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SCHOLARENA

Journal of Nanoscience and Nanotechnology Applications

RESEARCH ARTICLE

ISSN: 2577-7920

Preparation of Quercetin-Pd Nanoparticles and their Characterization

Shweta Gupta[1], Rupesh Kumar[2,*] and Dhanraj T Masram

[1]*Department of Chemistry, Kalindi College, University of Delhi, East Patel Nagar, Patel Nagar, New Delhi, Delhi-110008, India*

[2]*Department of Chemistry, Kirori Mal College, University of Delhi, Delhi-110007, India*

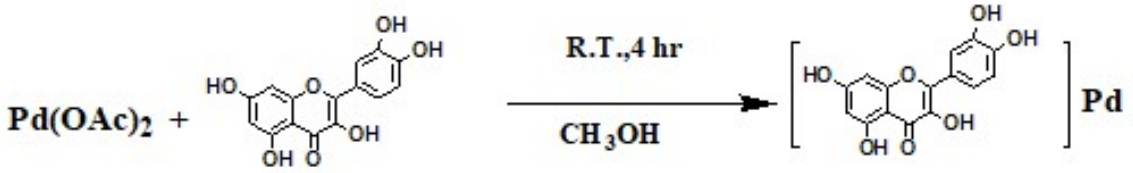
[3]*Department of Chemistry, University of Delhi, Delhi-110007, India*

[*]**Corresponding Author:** Rupesh Kumar, Department of Chemistry, Kirori Mal College, University of Delhi, Delhi-110007, India, Tel: 91-9818901344, E-mail: chembio005@yahoo.co.in

Citation: Shweta Gupta, Rupesh Kumar, Dhanraj T Masram (2024) Preparation of Quercetin-Pd Nanoparticles and their Characterization, J Nanosci Nanotechnol Appl 8: 101

Abstract

An efficient synthesis of Quercetin-Pd nanoparticles in water has been developed using methanol as solvent as well as reducing agent. In this work we described the synthesis and characterization of Quercetin capped palladium nanoparticles with low polydispersity in size.



Scheme: Synthesis of Quercetin-Pd Nanoparticles

Keywords: Palladium; Quercetin; 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 various methods. To this list proposed by Bradley [6] should be added 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].

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, 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. Quercetin is a pentahydroxyflavone having the five hydroxy groups placed at the 3-, 3'-, 4'-, 5- and 7-positions (Scheme 1). It is one of the most abundant flavonoids in edible vegetables, fruit and wine. In this work Querectin molecule has a role as a chelator as well as stabilizer due to presence of presence of six oxygen containing functional groups. We described the synthesis and characterization of polymer Quercetin capped palladium nanoparticles with low polydispersity in size. The development of chemical processes with minimal environmental impact has become a major area of interest in the scientific community.

The use of water as a solvent and the design of recyclable catalysts are some of the promising directions in this field. Among water--soluble catalysts, a great deal of attention has been focused on metal nanoparticles. Water-soluble Pd(0) nanoparticles are a promising class of catalysts in some organic processes, mainly in hydrogenation, oxidation and cross-coupling reactions for the formation of C-C bonds. A wide range of stabilizers for the preparation of nanoparticles are known, in order to prevent their aggregation. Among them, polymers provide stabilization by entrapment, both through their steric bulk and through the weak dative bonds between the nanoparticle surface and the hetero atoms present in the structure of the protective agent. In this context, our work has been focused on the use of Quercetin molecule as stabilizing agents for metal nanoparticles.

