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ORIGINAL ARTICLE

Dual probes of Ag/Pd bimetallic NPs facilely synthesized by green process using Catharanthus leaf extract on textile dye removal and free radical capability

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Abstract

Silver–palladium (Ag/Pd) bimetallic nanoparticles were synthesized by greener way using Catharanthus leaf extract. The synthesized silver/palladium bimetallic nanoparticles were used to degrade the safranin O textile dye through photo catalytic activity and the free radical scavenging property was evaluated by DPPH assay test. Silver/Palladium bimetallic nanoparticles were synthesized by biogenic reduction method using silver nitrate and palladium chloride precursors assisted with CRL extract. The synthesized Ag/Pd bimetallic nanoparticles' morphological and particle size were evaluated by the SEM/TEM image. The particle size was found to be within the nanoscale range of 15–30 nm. The 98% maximum dye degradation for 40 min time duration was achieved by the photocatalytic activity of silver/palladium bimetallic nanoparticles through UV light irradiation on safranin O textile dye and simultaneously antioxidant activity of silver/palladium bimetallic nanoparticles was also tested through DPPH assay test. The free radical scavenging efficiency was calculated for extract and extract with silver/palladium nanoparticles and was found to be 48.2% and 70.2%, respectively and revealed that the silver/palladium nanoparticles have 2.34 times higher scavenging activity when compared with Catharanthus leaf extract.

Keywords Ag–Pd bimetallic NPs · Green synthesis · X-ray diffraction · SEM/TEM · Safranin O · DPPH

Introduction

In present scenario antioxidants intake has been found to be an effective health impact. Free radicals are generated from the outcome of environmental factors such as cigarette smoke, air pollution and radiations etc., these free radicals are a serious problem to affect the human body and damaged the DNA cells leads to chronic infections, and degenerative diseases like cancer, arthritis, and atherosclerosis (Watters et al. 2007). Very few Synthetic antioxidants are found to be

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in dietary sources like butylated hydroxyl toluene, tertiary butylated hydroquinone & gallic acid are mostly toxic may absorb on the human body And also have adverse effects in bio-medical industries due to their limitations (Anagnostopoulou et al. 2006) and are also medicinal plants such as flavonoids, terpenoids, tannins, saponins, polyphenols and anthocyanins have also used good inhibiting free radical for antioxidant property. However noble metal nanoparticles (NPs) like silver, palladium, gold, platinum NPs have been synergistically improved by making them bi-metallic NPs on antioxidant activity (Bera et al. 2012; Yu et al. 2012).

Up to date the dye wastes derived from fabric, pigments, plastics, and textile, dye industries are highly hazardous to aquatic living systems as well as to cause very damage to the entire environment (Yu et al. 2012; Nasrollahzadeh et al. 2016).Dye effluents from the textile industries posses' serious threat to the environment and numbers of techniques are available to remove of dye such as aerobic and anaerobic microbial treatment, nano filtrations, activated carbon and using nanomaterials etc., Among the various methods can be influenced by dye removal techniques are coagulation, flocculation, oxidation, catalytic reduction, and photo catalytic dye degradation (Nasrollahzadeh et al. 2016; Ilunga and Meijboom 2016).

In recent research explored have shown that catalytic activity of noble bimetallic nanoparticles such as silver/gold, silver/palladium (Ag/Pd), silver/Nickel, gold/platinum were found to be more effective when compared with monometallic counterparts like silver, gold, platinum due to its unique properties and high surface area to the volume ratio and intermetallic interaction. Specially, Silver/palladium bimetallic nanoparticles has wide spectrum of applications due to their distinctive optical and electrical properties(Rostami-Vartooni et al. 2016).In this connection a lot of research work has been done on different noble bi-metallic nanoparticles using different precursors towards the size reduction and shape modification with wide optical properties and biomedical applications. Recently, Ag/Pd NPs has been synthesized by several researchers for various applications like: Chen et al. prepare the Ag–Pd NPs via laser irradiation and studied (Chen et al. 2002), Tong et al. prepared the Ag–Pd NPs via electro spinning route and presented their applications towards hydrogen generation (Tong et al. 2014), Damle et al. synthesized the Ag–Pd NPs via ion-entrapment route and studied (Damle et al. 2002), Shang et al. reported the synthesis of Ag/Pd NPs via chemical sonication and characterized for hydrolysis (Shang et al. 2016), Yang et al. synthesized the Ag/Pd NPs via reactive micelles route and presented its application for depositing the electroless Cu (Yang et al. 2004), Lee et al. reported the synthesis of CNT supported Ag/Pd NPs via self-regulation SDS reduction for electro catalysts applications (Lee et al. 2011), Yan et al. prepare the C coated Ag–Pd NPs via heat-treatment (Yan et al. 2004), Zhang et al. prepared the Ag–Pd NPs via thermal decomposition route and studied for catalytic applications (Zhang et al. 2015), Li et al. documented the GO decorated with bi-metallic Ag/Pd NPs for electrochemical sensing (Li et al. 2015), Vasan et al. chemically prepared the Ag–Pd NPs and studied (Vasan and Rao 1995), Pergolese et al. reported the bimetallic Ag/Pd NPs synthesis with improved SERS efficiency (Pergolese et al. 2007), He et al. reported the fabrication of Bimetallic Ag–Pd NPs in ultrathin film TiO_2-Gel via ion-exchange/reduction route and studied their shape and Catalytic nature (He et al. 2003), etc.

The reports reveal that the Ag/Pd NPs are having fascinating applications and green approach has not been employed to prepare these. Noble mono and bi-metallic nanoparticles have several synthetic routes like chemical reduction method (Njoki et al. 2007), solvothermal (Zhan et al. 2011), ɤ-ray radiation, micelles formations and Co-reduction methods but these all the methods having some limitations such as high expensive with toxicity, and face environmental problem due to byproduct formation. However, green approach preparation of metal NPs entities have considerable attention owed to their environment viability and owing to their biomedicinal applications. Hence, here in this present report we have focus on to synthesize silver/palladium bimetallic nanoparticles through green approach using methanolic Catharanthus leaf extract for the first time and evaluate its photo catalytic activity on dye degradation and also evaluate the performance antioxidant property by DPPH test.

Methodology

Collection of materials from plant and chemicals

The *Catharanthus roseus* (CR) leaves were collected in Government Arts College, Karur, Tamil Nadu, India and all the chemicals (Silver nitrate > 99.9% and palladium chloride 99.9%, AR grade) were purchased from Merck and used as such. Deionized water has been used in the entire experimental studies.

