crystals

MDPI

Article

Green Synthesis of Reduced Graphene Oxide-Supported Palladium Nanoparticles by *Coleus amboinicus* and Its Enhanced Catalytic Efficiency and Antibacterial Activity

Koduru Mallikarjuna [1,2], Lebaka Veeranjaneya Reddy [3], Sarah Al-Rasheed [4], Arifullah Mohammed [5,6,*], Sreedevi Gedi [7,*] and Woo Kyoung Kim [7,*]

1 Department for Management of Science and Technology Development, Ton Duc Thang University, Ho Chi Minh City 758307, Vietnam; koduru.mallikarjuna@tdtu.edu.vn
2 Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City 758307, Vietnam
3 Department of Microbiology, Yogi Vemana University, Kadapa 516005, India; lvereddy@gmail.com
4 Department of Botany and Microbiology, College of Science, King Saudi University, P.O. Box-2455, Riyadh 11451, Saudi Arabia; salrashed@ksu.edu.sa
5 Faculty of Agro-Based Industry, Universiti Malaysia Kelantan, Jeli 17600, Malaysia
6 Institute of Food Security and Sustainable Agriculture, Universiti Malaysia Kelantan, Jeli 17600, Malaysia
7 School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Korea
* Correspondence: aurifullah@umk.edu.my (A.M.); drsrvi9@gmail.com (S.G.); wkkim@ynu.ac.kr (W.K.K.)

check for updates

Citation: Mallikarjuna, K.; Reddy, L.V.; Al-Rasheed, S.; Mohammed, A.; Gedi, S.; Kim, W.K. Green Synthesis of Reduced Graphene Oxide-Supported Palladium Nanoparticles by *Coleus amboinicus* and Its Enhanced Catalytic Efficiency and Antibacterial Activity. *Crystals* **2021**, *11*, 134. https://doi.org/10.3390/cryst11020134

Academic Editor: Younes Hanifehpour

Received: 31 December 2020
Accepted: 24 January 2021
Published: 28 January 2021

Abstract: Novel reduced graphene oxide-supported palladium nanoparticles (RGO-PN) were synthesized under ultrasonication, a method that utilizes *Coleus amboinicus* as a bio-reduction agent. Green synthesized RGO-PN nanoparticles with a crystallite size in the range of 40–50 nm were confirmed in X-ray diffraction (XRD) spectra. RGO-PN show an absorption peak at 220 nm while reduced graphene oxide (RGO) shows its maximal absorbance at 210 nm. The scanning electron microscope image revealed that 40-nm-sized spherical-shaped palladium nanoparticles stick well to reduced graphene oxide sheets, which is consistent and correlated well with the XRD pattern. Moreover, a high-resolution morphological image of RGO-PN100 was obtained by TEM analysis, which shows the anchoring of palladium nanoparticles (PN) on RGO nanosheets. Green synthesized RGO-PN100 nanoparticles from *Coleus amboinicus* show better reduction kinetics for 4-nitrophenol at 40 min, suggesting that RGO-PN prepared from *Coleus amboinicus* serve as an excellent catalytic reducing agent. Furthermore, they show remarkable antibacterial activity against *Escherichia coli* (ATCC 25922). Thus, green synthesized RGO-supported palladium nanoparticles demonstrated that enhanced catalytic activity and antibacterial activity both play an important role in the environmental and medical disciplines.

Keywords: 4-Nitrophenol; *Coleus amboinicus*; palladium; RGO-PN; *Escherichia coli*; Ultrasonication

1. Introduction

Graphene is a 2D hexagonal single layer of graphite, which acts as a catalyst with high thermal and electrical conductivities [1–3]. Graphene and its derivatives, such as graphene oxide and reduced graphene oxide, can also act as catalysts, which support and stabilize metal nanoparticles [4,5]. Production of graphene oxide (GO) has attracted huge interest as a promising intermediate for the preparation of graphene in large quantities [6]. GO possesses several oxygen-based functional groups such as –OH, C=O, and –COOH attached to graphene layers. It is due to the presence of the hydroxyl and carboxyl groups in GO that exhibit better hydrophilicity, solubility, and dispersion in water than graphene and graphite powder [7]. After the elimination of the functional oxygen-containing groups in graphene oxide, reduced graphene oxide (RGO) was obtained through an improved and modified Hummers' method. The elimination of oxygen-containing groups, i.e., the reduction of GO, can be conducted by chemical, thermal, solvothermal, or microwave-initiated routes.

Metal nanoparticles have gained significant attention due to their novel physical and chemical properties compared to bulk metals, and their diverse potential applications in the field of catalysis [8–11]. Dispersion of metal nanoparticles on solid oxide prevents agglomeration and enhances the accessibility of substrate molecules, mechanical robustness, and so on. Solid oxide-supported nanoparticles have shown more catalytic efficiency, specificity, and selectivity compared to unsupported metal nanoparticles [12].

Palladium is a platinum group metal with wide applications in the medicinal, environmental, and material science disciplines. Palladium possesses unique metal properties and versatile catalytic applications at ambient temperatures in various industrial sectors. The synthesis of palladium nanoparticles by chemical and physical methods requires high pressure, precious metals, and high-toxicity chemicals [13]. Green mediated synthesis of RGO-PN nanoparticles has gained a lot of attention in recent years because of its cheaper and more eco-friendly approach [14]. Recently, numerous research efforts have focused on the green mediated synthesis of metal oxide nanoparticles inside the pores or walls of polymers for effective applications in catalysis. The large surface area of nanoparticles and their hybrid materials make them the perfect candidate for various catalytic applications [15,16].