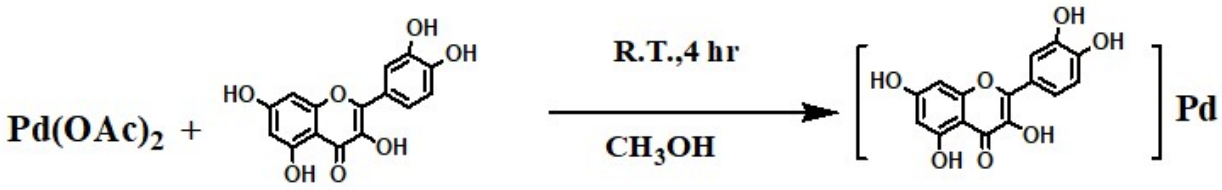
In this work, it has been synthesized a new Quercetin -Pd nanoparticles. The resulting material bearing quercetin molecules has been successfully used as stabilizer for the preparation of water-soluble palladium nanoparticles. We expect that also the present study can accelerate the investigation of Quercetin -Pd nanoparticles as a catalyst in organic synthesis. In the present study we used Quercetin as a stabilizer for palladium nanoparticles. We report a novel and facile route for the preparation of Pd nanoparticles by exploiting Quercetin molecule which was found to act as stabilizer.

The prepared Quercetin-Pd nanoparticles can be preserved for months under dark condition without any change of physical and chemical properties. Preparation of polymeric Quercetin-Pd nanoparticles was achieved successfully by the reaction a solution of Pd (OAc)2 in 1,4-dixoane with methanolic solution of quercetin in methanol at room temperature in a 30 ml closed vial for 4 hr. Pd(II) ions reduced to Pd(0) because of the presence of the terminal –OH functional group present methanol as solvent.

Experimental

Typical Experimental Procedure for Preparation of Quercetin-Pd Nanoparticles

Herein, we report a novel and facile route for preparation of Quercetin-Pd nanoparticles by mixing of Palladium acetate $Pd(OAc)_2$ ($5.09x10^{-3}$ M) solution and methanolic solution of Quercetin ($4.404x10^{-3}$ M) in methanol (15 ml) were stirred at room temperature for 4 hours (Scheme 1). With course of time the color of the solution turned from orange to brown and finally turned Yellowish-black, indicating the formation of Quercetin capped Pd(0) metal nanoparticles.



Scheme 1: Synthesis of Quercetin-Pd Nanoparticles

Size of prepared nanoparticles was characterized by QELS and TEM spectroscopic techniques. The reduction of Pd2+ ions could follow an analogous polyol process in the current study [34]. When Pd 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, where electron transfer between metal ions and the hydroxyl group of methanol leading to the reduction of Pd2+ to Pd (0). It is assumed that Pd(0) metal has interaction with negatively charged oxygen atoms of quercetin molecules at different sites.

Table 1: Preparation of Quercetin-Pd Nanoparticles

Sample No.	Volume of Quercetin($4.404x10^{-3}$ M) in ml	Volume of $Pd(OAc)_2$ ($5.09x10^{-3}$ M) in ml	Size in nm (using DLS)	Polydispersity (Standard deviation / $Mean^2$)
221-SG-1	0.2	0.8	38.26	1.145
221-SG-2	0.4	0.6	29.10	0.016
221-SG-3	0.5	0.5	31.32	0.067
221-SG-4	0.6	0.4	46.21	0.063
221-SG-5	0.8	0.2	134.6	6.368
221-SG-6	0.9	0.1	2095	3.988

In sample 221-SG-3 (Table 1) it was found that the monodisperse smallest size Quercetin-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 Quecetin, the concentration of the metal ions are systematically changed to achieve the smallest size Quercetin-Pd nanoparticles (Table 1; sample 229-SG-3).