Soxhlet extraction method

This procedure followed through literature with slight modified (Swamy et al. 2015). The strong and healthy *Catharanthus roseus* leaves were extracted by solvent extraction method at 70 °C. The collected CR leaves were meticulously washed several times in water & then the visible particles were removed by air dry. Air-dried bio-mass was transformed into powder through an electrical blender. Solvent extraction of 1 g CR leaves powder was treated with methanol in Soxhlet extractor. The extraction process was stopped after the period of about 6–7 cycles. The obtained

methanolic extracts were separated by petroleum ether and then with ethyl acetate washed three times and concentrated layer was evaporated. The ethyl acetate extracts was then stored at 4 °C. The prepared methanolic extract from CR leaves was employed as a capping agent and also as an agent for reduction for nanoparticles green preparation.

Flavonoid analysis

The existence of Flavonoids in extract has been tested by adding 5 drops of 5% NaOH solution with further addition of 2 mL of 10% HCl which change the color from the yellow into colorless that confirms the presence of flavonoids (structure of flavonoids is shown in Fig. 1).

Synthesis of co-nanocatalyst (CNC)

Silver–palladium (Ag/Pd) bi-metallic NPs were successfully prepared via green synthesis by employing extract of methanolic *C. Roses* leaf. A properly mixed bi-nary aqueous solution was readied 40 ml of 1 mM silver nitrate and 1 mM palladium chloride (1:1 ratio) solution. 10 ml of methanolic *C. Roses* leaf extract was then added to this solution with stirring for about 1 h in the nitrogen atmosphere where the rapidly reduction Ag^{+} to $(Ag/Pd)^{0}$ results in bi-metallic nanoparticles.

Photo catalysis method

The powerful tool of Ag/Pd bi-metallic NPs on safranin O dye removal was evaluated by photo catalysis. The mercury lamp (120w) was engaged as a UV light irradiation source. Aliquots 8 mg of the Ag–Pd bi-metallic NPs was mixed with 40 ml of (10 ppm/L) solution of safranin O dye. A blank safranin O dye solution was also kept for without nanoparticles. Prior to irradiation, the sample preparation was made by treating dye (10 ppm) with silver/palladium nanoparticles with the help of magnetically stirrer for 45 min to ensure the adsorption–desorption equilibrium of reaction mixtures. Later the color was changed from bright red to colorless when subjected to the reaction mixture under the UV light irradiation (mercury lamp 120w) with regular time intervals, aliquots of 4 ml suspensions were centrifuged at 5000 rpm for 20 min. The saturated solutions were subjected to Jasco-V-630 UV–Visible spectrophotometer for recording absorption spectra and rate of degradation of safranin O dye was observed by means of spontaneous reduction in absorption peak at ($\lambda_{max} = 519$ nm). The dye removal efficiency was calculated using the following formula;

$$(\%)\ \text{Removal efficiency} = \left(\left(C - C_0/C\right) \times 100\right) \quad (1)$$

where C—Initial dye concentration without nanoparticles on UV light irradiation, C_0—illumination of dye concentration on Ag–Pd bi-metallic nanoparticles.

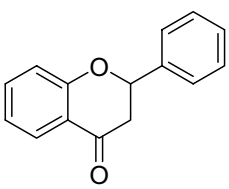

Fig. 1 Structure of flavonoids

Radical scavenging activity

This activity of Ag–Pd bi-metallic NPs was studied through DPPH assay test with slight modification (Villaño et al. 2007) in various concentration of Silver–Palladium bi-metallic nanoparticles (100, 200, 300 µl/ml) and it was mixed with 2 ml of 0.1 mM DPPH (1,1,2-diphenyl picryl hydroxyl radical) solution and the reaction blend was incubated under dark place for 30 min. The blank (DPPH) solutions were recorded at 517 nm against ethanol and compare this with standard solutions of CRL extract. Later, the dark purple color was disappeared into the yellow color solution which corresponds to the higher free radical scavenging activity of Silver/Palladium bi-metallic nanoparticles in presence of DPPH. The percentage of inhibition of free radical scavenging activity was calculated using this formula

$$(\%)\ \text{of radical Efficiency} = \frac{\text{OD in control solution} - \text{OD in reaction mixture}}{\text{OD in control solution}} \times 100 \quad (2)$$

Control—DPPH (without NPs) and Reaction mixture—DPPH @(Ag/Pd NPs).

Physio-chemical characterization

The development of Ag and Ag/Pd bi-metallic NPs was confirmed by UV–Visible spectrum analysis of (model Jasco-v-630), with optical resolution of 1 nm and the wavelength range between 300–800 nm. FTIR spectra were carried out using Agilent spectrometer. FTIR spectrophotometer in the wavelength range of 4000–650 cm^{-1} with the operating resolution of 4 $cm^{-1}$was employed to deduce the functional groups existing in pyto-compounds. The size, shape and morphological characteristics of synthesized silver/palladium bi-metallic nanoparticles were performed by NOVA-450 SEM and the percentage of an element was analyzed by energy dispersive spectroscopic techniques (EDX). TEM: size and shape of 2-optimum biogenic Ag@Pd NPs were inspected through TEM system operated at 200 kV furnished with SAED. The NPs colloid

specimens were placed as drop on a carbon coated at copper grid at room temperature. The structural and crystallite phase were characterized by XRD (powder X-ray diffraction) model (PW3050/60) using CuKα1 = 1.540 A0, Kα2 1.544 A0. (XPERT-PRO) software.

Results and discussion

Optical properties of bimetallic (Ag/Pd) nanoparticles

The formation of Ag, Pd mono and Ag/Pd bi-metallic NPs were inveterate via absorption spectra as revealed in Fig. 2a. Yellowish to brown color of bi-metallic colloids revealed that the surface plasmonic band arising due to the collective electron moiety induced by an interacting electromagnetic field (Song and Kim 2008). The spectra for CR leaf's extract possess no absorption band in 300–800 nm region, whereas the spectra measured through speedy reduction progression showed absorption peaks at 406 nm, and 372 nm, which are linked to surface Plasmon resonance (SPR) wavelength of Ag, Pd, and Ag/Pd bi-metallic NPs. These UV/Vis spectrum outcomes are well agreed to former reports (Wang and Cao 2007). The Ag/Pd bi-metallic NPs possess maximum absorption band at 372 nm, this is strongly agreed to Ag, monometallic nanoparticles (Ag/Pd) 1:1 proportion onwards (Wang and Cao 2007). Thus, the absorption profile confirms the development of Ag–Pd NPs.