Coleus amboinicus is a semi-succulent perennial herbaceous plant with different nutritional and therapeutic properties belonging to the Lamiaceae family. The plant is widely distributed in warmer tropical regions of Africa, Asia, and Australia. *Coleus amboinicus* is used as a traditional medicinal herbal medicine to treat cold, asthma, headache, and skin diseases [17]. It is often used in traditional food preparations as a food additive and a flavoring agent. *Coleus amboinicus* is rich in flavonoids, phenols, and terpenoids and has a wide range of pharmacological activities.

Nitroaromatic compounds (NAC) are huge classes of synthetic compounds currently being used in the different industrial production processes [18,19]. 4-Nitrophenol (4-NP) is one of the most important and widely used NAC [20–23]. 4-NP is principally utilized in industries routinely involved in the preparation of pharmaceuticals, pesticides, leather, and dyestuff. Additionally, 4-NP is released from the herbicide and pesticide industries, causing the contamination of groundwater resources. The acute toxicity and mutagenic potential of 4-NP cause significant environmental and public health risks. Therefore, it is necessary to find the cheapest alternative way to remove 4-NP pollutants in industrial wastewater effluents through the use of cheaper and more eco-friendly nanoparticles synthesized from the biological route.

The present study aims to synthesize reduced graphene oxide-supported palladium nanoparticles (RGO-PN) using the aqueous leaf extract of *Coleus amboinicus,* which is a bio-reducing agent, mediated through a cheaper and more eco-friendly ultrasonic-driven route. Secondary metabolites of the leaf extract of the plant *Coleus amboinicus* act as a reducing agent and convert palladium chloride into palladium nanoparticles. Additionally, the green synthesized RGO-PN nanoparticles were tested to confirm their catalytic efficiency of reduction reaction and their therapeutic applications to treat multiple drug resistance against human clinical pathogens.

2. Materials and Methods

2.1. Materials

Palladium chloride ($PdCl_2$), $NaBH_4$, graphite flakes, and 4-nitrophenol were procured from Sigma-Aldrich (USA) and utilized for the study. *Escherichia coli* (Catalogue No ATCC 25922) bacterial culture was obtained from the global bioresource center. The healthy leaves of *Coleus amboinicus* were collected from Gyeonsan, Republic of Korea, cleansed in double-distilled water, and then utilized for our study.

2.2. Methods

2.2.1. Preparation of the *Coleus amboinicus* Extract

Coleus amboinicus leaves were used as a reducing and capping agent for reduced graphene oxide-supported palladium nanoparticles. In brief, 5 g of dried leaf powder of *Coleus amboinicus* was kept in a 100 mL Erlenmeyer flask along with 50 mL of double-distilled water and mixed well. Then, the flask containing the leaf sample mixture was placed in an ultrasonicator (Power Sonica 410 bath sonicator, Hwashin Technology Co., Seoul, Korea). The mixture was subjected to ultrasonication by setting the frequency and power to 40 kHz and 150 W, respectively, for a 30 min duration at room temperature. The ultrasonicated plant extract was filtered and its filtrate was collected and kept in the refrigerator for further use.

2.2.2. Green Synthesis of Reduced Graphene Oxide-Supported Palladium Nanoparticles

Graphene oxide (GO) was obtained from graphite flakes using a modified Hummers' protocol [24]. For palladium-reduced graphene oxide (Pd-RGO) catalyst preparation, 1 g of graphene oxide in 70 mL distilled water was taken in an Erlenmeyer flask and kept under sonication for 30 min. The procedure for green synthesis of reduced graphene oxide-supported palladium nanoparticle (RGO-PN) preparation is as follows: the measured quantity of Pd-RGO catalyst, 10 mL of plant leaf extract of *Coleus amboinicus*, and 70 mL of deionized water were mixed in an Erlenmeyer flask. Three different concentrations of Pd-RGO catalyst (50, 100, and 150 mg) were taken to prepare three different reduced graphene oxide-supported palladium nanoparticle synthesis (RGO-PN50, RGO-PN100, RGO-PN150) from the leaf extract of *Coleus amboinicus*. Then, the reaction mixture was kept in ultrasonication (Power Sonica 410 bath sonicator) at room temperature for 8 h. The color change of a reaction mixture is the indication of reduced graphene oxide palladium nanoparticles (RGO-PN) synthesis.

2.2.3. Characterization Techniques

The obtained RGO-PN nanoparticle powder was subjected to the following characterization methods: the absorbance spectrum of RGO-PN was carried out using a UV–Visible spectrophotometer (Thermo Scientific Genesys 10S, Marietta, OH, USA) with a resolution of 1 nm in the range of 200−800 nm. The bio-reduced RGO-PN sample for X-ray diffraction (XRD) was prepared by drop-casting the solution on a glass slide. The XRD pattern of the prepared thin film was obtained using an InelC120 X-ray diffractometer. Diffraction data were collected using Cu-Kα radiation of 1.5406 Å in the 2θ range of 10–90 degrees. The particle size distribution and morphology of the prepared bio-reduced RGO-PN were studied using a field emission scanning electron microscope (SEM, S4800 Hitachi), and transmission electron microscope (TEM, H-7600 Hitachi, Tokyo, Japan), respectively. X-ray photoelectron spectroscopy (XPS) measurements were made in a Thermo scientific, using AlKα radiation. Further, the catalytic reduction of 4-nitro phenol to 4-amino phenol using a prepared RGO-PN suspension was visualized using the absorbance spectrum of 4-nitrophenol.