Results & Discussion

Characterization by QELS, TEM,SEM, & XRD Spectroscopic Techniques

QELS evaluation (Table 1; sample 221-SG-3). of the nanoparticles indicates that the size distributions of the particles are very narrow. Sample 221-SG-3 found to be smallest size 31.32 nm having polydispersity 0.067 (Table 1). We begin the studies with some preliminary investigations of the particle core size by using DLS (Figure 1a).Represented TEM images of Quercetin-Pd nanoparticles prepared using the chemical reduction method described in the experimental section is shown in Figure 1b.

a)

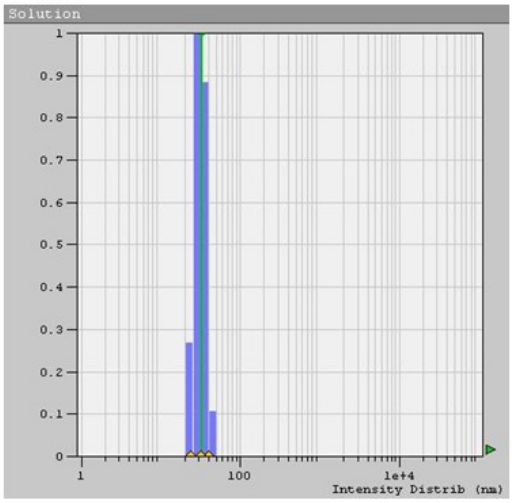


Figure 1a: (sample 221-SG-3) a) DLS data of Quercetin-Pd Nanoparticles

b)

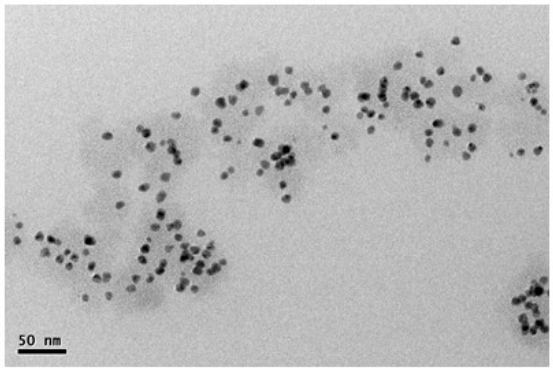


Figure 1b: (sample 221-SG-3) **b)** TEM image of Quercetin-Pd nanoparticles shows that 8-9 nm sized

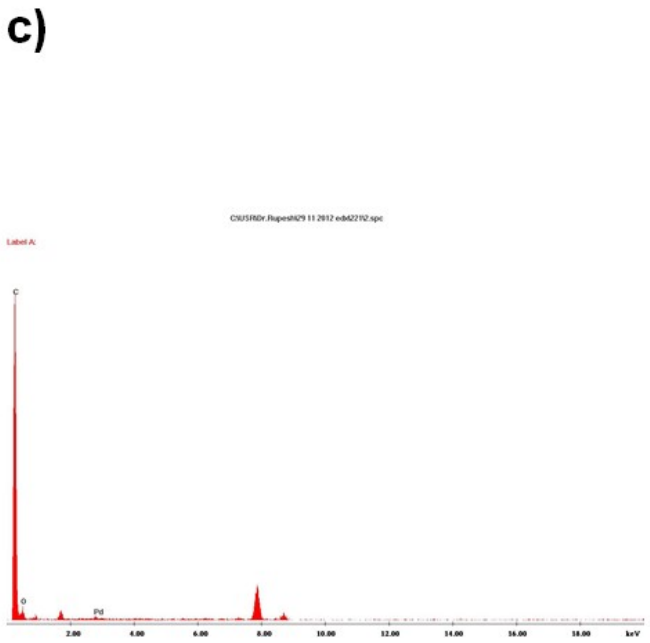


Figure 1c: (sample 221-SG-3) **c)** EDX Data of Synthesized Quercetin-Pd Nanoparticles.

Prepared nanoparticle possesses an average diameter of 8.0 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 TEM analysis implies that the individual nanoparticles are highly dispersed and circular in morphology without any agglomeration.The prepared Quercetin-Pd nanoparticles remained dispersed for several months with no obvious change in the size. The composition of Quercetin -Pd was further probed by EDX analysis (Figure1c). 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.

