methods. We have recently published a straightforward one-pot technique for producing a reusable palladium catalyst. This involves generating palladium nanoparticles from Pd(OAc)₂ and polyethylene glycol [27]. PEGs, which are simple and easily accessible polymers, have been utilized for numerous transformations due to their non-toxic, affordable, non-ionic, thermally stable, recoverable, and non-volatile properties. Transition metal nanoparticles are extensively used in several catalytic applications. Nevertheless, because of their expansive surface area and surface energy, these particles have a tendency to clump together during chemical reactions. As a result, it is necessary to stabilize them in order to ensure efficient usage. This study details the process of creating and analyzing polymer PEG12K capped palladium nanoparticles that are exceptionally tiny and have a low degree of variation in size.

2. EXPERIMENTAL

In this study, we present a new and simple method for synthesizing Pd nanoparticles using PEG with a molecular weight of 12000. It was found that this PEG molecule not only acts as a reducing agent but also as a stabilizer. The number is 27. In the standard procedure, a solution of Palladium acetate Pd(OAc)₂ (5.09×10^{-3} M) in 1,4-dioxane and a solution of PEG with a molecular weight of 12000 in methanol (2.0028%) were mixed together. The resulting mixture was agitated at room temperature for 5 h. Upon the immediate mixing of the two solutions, the resulting solution exhibited a faint yellow coloration and a slight turbidity, indicating the production of aggregates prior to the reduction of palladium ions. Over time, the solution's hue transitioned from orange to brown and ultimately to black, suggesting the creation of PEG12K capped Pd(0) metal nanoparticles (**Scheme 1**)



Scheme 1. Synthesis of polymeric PEG12K-Pd Nanoparticles.

The mixing ratio of the PEG12K and palladium ions (PEG12K/ [Pd²⁺]) affected the formation of the spherical aggregates of the palladium nanoparticles. The reduction of Pd²⁺ ions followed an analogous polyol process in the current study [28].

Table 1: Preparation of PEG12K-Pd Nanoparticles

Sample No.	Volume of PEG12K (2.047%) (mL)	Volume of Pd(OAc) ₂ (5.09×10^{-3} M) (mL)	Size (nm)	Polydispersity (S.D.)
232-SG-1	0.1	0.9	213.9	1.023
232-SG-2	0.2	0.8	158.1	1.403
232-SG-3	0.3	0.7	142.2	0.7
232-SG-4	0.4	0.6	55.43	0.122
232-SG-5	0.5	0.5	58.66	0.312
232-SG-6	0.6	0.4	225.4	251.5
232-SG-7	0.8	0.2	142.2	1.485
232-SG-8	0.9	0.1	242.4	3.39

When Pd(II) ions were added into the methanolic solution, electropositive palladium ions are rapidly trapped by electronegative oxygen forming weak metal ion complex followed by analogous polyol process. In this system electron transfer between metal ions and the hydroxyl group leads to the reduction of Pd²⁺ to Pd (0). In sample **232-SG-4** (**Table 1**) it was found that the monodisperse smallest size PEG12K-Pd nanoparticles were obtained which was characterized by the DLS study. (**Fig. 1a**). The desired size and monodispersity was not obtained in rest of the samples (**Table 1**). The experimental condition such as amount of protecting polymer, the concentration of the metal ions are systematically changed to achieve the smallest size PEG12K-Pd nanoparticles (**Table 1**; sample **232-SG-4**).

3. RESULTS & DISCUSSION

DLS evaluation (**Table 1**; sample **232-SG-4**). of the nanoparticles indicates that the size distributions of the particles are very narrow. Sample **232-SG-4** found to be smallest size 55.43 nm having polydispersity 0.122 (**Table 1**). We begin the studies with some preliminary investigations of the particle core size by using DLS (**Fig. 1a**). Represented TEM images of PEG12K-Pd nanoparticles prepared using the chemical reduction method described in the experimental section is shown in **Fig. 1b**.