2.2.4. Catalytic Reduction of 4-Nitrophenol by Pd-RGO

The enhanced catalytic reduction efficiency of RGO-PN was screened through a one step 4-nitrophenol reduction method. In brief, the reaction mixture consisting of 3.8 mL of 2 mM nitrophenol and 0.2 mL of 0.5 M sodium borohydride was taken in the cuvette and absorbance was measured in a UV-Vis spectrophotometer. The mixture of nitrophenol and NaBH4 produced a 4-nitrophenoxy ion, which generated a strong absorption peak at 400 nm. At this point, 0.5 mL (1 mg/mL) of green synthesized RGO-PN nanoparticles were added to the reaction mixture as a reduction reaction catalyst to speed up the reduction reaction kinetics. The reduction of 4-nitrophenol was monitored by a UV-Visible absorption spectrum pattern (200–550 nm) of the reaction mixture in four different time intervals from 10 to 40 min.

2.2.5. Antimicrobial Activity of Palladium-Reduced Graphite Oxide Nanoparticle

The agar well diffusion method was employed to screen the antimicrobial activity of green synthesized RGO-PN. The bactericidal effect of green synthesized RGO-PN has been attributed to its high ratio of surface to volume, which fine-tunes the size of nanoparticles with their bioactive molecules from plants, allowing them to interact very closely with microbial membranes. The overnight inoculated bacterial culture of *Escherichia coli* (ATCC 25922) was used as the test organism and seeded in sterile Petri plates using the spread plate technique. For agar well diffusion, five circular wells (5 mm) were made. Then it was loaded with a standard ampicillin antibiotic (10 μg) and the other wells were loaded with 10 μg samples of RGO, RGO-PN50, RGO-PN100, and RGO-PN150. Plates were then incubated at 37 °C overnight and triplicate plates were maintained, and finally, their results were recorded.

3. Result and Discussion

3.1. UV-Visible Spectroscopy

The UV-Visible absorption spectra of RGO and RGO-PN are presented in Figure 1. RGO showed its maximal peak of absorption at 210 nm whereas green synthesized RGO-PN50, RGO-PN100, and RGO-PN150 had strong and sharp absorption peaks at 220, 235, and 248 nm, respectively (Figure 1). This is due to the changes in the degree of bio-reduction of RGO-supported palladium nanoparticles by the phenolic and flavonoid constituents of *Coleus amboinicus*. From the absorption spectra, the RGO showed peak at 210 nm, and the absorption band shifted towards higher wavelength side with the addition of palladium nanoparticles to RGO. The obtained absorbance pattern of green synthesized RGO-PN confirms the formation of RGO-supported pure palladium nanoparticles in the reaction mixture suspension.

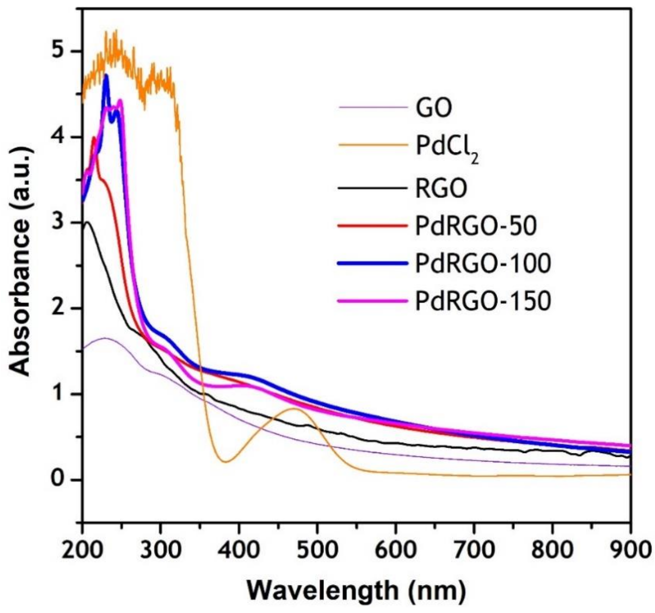

Figure 1. UV-Visible absorption pattern of graphene oxide (GO), $PdCl_2$, reduced graphene oxide (RGO), and green synthesized palladium-reduced graphene oxide (Pd-RGO) nanoparticles from *Coleus amboinicus.*

3.2. Structural Analysis of RGO-PN by XRD

X-ray diffraction patterns of RGO and RGO-PN with three different concentrations are shown in Figure 2. XRD patterns confirmed that the characteristic peaks of RGO-supported palladium nanoparticles correspond to the (111), (200), (220), (311), and (222) planes, which do not exist in RGO. Therefore, it confirms the spherical crystal structure of palladium nanoparticles, which matches well with the JCPDS card number (JCPDS: 01-087-0639), and proves the pure crystallite structure of RGO-supported palladium nanoparticles. A high-intensity peak at (111) indicates the cubic structure of green synthesized RGO-PN nanoparticles. The crystallite size of prepared Pd nanoparticles was calculated from the Debye–Scherrer's formula:

$$D = 0.9\lambda/\beta\cos\theta,$$

where D is the crystallite size of the sample, "0.9" is the shape factor (considered as spherical-shaped nanoparticles), β represents the full width at half maximum of corresponding diffraction peak, and θ is the diffraction angle. The average crystallite size of the prepared palladium nanoparticle for the (111) peak was calculated to be c.a. 21.1 nm.