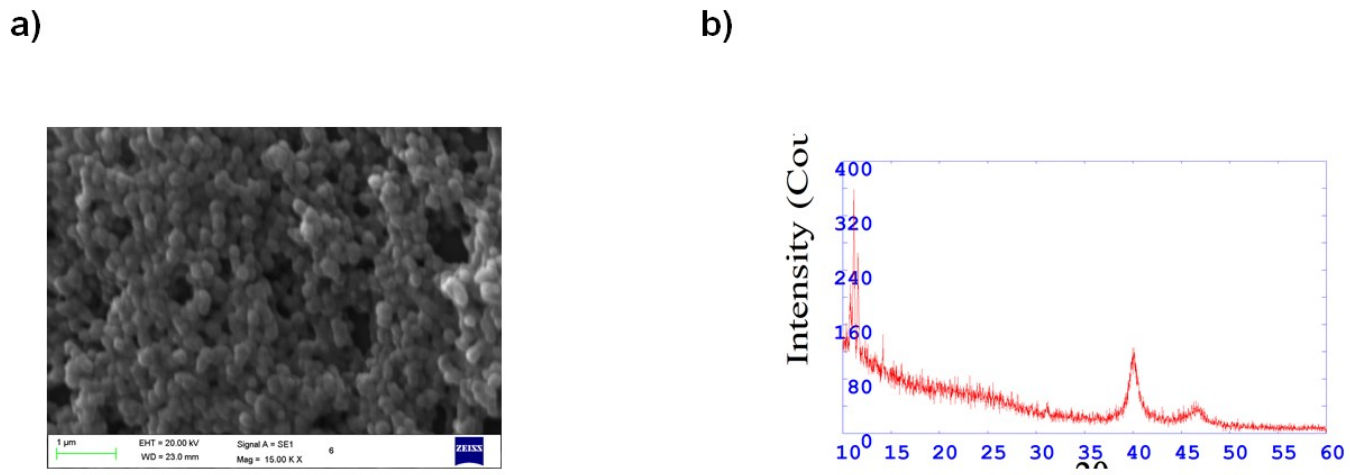


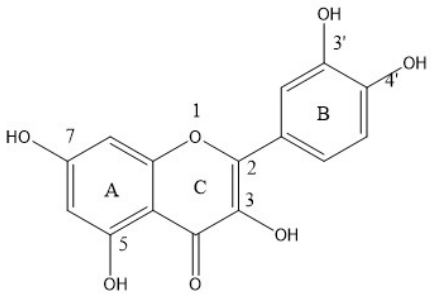
Figure 2: (Sample 221-SG-3): a) SEM Micrograph of Quercetin-PdNanoparticles b) XRD pattern of the synthesized Quercetin-Pd nanoparticles

From the Figure 2a. it is obvious a large amount of sample is dispersed on the slide .The average grain size was found to be 160 nm with round morphology. Agglomerated grain were attached on the polymer surface .The surface property was found out to be

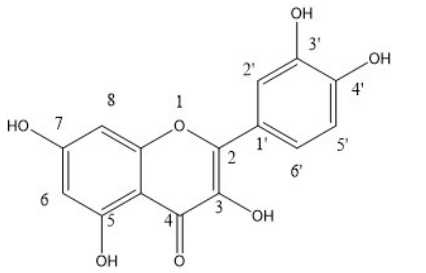
spherical geometry, rough without any specific pattern. The formation of nanoparticles is confirmed by observation of broad peaks in the XRD spectrum (Figure 2b). Reflections due to (111) and (200) planes at 2θ=39.64, and 45.62 confirmed the presence of palladium metal in the nanoparticles. EDX data (Figure 1c) shows the high content of carbon (98.3% by atomic weight) in the prepared nanoparticles. Presence of high carbon content shows that prepared Quercetin-Pd nanoparticles in the obtained powdered XRD (Figure 2b) are highly amorphous in nature.

