Radiation-Induced Synthesis and Immobilization of Palladium Nanoparticles on Polypropylene Non-Woven Fabric

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Abstract: A recyclable Pd-EDA-f-PP-g-PGMA fabric was synthesized using environment friendly gamma-induced reduction technique where Pd^{2+} was reduced and immobilized on ethylenediamine-functionalized polypropylene non-woven fabric using Co-60 gamma source. Palladium nanoparticles were successfully immobilized and stabilized through the diamine ligand present on the fabric support as confirmed by XPS and FTIR. XPS analysis identified the Pd components as surface Pd^0, bulk Pd^0, and some Pd^{2+}. The nanoparticle yield was found to increase with the radiation dose and the precursor concentration affording diameter sizes of 78.12 ±30 nm using 6.0 mM initial concentration at dose of 50 kGy. TGA analysis showed that the synthesized Pd-EDA-f-PP-g-PGMA has improved thermal stability, which can be suitable for applications such as catalysis in elevated temperature.

Key Words: Palladium; nanoparticles; grafted polypropylene

1. INTRODUCTION

Metallic nanoparticles (MNPs) are promising materials due to their size affording unique and improved chemical properties. Gamma radiation-induced synthesis of MNPs by reduction of metal ions is a less common technique because radiation facility is not readily available. The technique, however, is a very efficient approach because the reaction can be carried out in ambient pressure and temperature with high reproducibility. The synthesis is usually carried out in water as the solvent without addition of any toxic chemical reducing agents making it an environmentally advantageous process (Abedini et al., 2016). MNPs immobilized on a solid support has been shown to improve the stability of MNPs and to facilitate easy separation from the reaction mixture (Clifford et al., 2017). The usual solid supports for MNPs are metal oxides, graphene, carbon nanotubes, polymers, metal organic frameworks, and zeolites. A cursory survey of the literature showed minimal works on the use of polypropylene (PP) fabric as MNP support (Misra et al., 2018), hence this work. It is the objective of this work to synthesize and immobilize Pd nanoparticle on a non-woven PP fabric using radiation.

2. METHODOLOGY

2.1 Synthesis of EDA-f-PP-g-PGMA solid support

The non-woven PP fabric (40 cm x 20 cm^2; Agriculture & Supplies Corp. Phils.) was irradiated using electron beam at 40 kGy and was reacted with the monomer emulsion containing 5% (w/w) glycidyl methacrylate monomer (GMA, ≥99.7%, Aldrich) and

Tween 20 at 5:1 (w/w) ratio for 3.5 hours at 40° C. After grafting, the fabric sample was washed thoroughly with methanol to remove unreacted monomers then dried in vacuo overnight at 40° C. The resulting polypropylene-g-poly(glycidyl methacrylate) (PP-g-PGMA) was added into a solution of 50% (w/w) ethylenediamine (EDA,> 99%, Sigma- Aldrich) in isopropyl alcohol at 60°C. After 30 minutes, the sample was washed with methanol then dried in vacuo to afford EDA-functionalized PP-g-PGMA (EDA-f-PP-g-PGMA).

2.2 Synthesis and Immobilization of Pd on EDA-f-PP-g-PGMA solid support

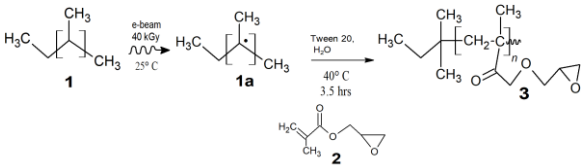
$PdCl_2$ (2.0 mM) was prepared in 2:1 H_2O/IPA solvent. Eight mL of $PdCl_2$ solution was transferred in a glass vial and the EDA-f-PP-g-PGMA support (1x2 cm^2) was immersed in the solution. The reaction was sealed with a septa, purged with N_2 gas, and subjected to gamma irradiation at the PNRI Multipurpose Irradiation Facility using a ^{60}Co source at a dose of 50 kGy and a dose rate range of 2.5-2.8 kGy/hr. After irradiation, the Pd-EDA-f-PP-g-PGMA sample was washed several times with deionized water to remove excess metals, stored in resealable bags, and purged with N_2 gas.