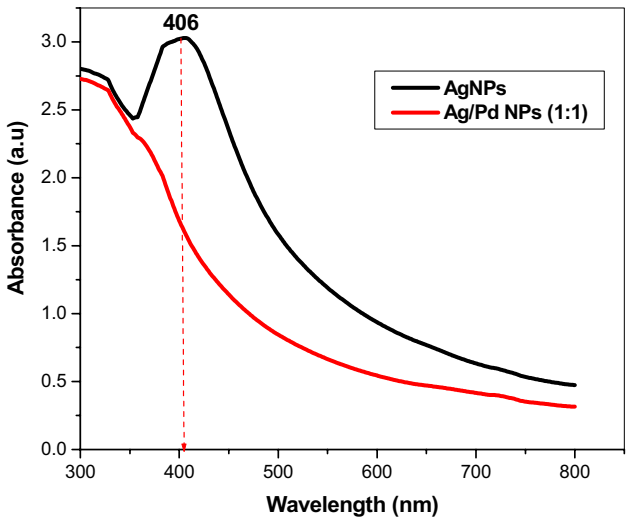

Fig. 2 UV–Visible absorption spectra of formation of AgNPs (light brown) and Ag/Pd (deep brown) nanoparticles 1:1 ratios using *C. roseus* leaf extract

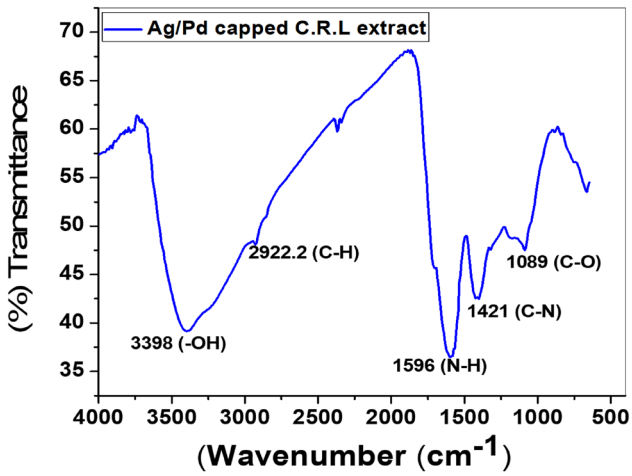

Fig. 3 FT IR spectrum of bio-synthesized silver/palladium bi-MNPs with capped methanolic extract of Catharanthus roseus leaf (CRL) extract

Functional group analysis and identification of crystal structure and size

FT IR spectral analysis was accomplished (Fig. 3) to the congruence of the pyto-molecules responsible for capping and stabilized silver/palladium bi-metallic nanoparticles. The silver/palladium bi-metallic alloy (or) core–shell nanoparticles were attributed strong and broad region at 3398 cm^{-1} was appropriate as υ(–OH) stretching vibration in presence of poly-phenols from CRL extract (Kasthuri et al. 2009). A region was observed at υ(2922.2 cm^{-1})that could be appropriated to the C-H stretching vibration of Methylene groups (Huang et al. 2007).The strong and middle of the absorption band at υ(1596 cm^{-1})was characteristic of amide II (N–H) band of protein. The present result revealed that proteins are interacting with pyto-capped silver/palladium bi-metallic nanoparticles using CRL extract and are also their secondary structure was not be affected during the reaction with Ag^{+}/Pd^{2+} ion (or) binding with Ag/Pd nanoparticles. The band at υ(1416 cm^{-1})correlated with to C–N stretching vibration of aromatic amine (Suman et al. 2013).

The synthesized silver, palladium monometallic and Ag/Pd bi-metallic NPs were in polycrystalline nature examined by PXRD patterns. XRD pattern of Ag/Pd bi-metallic NPs is displayed in Fig. 4. The four diffraction peaks had noted that and the appropriate the lattice planes such as (111)*, (200) and (311) correspond to Ag, palladium NPs and Ag/Pd bi-metallic NPs, correspondingly. The protuberant peak (111)* is agreed with Ag, Pd mono and silver/palladium bimetallic or core shell NPs, respectively (Mane Gavade et al. 2015; Kumar et al. 2016). The other intensity peaks were noted in primary pytochemical analysis of C.R leaf extract infers the presence of secondary metabolites group

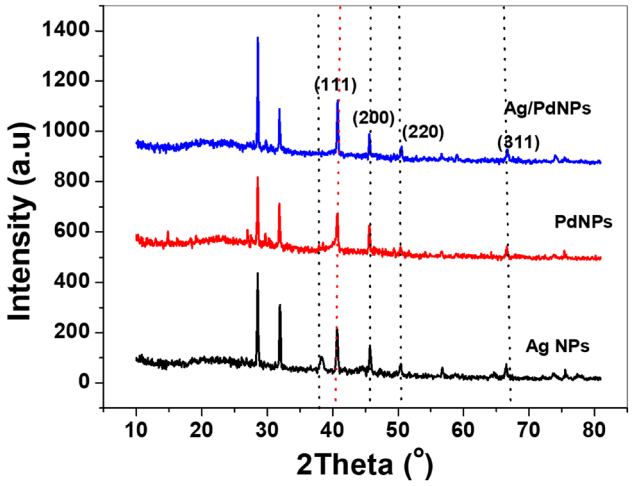

Fig. 4 Powder XRD patterns for Ag, Pd mono and Ag/Pd NPs using *C.R* leaf extract

such as flavonoids, anthocyanins and tannins were clearly located at 27.6 and 32.8° respectively (Bagherzade 2017). The JCPDS data (Ag 4–754; Pd 42–784; Ag/Pd 24–628) has been considered as an evident for indexing the predominant peak in XRD pattern.

The mean crystallite size (*D*) of the Ag–Pd bi-MNPs was calculated from Scherrer equation (Krishnan and Pradeep 2009).

$$D = 0.9\,\lambda/\beta\,\cos\theta \quad (3)$$

Here λ is wavelength and β is FWHM.

Morphological, elemental and particle size analysis

The surface morphological spectrum of silver, palladium &Ag/Pd bimetallic NPs is shown in Fig. 5a. From these SEM image were depicted in cubic like tetragons shaped with no agglomeration of poly-dispersed Ag–Pd bi-metallic nanoparticles respectfully. The average particles size was found to be 15–30 nm. And percentage of elemental composition silver/palladium bi-metallic or core shell nanoparticles was affirmed by EDX analysis. The successful development of bi-metallic NPs is publicized in Fig. 5b represented the strong signal in the Ag and Pd regions were confirmed at 3 keV. This was due SPR. The susceptible signal for chlorine, oxygen, and potassium was also examined which means that they are also absorbed poly-phenols present in the formation of silver/palladium bi-metallic nanoparticles.