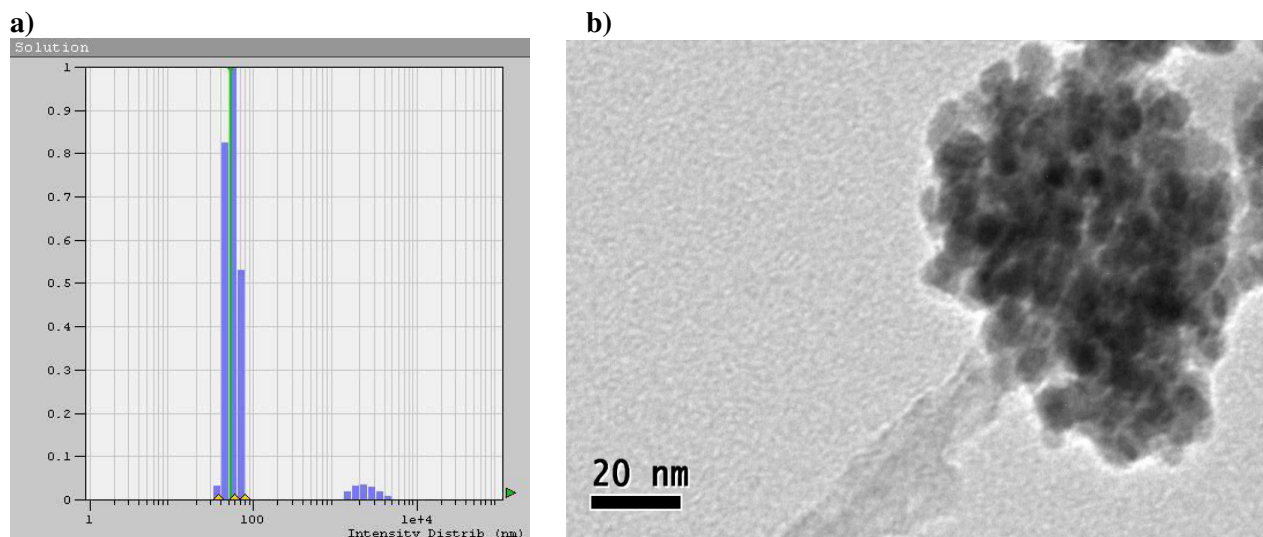


Fig. 1. (sample 232-SG-4) **a)** DLS data of PEG12K-Pd Nanoparticles **b)** TEM image shows that 9-10 nm sized PEG12K-Pd Nanoparticles.

c)

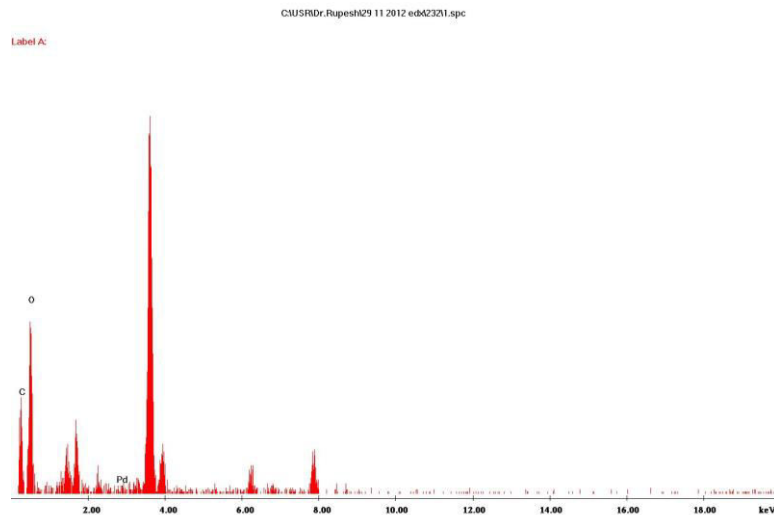


Fig. 1. (sample 232-SG-4) **c)** EDX Data of Synthesized PEG12K-Pd Nanoparticles.