Characterization by IR Spectroscopic Techniques

Quercetin have different key points due to which it is able to undergo metal complexation (Scheme 2.1). The interaction of quercetin with the palladium cluster surface mainly takes place through C5 OH/C4=O and C4=O/C3–OH groups placed in A-ring and C-ring (Scheme 2.2). The intermolecular interaction of nanoparticles system was established by FT-IR. Compared with the pure Quercetin molecules, Quercetin–Pd nanoparticles showed flattening of spectral band at around 2000 cm-1, which is assigned to presence of Pd (0)–O compounds.[3] It is observed that there is broadening of band at 3369.06 cm-1 due to binding of phenolic –OH groups with palladium metal which is further confirmed by broadening in the range 2400 to 1700 cm-1 (Scheme. 2.3).

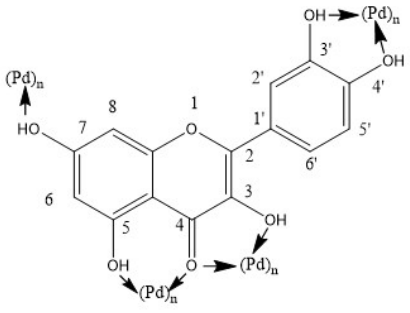


Scheme 2.1



2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-chromen-4-one

Scheme 2.2



Scheme 2.3

Figure 3(b) shows pure Quercetin presenting the characteristic intensities of -C= O absorption band at 1662.77 cm−1 and the OH stretch at 3321.05 cm−1. However, the spectra from the Quercetin-Pd nanoparticles (Figure 3(a)) showed that the C=O absorption band of Quercetin was shifted toward lower wavenumber [4] 1636.07 cm-1and the OH stretch of Quercetin shifted to higher wavenumber 3369.06 cm-1. This means oxygen atom of -C=O group of quercetin also involved binding with palladium metal and no intramolecular hydrogen bonding in nanoparticles with 3-OH of quercetin molecule (Scheme 2.3). A new sharp band appears in Quercetin-Pd nanoparticles at 1636.07 cm-1 (Scheme 2.3) which due –C=O group interaction with palladium metal. Bands at 1507.73 cm-1 and 1472.61 cm-1 peaks are present in Quercetin-Pd nanoparticles Figure 3(a) due to aromatic rings. Sharp band at 1293.41 cm-1 is due to -C-OH deformation vibrations. Bands due to C-OH stretching vibration are present in Quercetin-Pd nanoparticles (Figure 3(a)) at 1165.70 cm-1, 1086.59 cm-1 and 1044.30 cm-1 (Figure 3(a)).[5].

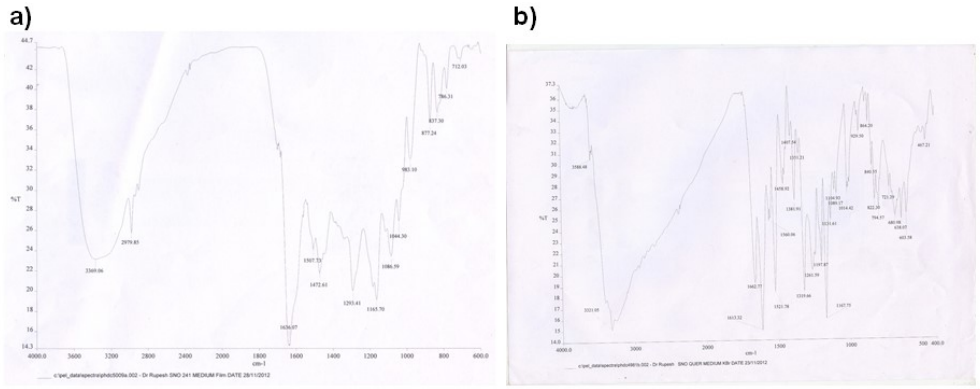


Figure 3: (Sample 221-SG-3): The FT-IR spectra of Quercetin-Pd nanoparticles. b) The FT-IR spectra of pure Quercetin

The palladium nanoparticles are capped with quercetin molecules that provided sufficient hydrophobicity to the nanoparticles. These nanoparticles are stable up to several months at room temperature under dark conditions. It is assumed that in Quercetin-Pd nanoparticles a single quercetin molecule interacted with palladium clusters from its functional groups (Scheme 2.3).