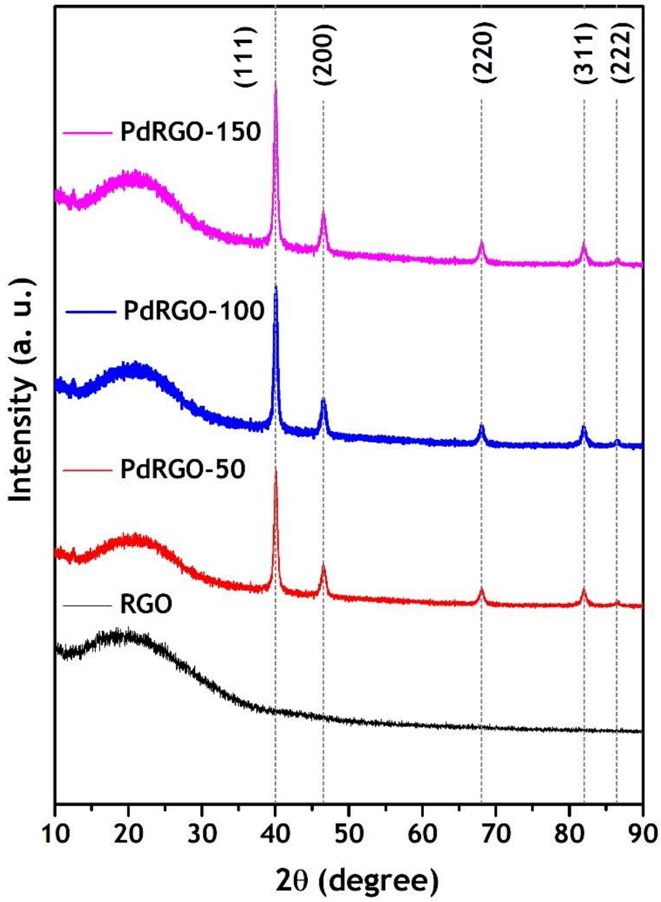

Figure 2. XRD patterns of RGO and green synthesized Pd-RGO nanoparticles from *Coleus amboinicus.*

3.3. SEM and TEM Analysis

SEM micrographs for green synthesized RGO-PN50, RGO-PN100, and RGO-PN150 were obtained by the mediation of *Coleus amboinicus* using an ultrasonic biological reduction process, as represented in Figure 3. All three SEM images depict that spherical-shaped green synthesized palladium nanoparticles are anchored with the reduced graphene oxide sheets. The size of green synthesized palladium nanoparticles was found to be 20–40 nm. The SEM images confirm that RGO-PN was successfully synthesized through the ultrasonic driven biological bio-reduction process using *Coleus amboinicus*. Moreover, the density of the palladium nanoparticles increased with an increasing molar ratio. As shown in Figure 4, high-resolution images of RGO and RGO-PN-100 samples were obtained by TEM analysis. Figure 4a revealed that the RGO has a 2D sheet-like structure, and Figure 4b shows that the palladium nanoparticles are anchored on the surface of the RGO nanosheets. The palladium nanoparticles showed a spherical shape with a diameter of 20–30 nm. It should be noted that smaller particles have a high surface area to volume ratio which influences the active sites for catalytic applications.

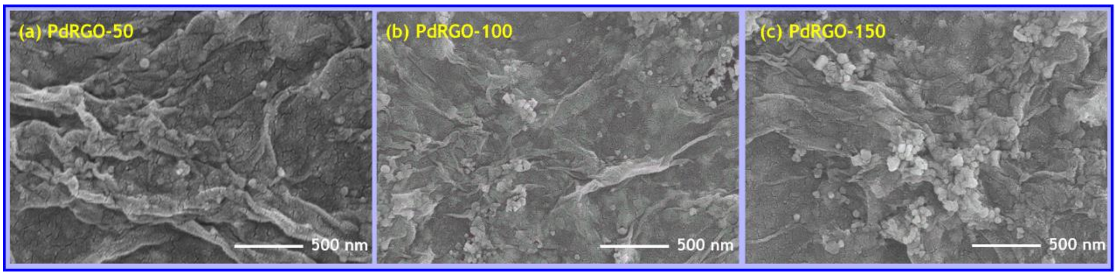

Figure 3. SEM micrographic images of green synthesized RGO-supported palladium nanoparticles with different concentrations: (**a**) RGO-PN-50, (**b**) RGO-PN-100, and (**c**) RGO-PN-150.

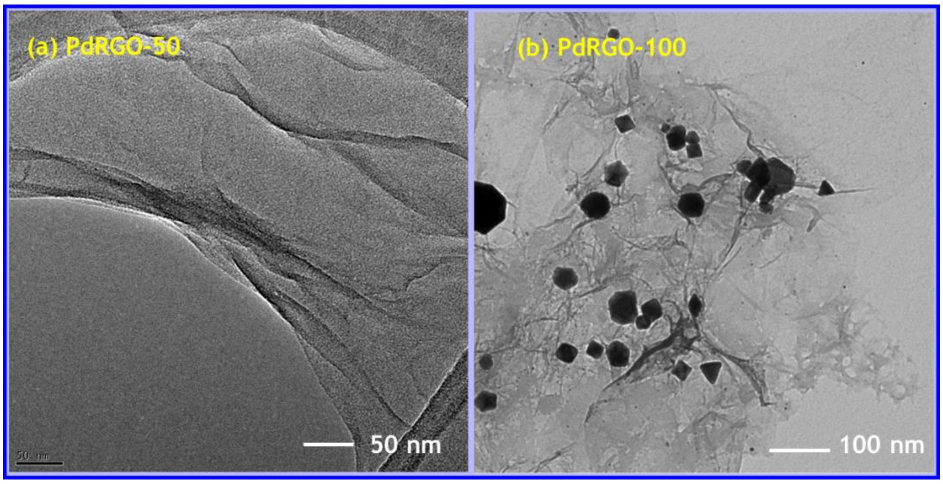

Figure 4. TEM images of green synthesized nanostructures: (**a**) RGO and (**b**) RGO-PN-100.

