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Research Article

Preparation of PEG12K-Pd Nanoparticles & Their Characterization

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Abstract

An efficient synthesis of PEG12K-Pd nanoparticles in water has been developed using PEG12K (Polyethylene ethylene glycol molecular weight 12000) as the capping agent. The stability of the prepared nanoparticles is due to protective polymer Polyethylene glycol molecular weight 12000 employed that fulfils the various requirements. Stable palladium nanoparticles developed by providing low cost high molecular weight polymer polyethylene glycol 12000.This polymer is cheaply available and low cost.

$$\mathrm{Pd(OAc)_2} + \mathrm{PEG12000} \xrightarrow{\text{R.T.,5 hr}} \mathrm{PEG12K\text{-}Pd}$$

Scheme. Synthesis of PEG12K-Pd Nanoparticles

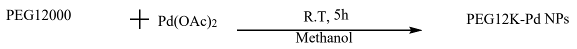
Keywords: Palladium, PEG12K, Nanoparticles, Monodisperse, Water soluble

Introduction

Nanoparticles have become attractive key materials in both academic and industrial areas because of their unique chemical and physical properties, such as catalytic, optical, and magnetic properties distinct from those of bulk metals or atoms [1-4]. Transition-metal nanoparticles have attracted a great deal of attention in the last 10 years; their preparation, structure determination, and applications are topics of current interest [5-18]. The smaller the cluster of atoms, the higher the percentage of atoms are on the surface, rendering nanoparticles very interesting in catalysis [10,15,18]. Metal nanoparticles are used for catalytic hydrogenation of nitroarenes over heterogeneous catalysts. The metal atoms constituting nanoparticles can be generated by (i) chemical reduction of a metal salt, (ii) thermal, photochemical, or sonochemical decomposition of a metal (0) complex, (iii) hydrogenation of a coordinating olefinic moiety, and (iv) vapor phase deposition. To this list proposed by Bradley [6] should be added (v) electrochemical reduction of higher valent species of the metal [13]. During generation of nanoparticles, the following steps have been identified: (i) generation of atoms as above; (ii) nucleation to form an initial cluster of atoms; (iii) growing of the cluster until a certain volume is reached; and (iv) surrounding the cluster by a protecting shell that prevents agglomeration. Therefore, nanoparticles should be formed in the presence of a protecting agent. These protectors can be broadly divided into two categories: those providing electrostatic and those providing steric stabilization. The electrostatic stabilization is based upon the double electric layer formed when ions of the same sign are adsorbed at the nanoparticle surface. It is well known that the catalytic properties of heterogeneous catalysts are dependent on the particle size of the metal and the surface structure of the supports [19]. Transition metal nanoparticles are effective catalysts for chemical transformations due to their large surface area and a unique combination of reactivity, stability, and selectivity. In most cases, the Controlling size and polydispersity of nanomaterials is a key requirement for most of their applications. PEG and PEO with different molecular weights find use in different applications and have different physical properties (e.g. viscosity) due to chain length effects, their chemical properties are nearly identical [20]. In transition metals noble metals have high Standard reduction potential i.e.palladium metal having reduction potential 0.938 V [21]. Nanoparticles have been immobilized on inorganic solid supports [22] or embedded in organic polymers [23], dendrimers [24], multilayer polyelectrolyte films [25], and ionic liquids for separation and reuse [26]. However, the immobilization often suffers from problems such as low reactivity, degradation, palladium leaching, and difficult synthetic procedures. Very recently, reported a simple one-pot method of making recyclable palladium catalyst through generation of palladium nanoparticles from $Pd(OAc)_2$ and Polyethylene glycol [27]. The use of simple and widely available polymers like PEGs as a non-toxic, inexpensive,non-ionic, thermally stable, recoverable, non-volatile polymers have been used for various transformations [28-33]. Transition metal nanoparticles have wide ranging applications in catalysis. However, due to their large surface area and surface energy, they tend to agglomerate during the reactions and therefore need to be stabilized for effective utilization. In this work we described the synthesis and characterization of polymer PEG12K capped palladium nanoparticles of smallest size with low polydispersity.