Prepared nanoparticle possesses an average diameter of 9.0 nm and a standard deviation ± 1 nm (calculated from the diameter of a sample of 40 nanoparticles); it is observed smaller monodispersed nanoparticle are obtained by chemical reduction method. The prepared PEG12K-Pd nanoparticles remained dispersed for several months with no obvious change in the size. The TEM analysis implies that the long chain structure of PEG could provide good stability and dispersing effects to the Pd nanoparticles and prevent its agglomeration. The composition of PEG12K-Pd was further probed by EDX analysis (**Fig.1c**). From the distribution of C, Pd, and O in the individual particles measured by EDX analysis, each element was non-uniformly distributed on the nanocomposites. These data gave a clue that the particles were nanocomposites consisting of Pd, C, and O. From the EDX spectra (**Fig. 1c**) we can see that the nanoparticles are composed of C, O and Pd; this confirms the presence of palladium metal.

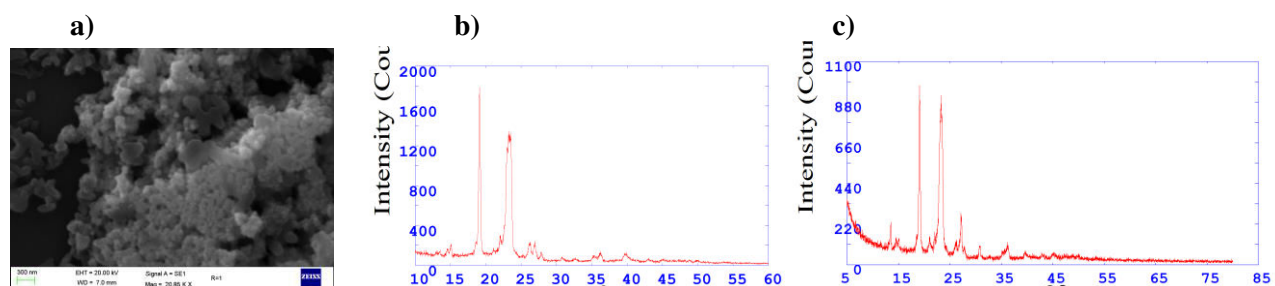


Fig. 2. (Sample 232-SG-4): **a)** SEM Micrograph of PEG12K-Pd Nanoparticles **b)** XRD pattern of the synthesized PEG12K-Pd nanoparticles **c)** XRD pattern of PEG12K polymer

From the **Fig. 2a**, it is obvious a large amount of sample is dispersed on the slide. The average grain size was found to be 100 nm with round morphology. Agglomerated grain were attached on the polymer surface. The surface property was found out to be distorted, rough without any specific pattern. The formation of nanoparticles is confirmed by observation of broad peaks in the XRD spectrum (**Fig. 2b**). Reflections due to (111) and (200) planes at $2\theta=39.64$, and 45.62 confirmed the presence of palladium metal in the nanoparticles. EDX data (**Fig. 1c**) shows the high content of carbon (48.6% by atomic weight) in the prepared nanoparticles. Presence of high

carbon content shows that prepared PEG12K-Pd nanoparticles in the obtained powdered XRD (Fig. 2b) are highly amorphous in nature. Pure PEG12K (Fig.2c) shows that the diffraction peaks between $2\theta = 19.16^\circ$, 23.24° , 27.2° , 30.76° and 36.25° . The peaks corresponding to the polymer still appears in the XRD pattern of prepared PEG12K-Pd nanoparticles (Fig. 2b). Compared with the pure polymer PEG12K, PEG12K-Pd nanoparticles (Fig. 3a) showed a new broad band at 1968.68 cm^{-1} , which is assigned to presence of Pd(0)-O compounds.^[35] It is observed that there is a increase in the IR frequency of pure ether linkage peak at 1100.33 cm^{-1} (Fig. 3a) bonded to the palladium metals. The methylene vibration modes at 2891.22 cm^{-1} , clearly seen in Fig. 3a and indicate that the hydrocarbon chains capping the palladium nanoparticles are closely packed without a significant density of defects in the chains [29]. A broad peak centered at 3435.86 cm^{-1} is observed and is assigned to the O-H stretch modes of vibration from the traces of uncoordinated PEG12K molecules remained.^[36] In addition, PEG12K-Pd nanoparticle (Fig. 3a) more bands at 1361.98 and 1343.00 corresponding to the vibration modes of methylene group C-H bending and OH bending modes. The absorption at 1467.32 cm^{-1} (Fig. 3b) is due to bending vibration of $-\text{CH}_2$ group which was found to be disappeared in the PEG12K-Pd nanoparticles (Fig. 3a). A sharp, strong band at 961.77 cm^{-1} and 842.17 cm^{-1} is due to the C-C stretching vibrations (Fig. 3a) [30] The above analysis establishes the formation of the polymer metal interaction.