3.4. XPS Analysis

The XPS patterns that were investigated to determine the chemical compositions and electronic structures of the elements on the prepared RGO-PN100 are displayed in Figure 5. The survey scan of the green synthesized RGO-PN100 suggested the Pd, C, and O were observed, which are depicted in Figure 5a. Moreover, in the enlarged spectra of the palladium 3d region depicted in Figure 5b, the peaks located at 337.8 eV and 342.7 eV are assigned to the Pd^0 species of $Pd3d_{5/2}$ and $Pd3d_{3/2}$ of green synthesized RGO-PN100 from *Coleus amboinicus*. Moreover, two peaks were observed at a lower region, which may be due to the presence of Pd^{2+} [25]. The enlarged C1s spectra denoted the four peaks at 284.0, 285.5, 286.3, and 288.4 eV (Figure 5c). The peak at 284.4 eV represents the C=C/C–C of graphitic or amorphous carbon, the peaks at 285.5 and 286.3 eV were attributed to the sp^2 carbon (C=O and C–OH), and the peak at 288.4 eV represents the carboxyl group (–COOH) [26]. Furthermore, the enlarged spectrum of oxygen (Figure 5d) denotes the peaks at 530.2, 531.8, 533.8, 535.0, and 536.4 eV, corresponding to the C=O, C–O, –OH, C–O–C, and –COO. Furthermore, the enlarged spectrum of N1s suggests the peaks at 399.3 and 401.0 eV can be attributed to the amines and amides (Figure 5e). The presence of the functional groups, such as amines and carboxylic and carbonyl groups, clearly suggests the presence of biomolecules in the synthesis of RGO-PN as capping and stabilizing materials.

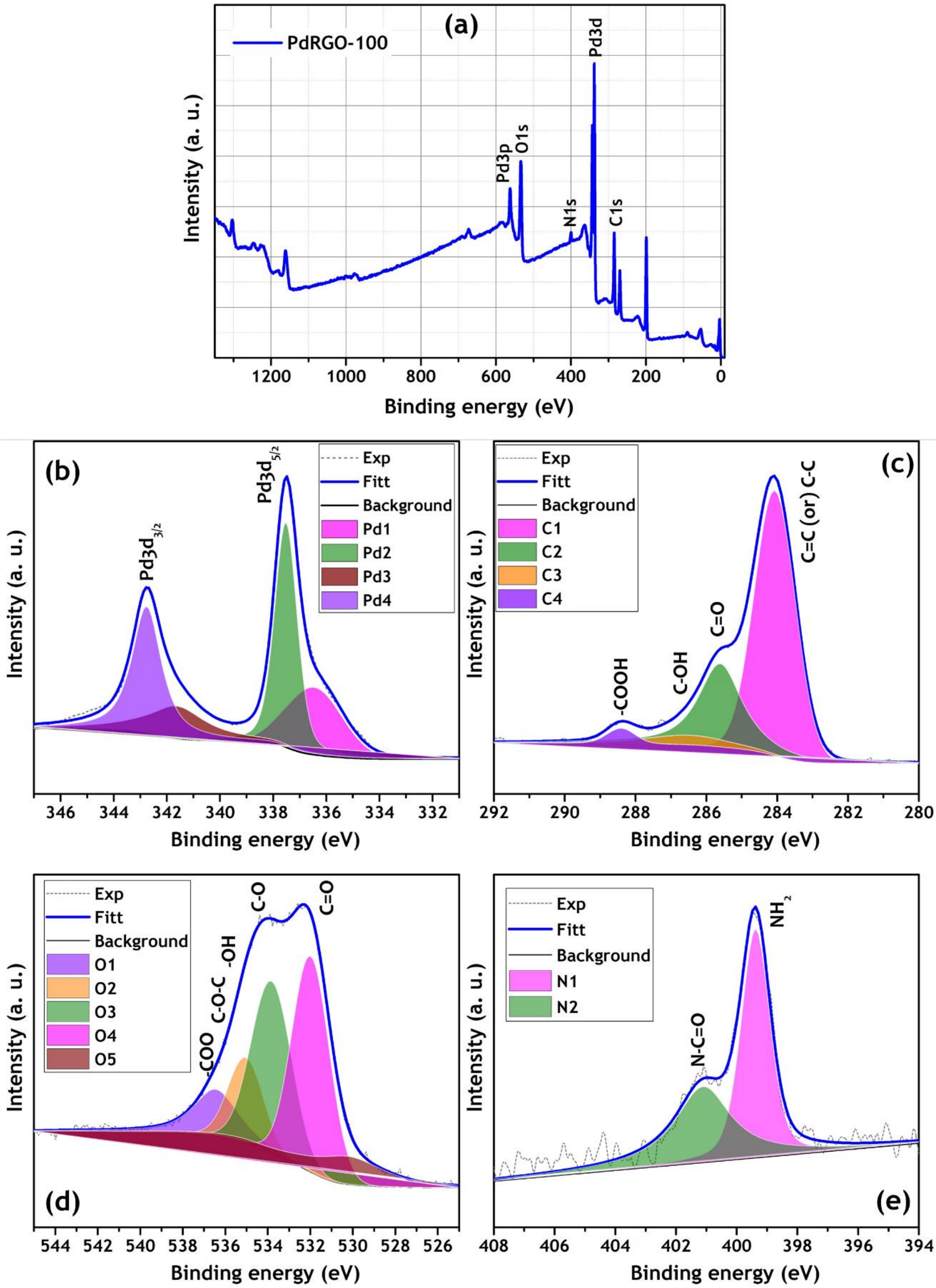

Figure 5. XPS spectra of RGO-PN100 for (**a**) survey scan, (**b**) palladium, (**c**) carbon, (**d**) oxygen, and (**e**) nitrogen elements.