Experimental

Herein, we report a novel and facile route for preparation of Pd nanoparticles by exploiting PEG molecular weight 12000(M.W.12K), which was found to act as both reducing agent and stabilizer [27]. In the typical experiment a mixture of Palladium acetate $Pd(OAc)_2$ ($5.09x10^{-3}$ M in 1,4-dioxane) solution and PEG, mol. wt. 12000 aqueous solution (2.0028%) in methanol (15 ml) were stirred at room temperature for 5 hours. Immediately after the two solutions were mixed, the solution became slightly yellow and slightly turbid, which indicated aggregate formation before the reduction of palladium ions. With course of time the color of the solution turned from orange to brown and finally turned black, indicating the formation of PEG12K capped Pd(0) metal nanoparticles. **(Scheme 1)**



Scheme 1. Synthesis of polymeic PEG12K-Pd Nanoparticles.

The mixing ratio of the PEG12K and palladium ions (PEG12K/$[Pd^{2+}]$) affected the formation of the spherical aggregates of the palladium nanoparticles. The reduction of Pd^{2+} ions followed an analogous polyol process in the current study [34].

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 anlogus polyol process. In this system electron transfer between metal ions and the hydroxyl group leads to the reduction of Pd^{2+} 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 (Figure 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).

Table 1: Preparation of PEG12K-Pd Nanoparticles.

Sample No.	Volume of PEG12K (2.047%) in ml	Volume of $Pd(OAc)_2$ ($5.09x10^{-3}$ M) in ml	Size in nm (using DLS)	Polydispersity (Standard deviation / $Mean^2$)
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

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 (Figure 1a). Represented TEM images of PEG12K-Pd nanoparticles prepared using the chemical reduction method described in the experimental section is shown in Figure 1b.

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 (Figure 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 (Figure 1c) we can see that the nanoparticles are composed of C, O and Pd; this confirms the presence of palladium metal.

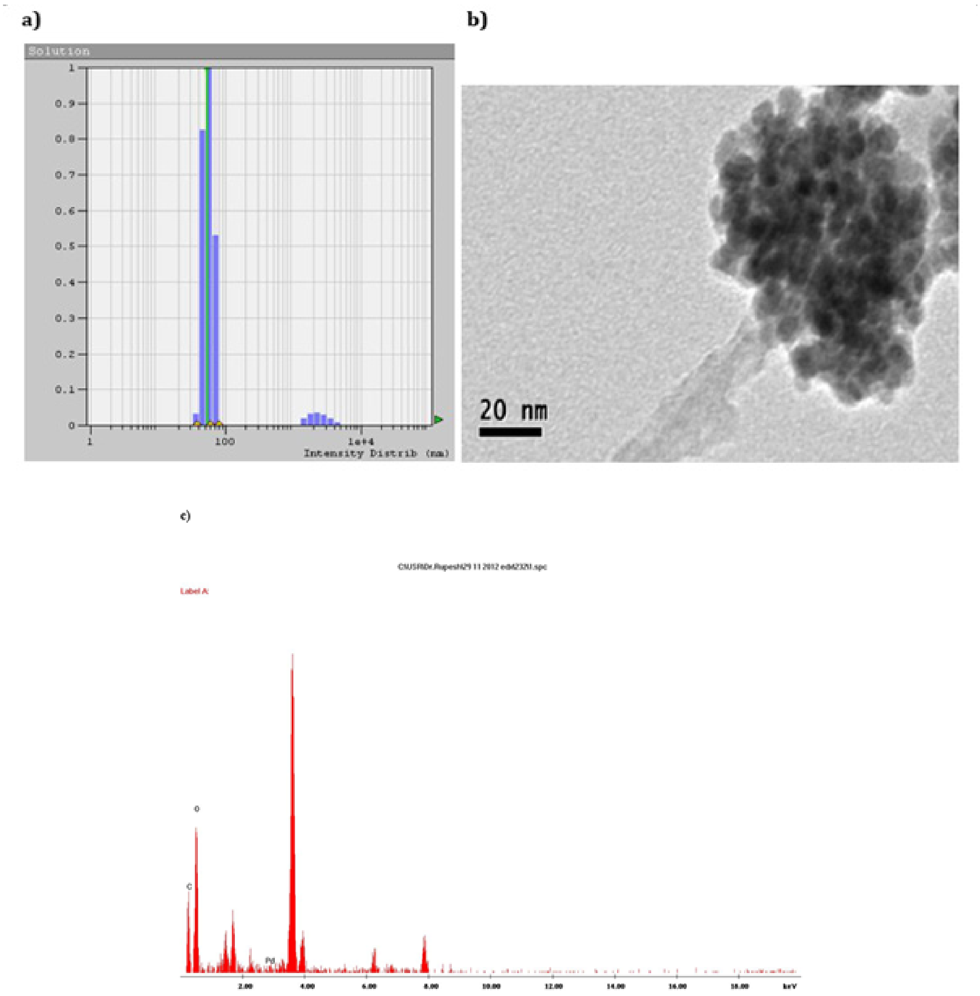


Figure 1: (sample 232-SG-4) c) EDX Data of Synthesized PEG12K-Pd Nanoparticles.