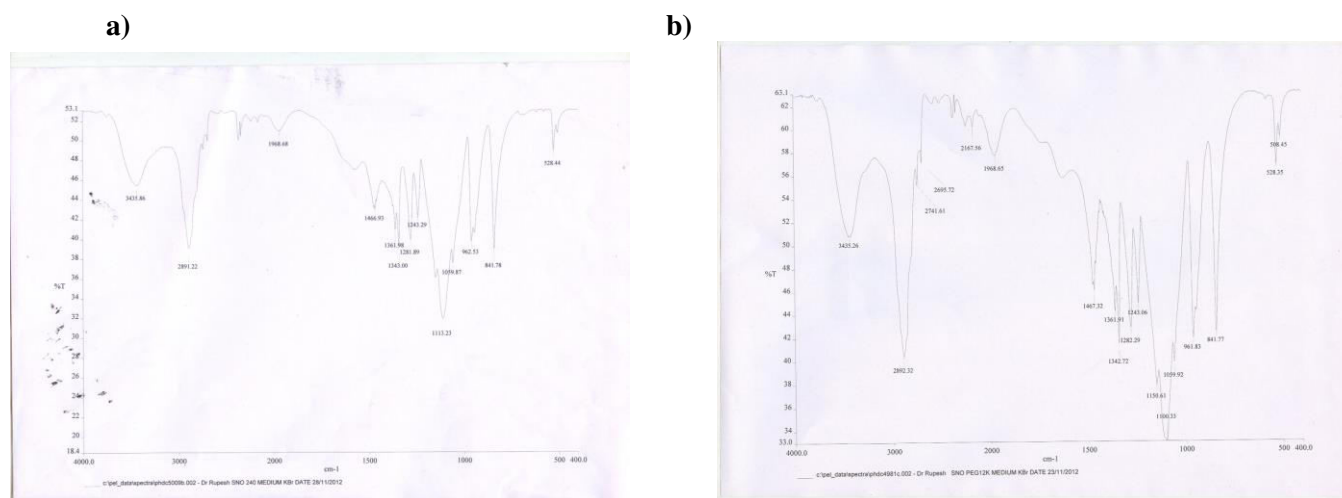


Fig. 3. (Sample 229-SG-6): The FT-IR spectra of PEG12K-Pd nanoparticles. b) The FT-IR spectra of pure polymer PEG12K

The nanoparticles of palladium are capped with molecules of PEG12K, which have provided the nanoparticles with an adequate amount of hydrophobic capability. When kept at room temperature, these nanoparticles can remain stable for a number of months. Analyses using thermo gravimetric techniques were carried out on purified samples in order to gain an understanding of the stability of these systems at higher temperatures. Fig. 4a depicts the TGA profile which was obtained for the PEG12K-Pd system. Desorption of PEG12K from the surface of the nanoparticles is responsible for prominent losses that occur between temperatures ranging from 201.56 to $364.36 \text{ }^\circ\text{C}$, which accounts for a total loss of 93.976% .