Characterization by TGA DSc & UV Techniques

To understand the stability of these systems at higher temperatures, thermo gravimetric analysis were performed on purified samples. The TGA profile for Quercetin-Pd system is shown in Figure 4(a). A continuous loss of 26.559% at 25.10 to 259.29°C indicates the detachment of the Pd metal the from two sites of the Quercetin molecule Scheme 2.3 (3'& 4' –OH groups of aromatic ring & 7 –OH group).[38] Further continuous losses occur between temperature range 259.29 and 596.70 °C, accounting for a total loss 23.229% which is assumed due to complete breakdown six and five membered rings of quercetin with the palladium metal (Scheme 2.3). A deep curve at 62.32 °C and enthalpy 27.2828 J/g shows detachment of the Pd metal from two sites of the Quercetin molecule Scheme 2.3 (3'& 4' –OH groups of aromatic ring & 7 –OH group). Second peak around 199.63°C having enthalpy 67.2477 J/g shows the separation of six and five membered rings of quercetin with the palladium metal (Scheme 2.3). The UV–Vis spectrum of Quercetin –stabilized palladium shows absorption maximum at 290 nm & 230nm (Figure 4 (c)). Whereas Quercetin shows the band at 370 & 250 nm. So there is a blue shift in the wavelength. From the UV–Vis spectra it is concluded that Quercetin capped the palladium metal

which is also supported by the TGA data (Figure 4(a)).

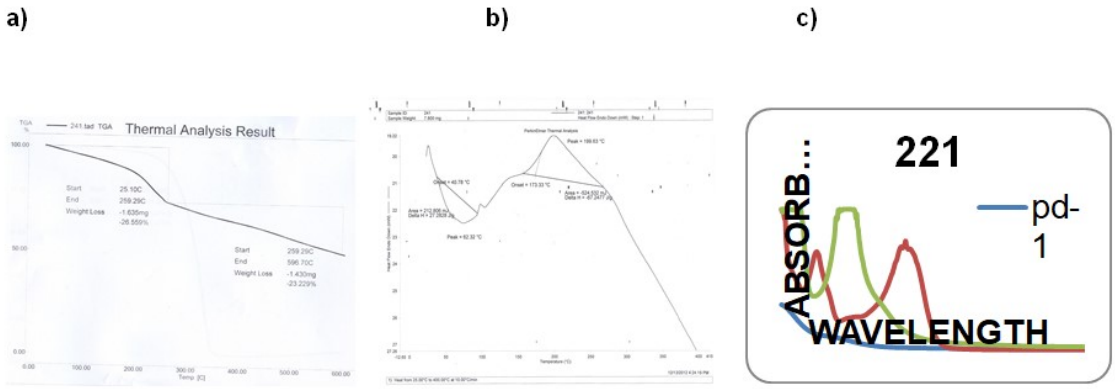


Figure 4: (Sample 221-SG-3):a) TGA curve for Quercetin-Pd nanoparticles. b) Differential Scanning Calorimetry of Quercetin-Pd nanoparticles.c) UV spectra of Quercetin-Pd nanoparticles

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 Quercetin-Palladium nanoparticles by using Quercetin molecule to control the synthesis. This enables properties such as the size, shape, solubility and surface functionality of the resulting nanoparticles to be carefully tuned. Quercetin-Pd nanoparticles can be explored in future studies for many different applications, especially in catalysis, drug delivery, anti-oxidant and sensing where palladium can effectively alter the desired properties of Quercetin molecule.

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

Acknowledgements

We are pleased to acknowledge financial support from UGC No.F.30.-109/2015 (BSR) for this investigation. We are also thankful to Department of Chemistry,Kirori Mal College, University of Delhi and USIC of D.U for providing technical support.

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