3.5. Catalytic Reduction of 4-Nitrophenol by Pd-RGO100 Nanoparticles

The catalytic efficiency of green synthesized RGO-supported palladium nanoparticles was elucidated through a reliable one-step catalytic reduction of the 4-nitrophenol method (Figure 6). The characteristic absorption peak of the nitrophenol and $NaBH_4$ mixture was identified near 400 nm and showed the maximum intensity at 0 min, i.e., before the reaction. As the reaction time increased up to 40 min, the intensity of the absorption peak at 400 nm monotonically decreased, which presumably is due to the addition of RGO-supported palladium nanoparticles to the reaction mixture. Therefore, it is believed that RGO-PN100 can accelerate the reduction of 4-nitrophenol to 4-aminophenol. It is also noted that at the end of the 40 min reaction, the characteristic absorption peak at 400 nm was not detected anymore, and instead another small peak was identified at 294 nm, which confirmed the complete reduction of 4-nitrophenol to 4-aminophenol. Thus, green synthesized RGO-PN100 nanoparticles showed a comparatively desirable reduction time of 40 min, which demonstrated that RGO-PN prepared from *Coleus amboinicus* served as an excellent catalytic reducing agent. Moreover, the dye degradation results were fitted using a pseudo-first-order equation and the rate of reaction was estimated based on the Langmuir–Hinshelwood reaction model equation: $\text{Log}(C_t/C_0) = -kt$, where t is the time of reaction, C_0 and C_t are the concentration of solution at initial and regular intervals, and k is the apparent reaction rate constant. The estimated apparent rate of reaction constant of RGO-PN100 was 0.104×10^{-2} s^{-1} and is compared with the recent literature in Table 1 [22–25].

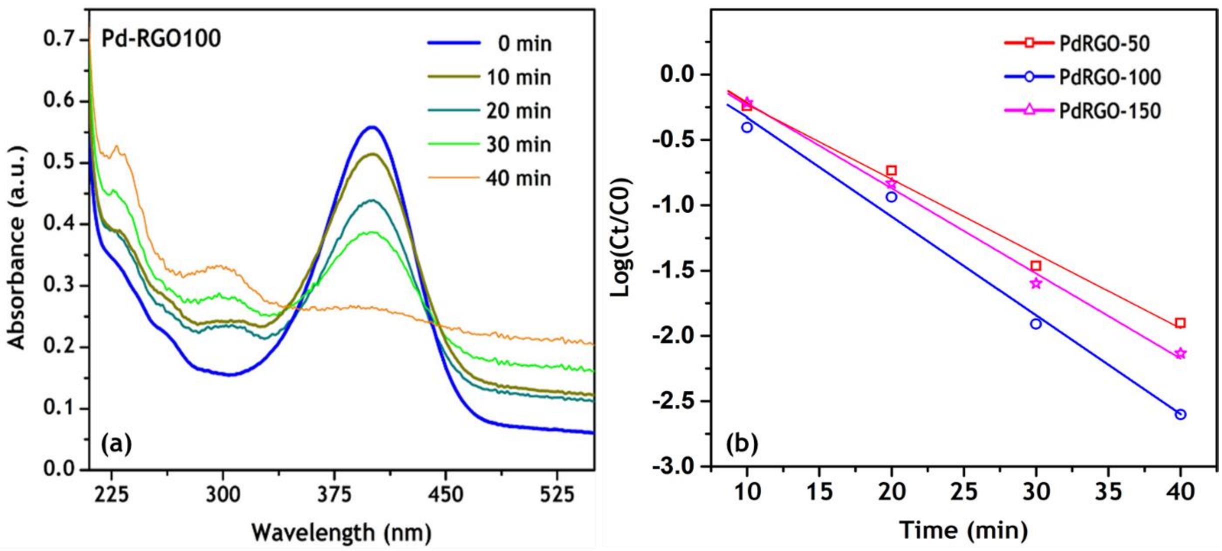

Figure 6. (**a**) Degradation kinetics of 4-nitrophenol using green synthesized RGO-PN100 from *Coleus amboinicus* (**b**) plots of reaction time versus Log (C_t/C_0).

Table 1. Comparison of rate of reaction constant (k) with recent literature.

Catalyst	[Dye] (mM)	[$NaBH_4$] mM	k ($\times 10^{-2}$ s^{-1})	References
Pd-Au/MCA	[4NP]0.54	47.1	0.47	[27]
Cu-Fe_2O_3/RGO	[4NP]10	1.85	0.11	[28]
Pd@C	[Nitrobenzene]0.4	200	0.013	[29]
Pt-Pd supported on Fe_3O_4@C	[4NP]30	300	0.0023	[30]
RGO -PN100	[4NP]2	500	0.104	Present work

3.6. Antimicrobial Activity

The results of antimicrobial activities of RGO-PN against human pathogenic strains of *E. coli* were shown in Figure 7. The results revealed that green synthesized Pd-RGO showed effective antibacterial activity against *E. coli*. Standard antibiotic streptomycin (10 µg) showed the maximal zone of inhibition at 18 mm, whereas the 10 µg of green synthesized RGO (point 1), RGO-PN50 (point 2), RGO-PN100 (point 4), and RGO-PN150 (point 3) nanoparticles showed a gradual increase in zone of inhibition at 2 mm (RGO), 4 mm (RGO-PN50), 12 mm (RGO-PN100), and 10 mm (RGO-PN150), respectively. Green synthesized RGO-PN from the leaf extract of *Coleus amboinicus* showed remarkable antibacterial activity against *E. coli.*

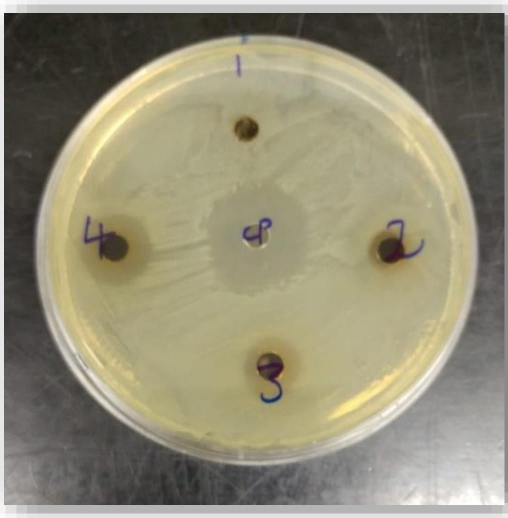

Figure 7. The zone of inhibition (ZOI) formed by green synthesized RGO-PN100 from *Coleus amboinicus* against the human bacterial pathogen *E. coli* (ATCC25922): (1) RGO, (2) RGO-PN50, (3) RGO-PN150, and (4) RGO-PN100.