TEM analysis

Figure 6 demonstrates the TEM images of Ag/Pd NPs along with SAED profile having concentric rings that signify a polycrystalline Ag/Pd core shell structure (Fig. 6b). The Ag/Pd core shell NPs represents non-agglomerated Ag/Pd bi-metallic NPs and quasi-spherical shape. The observed particle size for bimetallic nanoparticles according to the

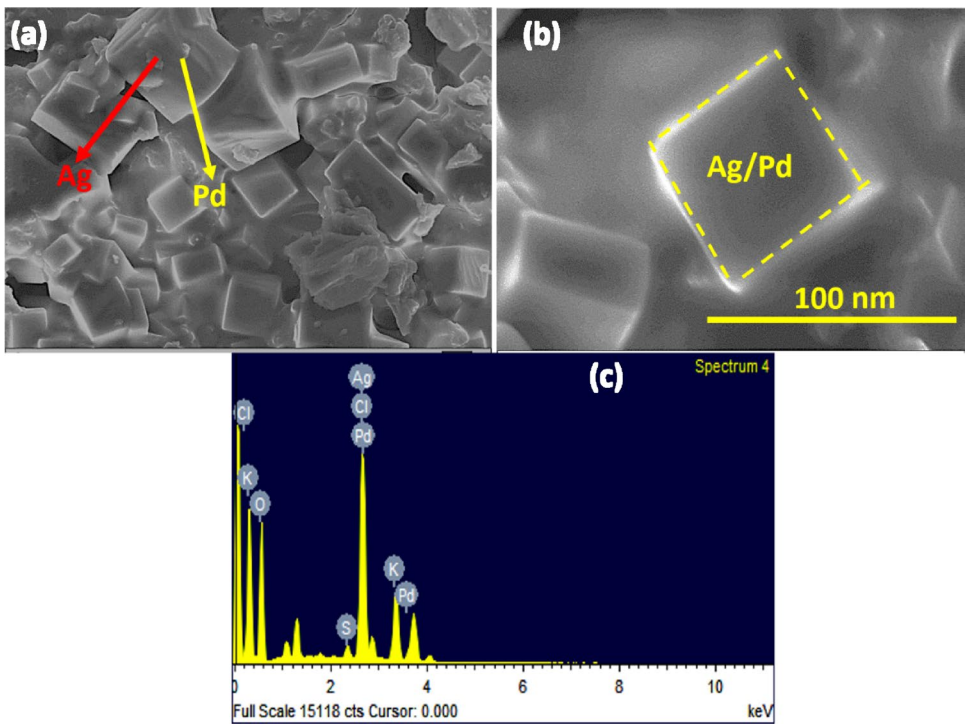

Fig. 5 **a** and **b** different resolutions of Ag/Pd core shell nanoparticles FESEM images; **c** elemental identification of bio-synthesized bi-metallic nanoparticles using *CR* leaf extract

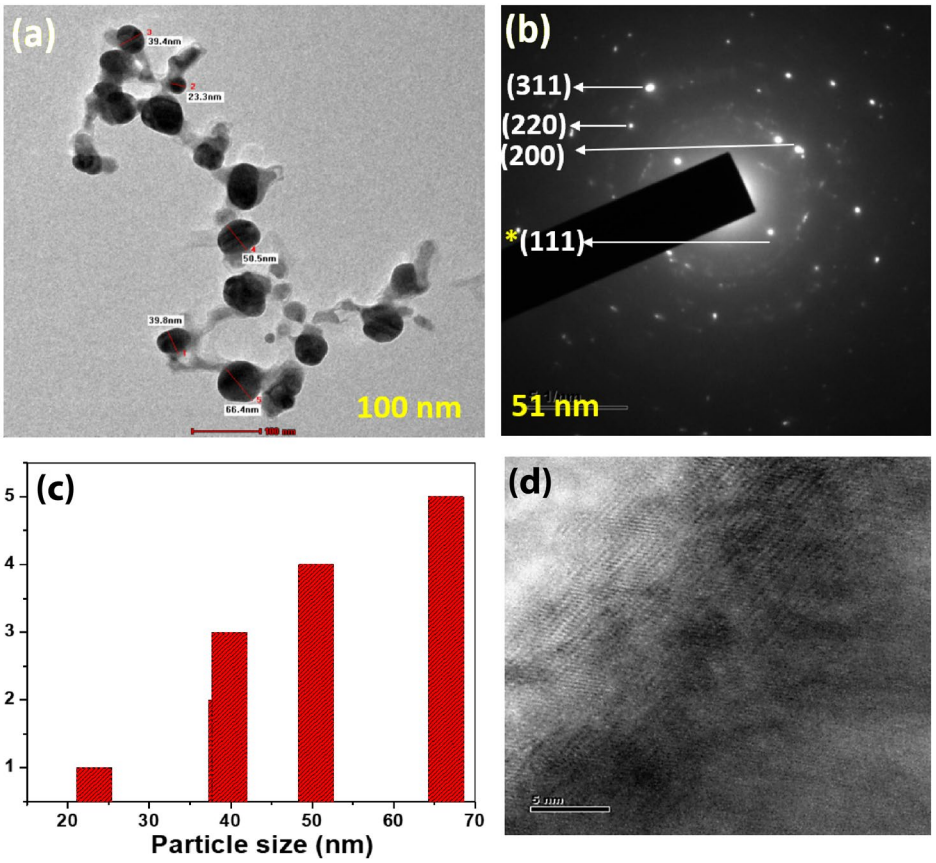

Fig. 6 **a** TEM image of spherical shaped silver/palladium core shell NPs; **b** selected electron diffraction patterns of Ag/Pd NPs; **c** particle size distribution; and **d** HRTEM image

histogram is 23–64 nm and it was shown in Fig. 6c. The HRTEM image of the prepared Ag/Pd metallic nanoparticles is shown in Fig. 6d. The observed inter-planar distance of 0.235 nm and 0.246 nm related to the (111) plane of Ag and Pd, respectively. This HRTEM result clearly demonstrated the existence of heterojunction between the Ag and Pd nanoparticles.