From Figure 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 (Figure 2b). Reflections due to (111) and (200) planes at 2θ=39.64, and 45.62 confirmed the presence of palladium metal in the nanoparticles. EDX data (Figure 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 (Figure 2b) are highly amorphous in nature. Pure PEG12K (Figure 2c) shows that the diffraction peaks between 2θ = 19.16º , 23.24º , 27.2º ,30.76º and 36.25º . The peaks corresponding to the polymer still appears in the XRD pattern of prepared PEG12K-Pd nanoparticles (Figure 2b). Compared with the pure polymer PEG12K, PEG12K–Pd nanoparticles (Figure 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 (Figure 3a) bonded to the palladium metals. The methylene vibration modes at 2891.22 cm^{-1}, clearly seen in Figure 3a and indicate that the hydrocarbon chains capping the palladium nanoparticles are closely packed without a significant density of defects in the chains [36]. 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 (Figure 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 around 1467.32 cm^{-1} (Figure 3b) is due to bending vibration of -CH2 group which was found to be disappeared in the PEG12K-Pd nanoparticles (Figure 3a). A sharp, strong band at 961.77 cm^{-1} and 842.17 cm^{-1} is due to the C-C stretching vibrations (Figure 3a) [37]. The above analysis establishes the formation of the polymer metal interaction.

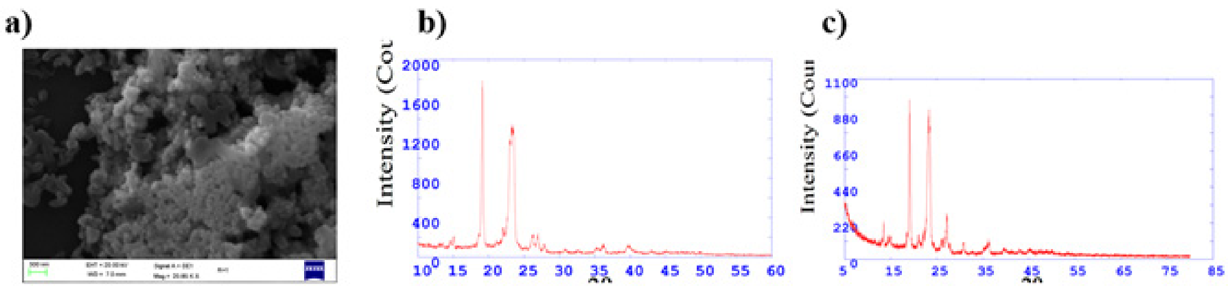


Figure 2: (Sample 232-SG-4): a) SEM Micrograph of PEG12K-PdNanoparticles b) XRD pattern of the synthesized PEG12K-Pd nanoparticles c) XRD pattern of PEG12K polymer.