4. Conclusions

Eco-friendly reduced graphene oxide-supported palladium nanoparticles with diverse applications in both environmental and medical fields were synthesized using *Coleus amboinicus* through the biological green synthetic protocol. The SEM and XRD results affirmed that green synthesized palladium nanoparticles are spherical in shape with a diameter of 40–50 nm and stick well to the surface of reduced graphene oxide. The maximal peak of absorption at the UV region of 240 nm by nanoparticle suspension confirms the reduction of palladium ions into palladium nanoparticles by the *Coleus amboinicus* plant extract. Green synthesized RGO-PN100 possessed its catalytic efficiency of 4-nitrophenol reduction at 40 min and further showed antimicrobial activit y against the human pathogenic microorganism *E.coli* by producing a 12-mm zone of inhibition. Finally, the RGO-supported palladium nanoparticles obtained from the eco-friendly green synthetic protocol using *Coleus amboinicus* can be used as bio-reduction agents. Moreover, the synthesized RGO-PN has a dual application in both environmental clean-up and pharmaceuticals.

Author Contributions: K.M. performed the experimental work and writing and review, L.V.R. performed the antibacterial study; S.A.-R. provided the resource and funding, A.M. analyzed the data and supervision, S.G. provided the instrumentation, writing, and editing, and W.K.K. supervision, editing the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available on request due to restrictions e.g., privacy or ethical.

Acknowledgments: The authors extend their appreciation to the researchers supporting project number (RSP-2020/200), King Saud University, Riyadh, Saudi Arabia, and Priority Research Centers Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education (2014R1A6A1031189).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Pd-RGO—Reduced Graphene Oxide-Palladium Complex, RGO-PN—Reduced Graphene Oxide-Palladium Nanoparticles, NAC—Nitro Aromatic Compounds, 4-NP—4 Nitro Phenol, XPS—X-ray photoelectron spectroscopy, SEM—scanning electron microscopy, TEM—Transmission electron microscopy.

References

1. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Kalsnelson, M.I.; Grigorieva, I.V.; Dubonos, S.V.; Firsov, A.A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438*, 197–200. [CrossRef] [PubMed]
2. Balandin, A.A.; Suchismita, G.; Wenzhong, B.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C.N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett.* **2008**, *8*, 902–907. [CrossRef] [PubMed]
3. Bao, Y.; Yan, Q.; Ji, J.; Qiu, B.; Zhang, J.; Xing, M. Graphene-Based Photo-Fenton Catalysts for Pollutant Control. *Trans. Tianjin Univ.* **2021**, 1–17. [CrossRef]
4. Tran, T.P.N.; Nguyen, T.N.; Taniike, T.; Nishimura, S. Tailoring Graphene Oxide Framework with N-and S-Containing Organic Ligands for the Confinement of Pd Nanoparticles Towards Recyclable Catalyst Systems. *Catal. Lett.* **2020**, *151*, 247–254. [CrossRef]
5. Shen, Y.; Lu, S.; Xu, W.; Lv, A.; Wang, Z.; Wang, H.; Liu, G.; Zhang, Y. Fabrication of Composite Material with Pd Nanoparticles and Graphene on Nickel Foam for Its Excellent Electrocatalytic Performance. *Electrocatalysis* **2020**, *11*, 522–535.
6. Kovtyukhova, N.I.; Ollivier, P.J.; Martin, B.R.; Mallouk, T.E.; Chizhik, S.A.; Buzaneva, E.V.; Gorchinskiy, A.D. Layer-by-Layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem. Mater.* **1999**, *11*, 771–778. [CrossRef]
7. Kole, A.K.; Biswas, S.; Tiwary, C.S.; Kumbhakar, P. A facile synthesis of graphene oxide–ZnS/ZnO nanocomposites and observations of thermal quenching of visible photoluminescence emission and nonlinear optical properties. *J. Lumin.* **2016**, *179*, 211–221. [CrossRef]
8. Jayakumar, A.; Vedhaiyan, R.K. Rapid synthesis of phytogenic silver nanoparticles using Clerodendrum splendens: Its antibacterial and antioxidant activities. *Korean J. Chem. Eng.* **2019**, *36*, 1869–1881. [CrossRef]
9. Mori, K.; Kumami, A.; Tomonari, M.; Yamashita, H. A pH-Induced Size Controlled Deposition of Colloidal Ag Nanoparticles on Alumina Support for Catalytic Application. *J. Phys. Chem. C* **2009**, *113*, 16850–16854.
10. Saha, S.; Pal, A.; Kundu, S.; Basu, S.; Pal, T. Photochemical Green Synthesis of Calcium-Alginate-Stabilized Ag and Au Nanoparticles and Their Catalytic Application to 4-Nitrophenol Reduction. *Langmuir* **2010**, *26*, 2885–2893. [CrossRef]
11. Zhang, Z.; Shao, C.; Zou, P.; Zhang, P.; Zhang, M.; Mu, J.; Guo, Z.; Li, X.; Wang, C.; Liu, Y. In situ assembly of well-dispersed gold nanoparticles on electrospun silica nanotubes for catalytic reduction of 4-nitrophenol. *Chem. Commun.* **2011**, *47*, 3906–3908. [CrossRef]
12. Jin, Z.; Xiao, M.; Bao, Z.; Wang, P.; Wang, J. A General Approach to Mesoporous Metal Oxide Microspheres Loaded with Noble Metal Nanoparticles. *Angew. Chem. Int. Ed.* **2012**, *51*, 6406–6410. [CrossRef] [PubMed]
13. Shargh, A.Y.; Sayadi, M.H.; Heidari, A. Green Biosynthesis of Palladium Oxide Nanoparticles Using Dictyota indica Seaweed and its application for adsorption. *J. Water Environ. Nanotechnol.* **2018**, *3*, 337–347.
14. Mahdavi, H.; Rezaei, M.; Ahmadian-Alam, L.; Amini, M.M. A novel ternary Pd-GO/N-doped TiO2 hierarchical visible-light sensitive photocatalyst for nanocomposite membrane. *Korean J. Chem. Eng.* **2020**, *37*, 946–954. [CrossRef]
15. Bhuyan, D.; Saikia, M.; Saikia, L. Magnetically recoverable Fe3O4@SBA-15: An improved catalyst for three component coupling reaction of aldehyde, amine and alkyne. *Catal. Commun.* **2014**, *58*, 158–163. [CrossRef]
16. Feng, X.; Yan, M.; Zhang, T.; Liu, Y.; Bao, M. Preparation and application of SBA-15-supported palladium catalyst for Suzuki reaction in supercritical carbon dioxide. *Green Chem.* **2010**, *12*, 1758–1766. [CrossRef]
17. Arumugam, G.; Swamy, M.K.; Sinniah, U.R. *Plectranthus amboinicus* (Lour.) Spreng: Botanical, Phytochemical, Pharmacological and Nutritional Significance. *Molecules* **2016**, *21*, 369. [CrossRef]
18. Ju, K.S.; Parales, R.E. Nitroaromatic Compounds, from Synthesis to Biodegradation. *Microbiol. Mol. Biol. Rev.* **2010**, *74*, 250–272. [CrossRef]
19. Tomei, M.C.; Annesini, M.C.; Rita, S.; Daugulis, A.J. Two-Phase Partitioning Bioreactors Operating with Polymers Applied to the Removal of Substituted Phenols. *Environ. Sci. Technol.* **2010**, *44*, 7254–7259.