The particles size and distribution of synthesized silver/palladium nanoparticles was analyzed by hydrodynamic light scattering method (Adavallan and Krishnakumar 2014). The resulted silver/palladium nanoparticles

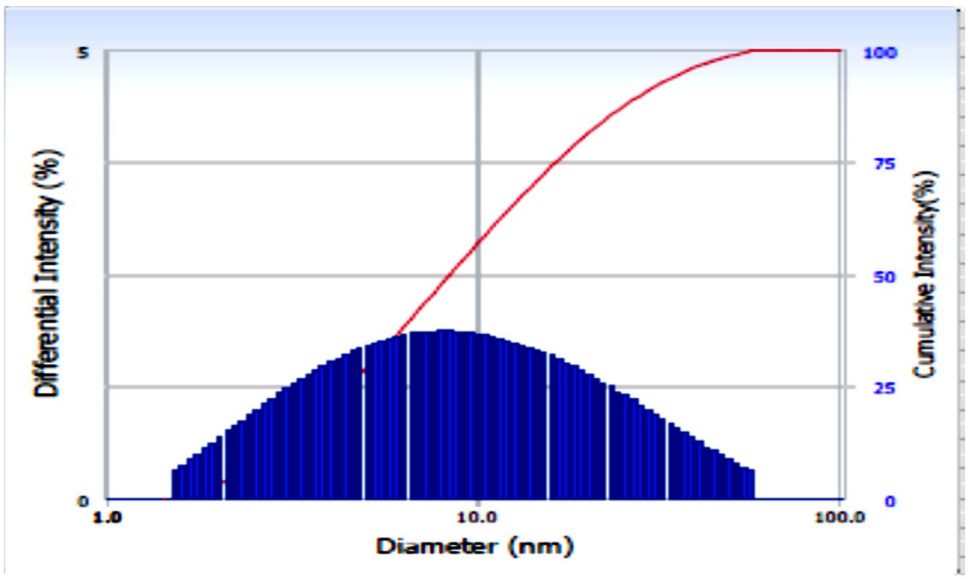

Fig. 7 Particle size distributed by dynamic light scattering techniques

correspond to the particle size distributed from 2–28 nm with maximum size distribution is around 28 nm was shown in Fig. 7.

Effect of anti-radical activity

The Effect of Ag–Pd bi-metallic NPs capped with C.R leaf extract and C.R leaf extract both as exhibited the radical scavenging activity was shown in Fig. 8a. Ag/Pd NPs showed the strong free radical scavenging activity (70.2%) alone CR leaf extract (48.2%) (see Table 1). The possible reason for antioxidant activity of leaf extract may be correlated in the presence of total poly-phenol groups interacted with metal ions during nanoparticles synthesis may result in the effect of free radical scavenging properties. In addition, to the electrostatic attractions of Ag/Pd bi-metallic NPs functionalized as synergistically to improve the bioactivity molecules (Mohanty et al. 2014; Sudipta et al. 2012). As earlier studies have also suggested that the anti-radical scavenging activity spontaneously increases with the increase in the treated dosages (Fig. 8b) (Mohanty et al. 2014; Dipankar and Murugan 2012; Shahwan et al. 2011).

Effect of PCA and mechanisms of photocatalytic activity (PCA) and quantum yield (QY) of Ag/Pd NPs on degradation of safranin O dye

Safranin O dye removal was tested by photo catalytic activity of co-catalyst silver/palladium nanoparticles under UV light irradiation. Figure 9a shows Safranin O dye exhibit an absorption peak at $\lambda_{max} = 518$ nm which revealed the presence of $\pi - \pi^*$ and $n - \pi^*$ electronic transition and R* band (Saeed et al. 2016).The absorption peak was spontaneously decreased at regular time intervals under UV light irradiation in presence of Ag/Pd NPs. The control test solutions (without Ag/Pd NPs) were also carried out under UV light irradiation and observed no dye degradation but in presence

Table 1 Radical scavenging activity of *Catharanthus* leaf extract (*CRL*) and along with synthesized silver–palladium Co-Nanocatalyst using DPPH assays

S. No	Plant extract/core shell nanoparticles	Different concentration (µl)	Free radical efficiency (%)
1	DPPH@*CR*L Extract	100	23.4
		200	44.1
		300	48.2
2	DPPH @ Ag/Pd NPs @ *CR*L Extract	100	62.5
		200	68.2
		300	70.2

of Ag/Pd NPs enhanced faster reaction rate and complete the dye degradation on safranin O dye within 40 min with 98% efficiency. The UV light irradiation on effective dye removal was due to the presence of chromophoric azo groups (N = N) in the saffranin O dye. As early study was reported GNs/Sn-Pt nanocomposite and its Basic Green 5 dye degradation wasachieved80% for about 8 h. Khalid Saeed et al. and Adeel Ahmed et al. reported Fe NPs showed photocatalytic activity and up to 93.7% of the dye was degraded in 42 h (Ahmed et al. 2020; Ramakrishnan et al. 2018). Ramakrishnan et al. 2018 reported the synthesis of $Ag@TiO_2$ NPs and applications of different dyes degradation was achieved 96.3% and 97% for MB and MO dyes under UV light irradiation. The above discussion previous literature was clearly from that synthesized Ag/Pd nanoparticles and its textile dye degradation was achieved 40 min with 98% have potential efficiency of compared to one (Saeed et al. 2016; Ahmed et al. 2020; Ramakrishnan et al. 2018).

The mechanism for dye degradation by silver/palladium is shown in Fig. 10. When UV light irradiation, it can be adsorbed by the photocatalyst as well as dye molecules. Upon the light irradiation silver/palladium nanoparticles

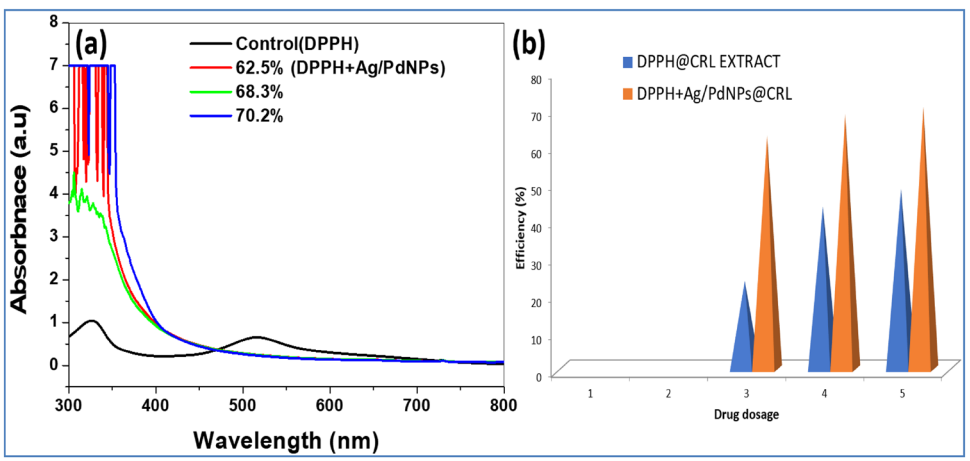

Fig. 8 **a** UV–Visible absorbance spectrum; **b** antioxidant activity on silver–palladium NPs using DPPH assay