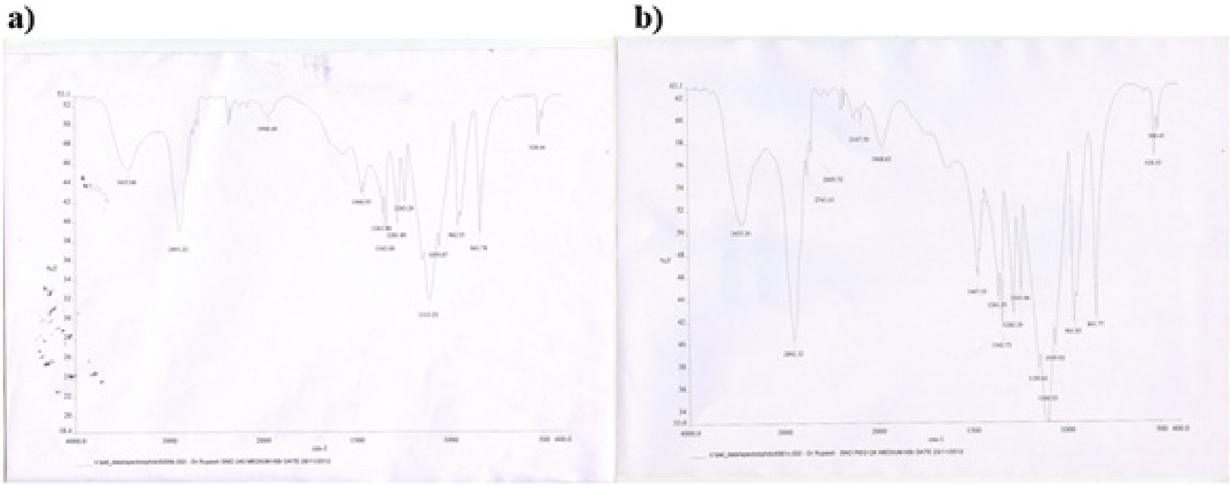


Figure 3: (Sample 229-SG-6): The FT-IR spectra of PEG12K-Pd nanoparticles. b) The FT-IR spectra of pure polymer PEG12K.

The palladium nanoparticles are capped with PEG12K molecules that provided sufficient hydrophobicity to the nanoparticles. These nanoparticles are stable up to several months at room temperature. To understand the stability of these systems at higher temperatures, thermo gravimetric analysis was performed on purified samples. The TGA profile for PEG12K-Pd system is shown in Figure 4a. Prominent losses occur between temperature range 201.56 and 364.36°C, accounting for a total loss 93.976% which is due to desorption of PEG12K from the surface of the nanoparticles.

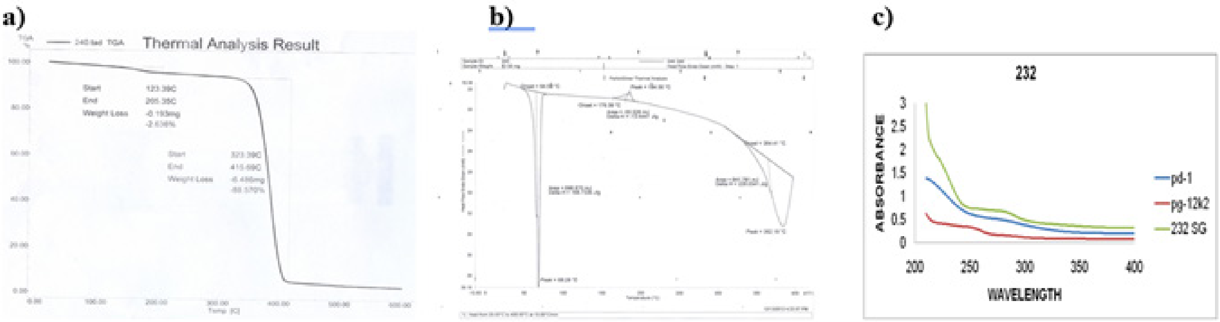


Figure 4: (Sample 232-SG-4): a) TGA curve for PEG12K-Pd nanoparticles. b) Differential Scanning Calorimetry of PEG12K-Pd nanoparticles.c) UV spectra of PEG12K-Pd nanoparticles.

The TGA profile for PEG12K-Pd system is shown in Figure 4a. A minor loss of 2.636% at 123.39 to 205.35°C 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 [38]. 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. Figure 4b. shows the enthalpies of transitions of PEG12K-Pd nanoparticles. A sharp peak at 68.28^0C and enthalpy 168.7336 J/g shows the melting of polymer (Tm). Second peak around 184.56^0C having enthalpy 13.4447J/g shows the separation of the polymer from the Palladium metal from one binding site. Third peak (364.41 to 382.81^0C) 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, (Figure 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.

Conclusion

The utilisation of nanodimensional materials offers significant benefits in a range of different applications. In order to maximise their usefulness, reliable synthesis are required that can generate well-defined nanoparticles with a high degree of monodispersity. This aim is being achieved in the synthesis of PEG12K-Palladium nanoparticles by using polyethylene glycol 12,000 sterically bulky molecules to control the synthesis. This enables properties such as the size, shape, solubility and surface functionality of the resulting nanoparticles to be carefully tuned. Such materials are being explored for many different applications, especially in catalysis, where palladium can effectively catalyse a range of different transformations.

Author Contributions

SG: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - review & editing, Writing - original draft.

DTM: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Validation.

RK: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft, Funding acquisition, Supervision, Validation, Visualization.

Conflicts of Interest

There are no conflicts to declare.

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