20. Yi, S.; Zhuang, W.Q.; Wu, B.; Tay, S.T.L.; Tay, J.H. Biodegradation of p-Nitrophenol by Aerobic Granules in a Sequencing Batch Reactor. *Environ. Sci. Technol.* **2006**, *40*, 2396–2401. [CrossRef]
21. Aditya, T.; Pal, A.; Pal, T. Nitroarene reduction: A trusted model reaction to test nanoparticle catalysts. *Chem. Commun.* **2015**, *51*, 9410–9431. [CrossRef] [PubMed]
22. Podeh, M.R.H.; Bhattacharya, S.K.; Qu, M. Effects of nitrophenols on acetate utilizing methanogenic systems. *Water Res.* **1995**, *29*, 391–399. [CrossRef]
23. Sarkar, S.; Sinha, A.K.; Pradhan, M.; Basu, M.; Negishi, Y.; Pal, T. Redox Transmetalation of Prickly Nickel Nanowires for Morphology Controlled Hierarchical Synthesis of Nickel/Gold Nanostructures for Enhanced Catalytic Activity and SERS Responsive Functional Material. *J. Phys. Chem. C* **2011**, *115*, 1659–1673. [CrossRef]
24. Hummers, W.S.; Offeman, R.E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339. [CrossRef]
25. Zhou, J.C.; Soto, C.M.; Chen, M.S.; Bruckman, M.A.; Moore, M.H.; Barry, E.; Ratna, B.R.; Pehrsson, P.E.; Spies, B.R.; Confer, T.S. Biotemplating rod-like viruses for the synthesis of copper nanorods and nanowires. *J. Nanobiotechnol.* **2012**, *10*, 18. [CrossRef] [PubMed]
26. Kwan, Y.C.G.; Ng, G.M.; Huan, C.H.A. Identification of functional groups and determination of carboxyl formation temperature in graphene oxide using the XPS O 1s spectrum. *Thin Solid Films* **2015**, *590*, 40–48. [CrossRef]
27. Jiang, F.; Li, R.; Cai, J.; Xu, W.; Cao, A.; Chen, D.; Zhang, X.; Wang, C.; Shu, C. Ultrasmall Pd/Au bimetallic nanocrystal embedded in hydrogen-bonded supramolecular structures: Facile synthesis and catalytic activities in the reduction of 4-niteophenol. *J. Mater. Chem. A* **2015**, *3*, 19433–19438. [CrossRef]
28. Xu, R.; Bi, H.; He, G.; Zhu, J.; Chen, H. Synthesis of Cu-Fe_3O_4@graphene composite: A magnetically separable and efficient catalyst for the reduction of 4-nitrophenol. *Mater. Res. Bull.* **2014**, *57*, 190–196. [CrossRef]
29. Kim, Y.; Ma, R.; Reddy, D.A.; Kim, T.K. Liquid-phase pulsed laser ablation synthesis of graphitized carbon-encapsulated palladium core-shell nanospheres for catalytic reduction of nitrobenzene to aniline. *Appl. Surf. Sci.* **2015**, *357*, 2112–2120. [CrossRef]
30. Zhang, P.; Li, R.; Huang, Y.; Chen, Q. A novel approach for the in situ synthesis of Pt-Pd nanoalloys supported on Fe_3O_4@C core-shell nanoparticles with enhanced catalytic activity for reduction reactions. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2671–2678. [CrossRef]