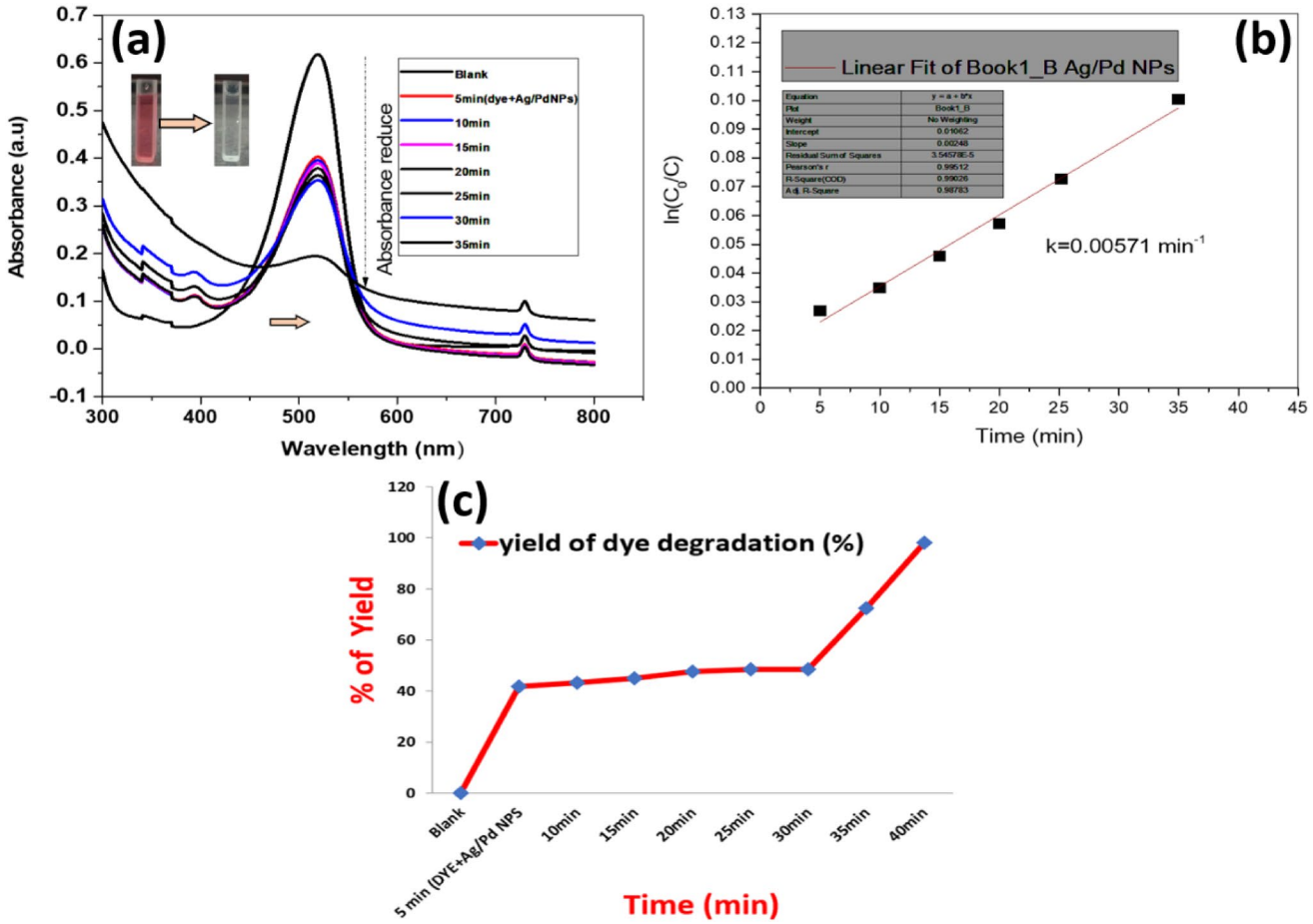

Fig. 9 **a** UV–Visible absorption spectrum of textile dye removal using photo catalysis method (PCA); **b** Kinetic plot of textile dye removal; **c** percentage of yield of dye removal on silver/palladium NPs

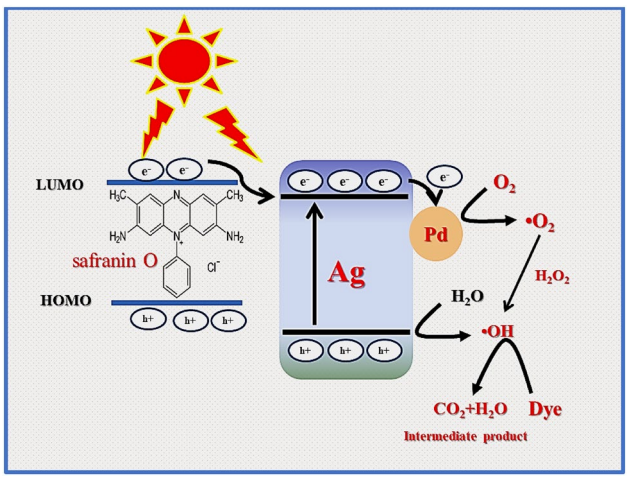

Fig. 10 Possible reaction mechanism

are produce the electron–hole pairs due to the surface plasmon resonance. The dye molecules adsorbed by the nanoparticle surface, which act as a photosensitizer. During the light irradiation, dye molecules get excited and donate their electron to conduction band of the silver nanoparticle. This conduction band electron was further trapped by palladium nanoparticle and it prevents the electron–hole recombination during the light irradiation. Conduction band electrons further trapped by surface adsorbed molecular oxygen and it generates the superoxide radicals and H_2O_2 molecules. The combination of Ag to Pd nanoparticles gave away Ag/Pd alloy and it forms redox couple in which Ag is more anodic to Pd and hence the electron transfer from Ag to Pd produce much amount of H_2O_2. Besides, the photo-generated holes are directly reacting with the adsorbed dye molecules or water molecules and it produces the hydroxyl radicals or hydroxyl ions respectively. These active radicals helps to mineralize the dye molecules with liberation of clinical products such as CO_2, H_2O_2, and NO_2 and this part has well agreed with the previous reports (Dipankar and Murugan 2012; Shahwan et al. 2011; Mohan and Devan 2019; Mavaei et al. 2020; Palanivel and Mani 2020; Palanivel et al. 2021).