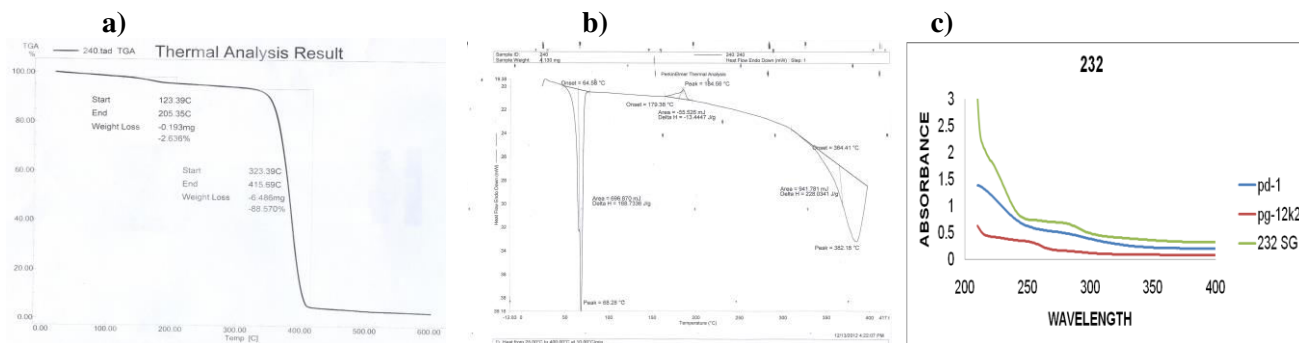


Fig.4. (Sample 232-SG-4):**a)** TGA curve for PEG12K-Pd nanoparticles. **b)** Differential scanning calorimetry of PEG12K-Pd nanoparticles; and c) UV spectra of PEG12K-Pd nanoparticles

The TGA profile for PEG12K-Pd system is shown in **Fig. 4a**. A minor loss of 2.636% at 123.39-205.35 °C temperature range indicates the detachment of the polymer PEG12K from the Pd metal. Prominent losses occur between temperature range 323.39 and 415.69 °C, accounting for a total loss 88.57% which is due to desorption of PEG12K from the surface of the nanoparticles. However the weight loss found (88.57%) seems to be large for decomposition of PEG12K monolayer formed at Pd nanoparticle surface [30]. This indicates that the observed weight loss would include loss of not only PEG12K bound to Pd particles, but also unbound PEG12K molecules and traces of solvent molecules. The presence of two distinct temperatures at which weight loss occurs indicates the possibility of two different modes of binding of the PEG12K molecules with the palladium nanoparticle surface. **Fig. 4b** shows the enthalpies of transitions of PEG12K-Pd nanoparticles. A sharp peak at 68.28 °C and enthalpy 168.7336 J/g shows the melting of polymer (T_m). Second peak around 184.56 °C having enthalpy 13.4447J/g .shows the separation of the polymer from the Palladium metal from one binding site. Third peak (364.41 to 382.81 °C) having enthalpy 228.0341J/g shows the complete separation and degradation of polymer from the entire binding site from the metal. It concludes that as the temperature increases, the state of polymer changes from solid to liquid and finally breakdown of the polymer chain take place. The UV-Vis spectrum of PEG12K stabilized palladium shows absorption maximum at around 272 nm (Fig. 4c) which is characteristic of prepared PEG12K-Pd nanoparticles. From the UV-Vis spectra, it is concluded that PEG has capped the palladium metal, which is also supported by the TGA data.

4. CONCLUSION

The usage of nanodimensional materials provides considerable benefits in a variety of applications that are all different from one another. It is necessary to have a dependable synthesis that is capable of producing nanoparticles that are specifically defined and have a high degree of monodispersity in order to make the most of their utility. The production of PEG12K-Palladium nanoparticles is effectively accomplishing this objective by the utilization of polyethylene glycol 12,000 molecules that are sterical bulky in order to manage the synthesis. This makes it possible to fine-tune the attributes of the nanoparticles that are produced, including their size, shape, solubility, and surface functionality. Examples of such materials are now being investigated for a wide variety of applications, particularly in the field of catalysis, where palladium has the ability to catalyze a wide variety of chemical transformations.

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