The QY of Ag/Pd bimetallic NPs on degradation of safranin O dye were evaluated by:

$$\Phi = \frac{\text{No of molecules decomposed}}{\text{No of photon absorbed}} \quad (4)$$

The QY of Ag/Pd NPs is noticed to be (Φ) = 2.37, this reveals that the QY is > 1 which means that on absorbing the per quantum of photon, the huge quantity of reactant atoms (dye) will undergo to decomposition.

Conclusion

We have explored our report that the silver modified silver–palladium core–shell nanoparticles were successfully synthesized through flavonoids present in CRL extract. The flavonoids present in CR leaves extract have functionalized as reducing & capping agents for synthesizing the bimetallic nanoparticles. The Ag modified Ag–Pd bi-metallic NPs were studied through UV–Vis, FTIR, SEM/EDX, and XRD systems. The morphological size and shape were analyzed by scanning electron microscopy with an average particle size of 30 nm and cubic like tetragons shape. Thus the free radical scavenging activity of silver/palladium bimetallic or alloy nanoparticles along with extract and compared with CR leaf extracts. The results of our study revealed that the leaf extract and synthesized Ag–Pd NPs both exhibited radical scavenging activity. However, Ag/Pd NPs showed the strong free radical scavenging activity (70.2% of 300 µL/ml) compare with leaf extract (48.2% of 300 µl/ml). Moreover, the increase in antioxidant activity strongly recommended for cytotoxic activity towards the cell lines treating anticancer activities. Finally, the overall report concluded that the silver modified silver/palladium nanoparticles have multi-functionalized as a potential candidate for both textile dye removal and scavenging free radicals for anticancer activities.

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Declarations

Conflict of interest The authors declare that there is no conflict of interest.

References

Adavallan K, Krishnakumar N (2014) Mulberry leaf extract mediated synthesis of gold nanoparticles and its anti-bacterial activity against human pathogens. Adv Nat Sci: Nanosci Nanotechnol 5:025018

Ahmed A, Usman M, Yu B, Ding X, Peng Q, Shen Y, Cong H (2020) Efficient photocatalytic degradation of toxic Alizarin yellow R dye from industrial wastewater using biosynthesized Fe nanoparticle and study of factors affecting the degradation rate. J Photochem Photobiol, B 202:111682

Anagnostopoulou MA, Kefalas P, Papageorgiou VP, Assimopoulou AN, Boskou D (2006) Radical scavenging activity of various extracts and fractions of sweet orange peel (Citrus sinensis). Food Chem 94:19–25

Bagherzade G (2017) Mohmmed Hasan Namaei, Green synthesis of silver nanoparticles using aqueous extract of saffron (*Crocus sativus* L) wastages and its antibacterial activity against six bacteria. Asia Pacific J Trop Biomed 7(3):227–233

Bera TK, Chatterjee K, Jana K, Ali KM, De MSD, Ghosh D (2012) Antihepatotoxic effect of "Livshis", a polyherbal formulation against carbon tetrachloride-induced hepatotoxicity in male albino rat. J Nat Pharm 3:17–24

Chen Y-H, Tseng Y-H, Yeh C-S (2002) Laser-induced alloying Au–Pd and Ag–Pd colloidal mixtures: the formation of dispersed Au/Pd and Ag/Pd nanoparticles. J Mater Chem 12:1419–1422

Damle C, Kumar A, Sastry M (2002) Synthesis of Ag/Pd nanoparticles and their low-temperature alloying within thermally evaporated fatty acid films. J Phys Chem B 106:297–302

Dipankar C, Murugan S (2012) The green synthesis, characterization and evaluation of the biological activities of silver nanoparticles synthesized from Iresine herbstii leaf aqueous extracts. Colloids Surf, B 98:112–119

He J, Ichinose I, Kunitake T, Nakao A, Shiraishi Y, Toshima N (2003) Facile fabrication of Ag−Pd bimetallic nanoparticles in ultrathin TiO_2-gel films: nanoparticle morphology and catalytic activity. J Am Chem Soc 125:11034–11040

Huang J, Li Q, Sun D, Lu Y, Su Y, Yang X, Wang H, Wang Y, Shao W, He N, Hong J, Chen C (2007) Biosynthesis of silver and gold nanoparticles by novel sundriedCinnamomum camphoraleaf. Nanotechnology 18:105104

Ilunga AK, Meijboom R (2016) Catalytic oxidation of methylene blue by dendrimer encapsulated silver and gold nanoparticles. J Mol Catal A: Chem 411:48–60

Kasthuri J, Veerapandian S, Rajendiran N (2009) Biological synthesis of silver and gold nanoparticles using apiin as reducing agent. Colloids Surf, B 68:55–60

Krishnan D, Pradeep T (2009) Precursor-controlled synthesis of hierarchical ZnO nanostructures, using oligoaniline-coated Au nanoparticle seeds. J Cryst Growth 311:3889–3897

Kumar VA, Uchida T, Mizuki T, Nakajima Y, Katsube Y, Hanajiri T, Maekawa T (2016) Synthesis of nanoparticles composed of silver and silver chloride for a plasmonic photocatalyst using an extract from a weed *Solidago altissima* (goldenrod). Adv Nat Sci: Nanosci Nanotechnol 7:015002

Lee C-L, Chiou H-P, Chang K-C, Huang C-H (2011) Carbon nanotubes-supported colloidal Ag–Pd nanoparticles as electrocatalysts toward oxygen reduction reaction in alkaline electrolyte. Int J Hydrogen Energy 36:2759–2764

Li J, Feng H, Li J, Jiang J, Feng Y, He L, Qian D (2015) Bimetallic Ag-Pd nanoparticles-decorated graphene oxide: a fascinating three-dimensional nanohybrid as an efficient electrochemical sensing platform for vanillin determination. Electrochim Acta 176:827–835

Mane Gavade SJ, Nikam GH, Dhabbe RS, Sabale SR, Tamhankar BV, Mulik GN (2015) Green synthesis of silver nanoparticles by using carambola fruit extract and their antibacterial activity. Adv Nat Sci: Nanosci Nanotechnol 6:045015

Mavaei M, Chahardoli A, Shokoohinia Y, Khoshroo A, Fattahi A, Iso-imperatorin O-S (2020) Evaluation of photocatalytic, and electrochemical activities. Sci Rep 10:1762

Mohan S, Devan MV (2019) Photocatalytic activity of Ag/Ni bimetallic nanoparticles on textile dye removal. Green Process Synth 8:895–900

Mohanty SK, Mallappa KS, Godavarthi A, Subbanarasiman B, Maniyam A (2014) Evaluation of antioxidant, in vitro cytotoxicity of micropropagated and naturally grown plants of *Leptadenia reticulata* (Retz.) Wight & Arn.—an endangered medicinal plant. Asian Pacific J Trop Med 7:S267–S271

Nasrollahzadeh M, Atarod M, Jaleh B, Gandomirouzbahani M (2016) In situ green synthesis of Ag nanoparticles on graphene oxide/TiO_2 nanocomposite and their catalytic activity for the reduction of 4-nitrophenol, congo red and methylene blue. Ceram Int 42:8587–8596

Njoki PN, Lim IIS, Mott D, Park H-Y, Khan B, Mishra S, Sujakumar R, Luo J, Zhong C-J (2007) Size correlation of optical and spectroscopic properties for gold nanoparticles. J Physical Chemistry C 111:14664–14669

Palanivel B, Mani A (2020) Conversion of a type-II to a Z-scheme heterojunction by intercalation of a 0D electron mediator between the integrative $NiFe_2O_4$/g-C_3N_4 composite nanoparticles: boosting the radical production for photo-fenton degradation. ACS Omega 31:19747–19759

Palanivel B, Lallimathi M, Arjunkumar B, Shkir M, Alshahrani T, Al-Namshah KS, Hamdy MS, Shanavas S, Venkatachalam M, Ramalingam G (2021) rGO supported g-C_3N_4/$CoFe_2O_4$ heterojunction: Visible-light-active photocatalyst for effective utilization of H_2O_2 to organic pollutant degradation and OH• radicals production. J Environ Chem Eng 9:104698

Pergolese B, Muniz-Miranda M, Bigotto A (2007) Catalytic activity of Ag/Pd bimetallic nanoparticles immobilized on quartz surfaces. Chem Phys Lett 438:290–293

Ramakrishnan VM, Natarajan M, Santhanam A, Asokan V, Velauthapillai D (2018) Size controlled synthesis of TiO_2 nanoparticles by modified solvothermal method towards effective photo catalytic and photovoltaic applications. Mater Res Bull 97:351–360

Rostami-Vartooni A, Nasrollahzadeh M, Alizadeh M (2016) Green synthesis of seashell supported silver nanoparticles using *Bunium persicum* seeds extract: application of the particles for catalytic reduction of organic dyes. J Colloid Interface Sci 470:268–275

Saeed K, Khan I, Sadiq M (2016) Synthesis of graphene-supported bimetallic nanoparticles for the sunlight photodegradation of basic green 5 dye in aqueous medium. Sep Sci Technol 51:1421–1426

Shahwan T, Abu Sirriah S, Nairat M, Boyacı E, Eroğlu AE, Scott TB, Hallam KR (2011) Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. Chem Eng J 172:258–266

Shang N-Z, Feng C, Gao S-T, Wang C (2016) Ag/Pd nanoparticles supported on amine-functionalized metal–organic framework for catalytic hydrolysis of ammonia borane. Int J Hydrogen Energy 41:944–950

Song JY, Kim BS (2008) Biological synthesis of bimetallic Au/Ag nanoparticles using Persimmon (Diopyros kaki) leaf extract. Korean J Chem Eng 25:808–811

Sudipta K, Lokesh P, Rashmi W, Vijay R, Ssn K (2012) Phytochemical screening and in vitro antimicrobial activity of Bougainvillea spectabilis flower extracts. Int J Phytomed 4:375

Suman TY, Radhika Rajasree SR, Kanchana A, Elizabeth SB (2013) Biosynthesis, characterization and cytotoxic effect of plant mediated silver nanoparticles using Morinda citrifolia root extract. Colloid Surf B: Biointerface 106:74–78

Swamy MK, Akhtar MS, Mohanty SK, Sinniah UR (2015) Synthesis and characterization of silver nanoparticles using fruit extract of Momordica cymbalaria and assessment of their in vitro antimicrobial, antioxidant and cytotoxicity activities. Spectrochim Acta Part A Mol Biomol Spectrosc 151:939–944

Tong Y, Lu X, Sun W, Nie G, Yang L, Wang C (2014) Electrospun polyacrylonitrile nanofibers supported Ag/Pd nanoparticles for hydrogen generation from the hydrolysis of ammonia borane. J Power Sources 261:221–226

Vasan HN, Rao CNR (1995) Nanoscale Ag–Pd and Cu–Pd alloys. J Mater Chem 5:1755–1757

Villaño D, Fernández-Pachón MS, Moyá ML, Troncoso AM, García-Parrilla MC (2007) Radical scavenging ability of polyphenolic compounds towards DPPH free radical. Talanta 71:230–235

Wang W, Cao G (2007) Synthesis and structural investigation of Pd/Ag bimetallic nanoparticles prepared by the solvothermal method. J Nanopart Res 9:1153–1161

Watters JL, Satia JA, Kupper LL, Swenberg JA, Schroeder JC, Switzer BR (2007) Associations of antioxidant nutrients and oxidative DNA damage in healthy African-American and White adults. Cancer Epidemiol Prevent Biomark 16:1428–1436

Yan X, Xu T, Xu S, Wang X, Yang S (2004) Fabrication of polymer-converted carbon films containing Ag, Pd nanoparticles. Nanotechnology 15:1759–1762

Yang C-C, Wan C-C, Wang Y-Y (2004) Synthesis of Ag/Pd nanoparticles via reactive micelles as templates and its application to electroless copper deposition. J Colloid Interface Sci 279:433–439

Yu K, Yang S, Liu C, Chen H, Li H, Sun C, Boyd SA (2012) Degradation of organic dyes via bismuth silver oxide initiated direct oxidation coupled with sodium bismuthate based visible light photocatalysis. Environ Sci Technol 46:7318–7326

Zhan G, Huang J, Du M, Abdul-Rauf I, Ma Y, Li Q (2011) Green synthesis of Au–Pd bimetallic nanoparticles: Single-step bioreduction method with plant extract. Mater Lett 65:2989–2991

Zhang B, Yuan Y, Philippot K, Yan N (2015) Ag–Pd and CuO–Pd nanoparticles in a hydroxyl-group functionalized ionic liquid: synthesis, characterization and catalytic performance. Catal Sci Technol 5:1683–1692