2.3 Characterization of PdNPs immobilized on EDA-f-PP-g-PGMA solid support

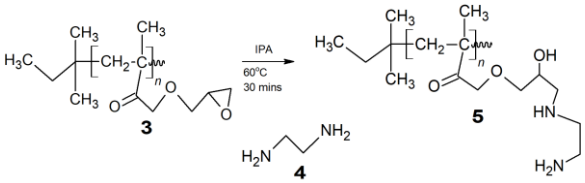
Characterization of PdNPs was done using X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX) following standard protocols. Nanoparticle dimensions were measured using ImageJ software using n=100 readings)

3. RESULTS AND DISCUSSION

The irradiated non-woven polypropylene (PP) fabric **1** formed free radicals on the tertiary carbon of PP, which are highly reactive species that served as the initiation site for the incorporation of GMA **2.** The doses for irradiation have been optimized as previously reported (Madrid et al., 2017). The carbon-carbon double bond in **2** will be attacked by the free radical forming a new covalent bond between the initiator carbon on **1a** and GMA **2** monomer. The polymerization process proceeds until another radical reacts and the termination step occurred. The degree of grafting (Dg) in the resulting fabric **3** having a dimension of 40 x20 cm^2, was gravimetrically obtained and was calculated to be 200%.



The PP-g-PGMA **3** fabric was further functionalized with ethylenediamine (EDA) **4**, which resulted in the introduction of amine functional groups by ring-opening of the epoxy moiety in **3** to obtain the EDA-f-PP-g-PGMA **5**. The ethylenediamine **4** nucleophile, bearing unpaired electrons, attacks the less hindered epoxide carbon on **3**, breaking the C-O bond, leaving the oxygen negatively charged. The oxygen then abstracts H from isopropanol forming the product **5**.



The FTIR spectra of the pristine **1**, grafted **3**, and functionalized PP **5** highlights the comparison between the peaks (Fig. 1). The incorporation of GMA on the PP chain gives rise to the strong bands at 1700 cm^{-1} and 1260 cm^{-1}, which are unique to the C=O group and C-O stretch of the GMA moieties. Moreover, intense bands around 900 cm^{-1} and 800 cm^{-1} are present, which corresponds to the epoxide groups of the GMA moiety. Upon functionalization with EDA, the epoxide bands from this region disappeared from the spectrum, indicating the successful incorporation of ethylenediamine through the ring-opening of the epoxide group. This is confirmed by the new bands that appeared at 1570 cm^{-1} and 1600 cm^{-1}, which corresponds to the presence of N-H bending from the amine group. More importantly, the broad peak at 3500-3100 cm^{-1} confirms the successful reaction of

EDA on GMA grafted PP as this band corresponds to the overlap of the N-H and O-H peaks.

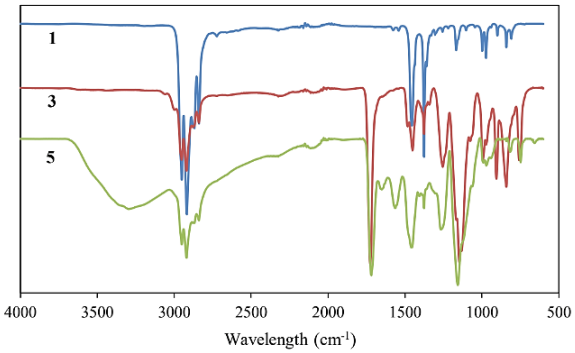


Fig.1 FTIR spectra of PP (**1**) PP-g-PGMA (**3**), and EDA-f-PP-g-PGMA (**5**)

The in-situ reduction of Pd by immobilization to the synthesized support **5** to produce **6** was done using gamma irradiation (Misra et al., 2018). The appearance of black coloration on the support after the irradiation confirmed the reduction and simultaneous immobilization of Pd (Fig. 2).

Fig. 2 EDA-f-PP-g-PGMA in 6.0 mM $PdCl_2$ before and after gamma irradiation

The IR spectra of the EDA-f-PP-g-PGMA **5** and Pd-EDA-f-PP-g-PGMA **6** (Figure 3-A) showed the differences in absorbance. The band around 3293 cm^{-1} corresponds to the N-H, O-H overlap stretchings of the amine and hydroxyl group in the bare support. With Pd immobilized on the support, a shift of these stretching vibrations to lower wavenumber around 3210 cm^{-1} is observed due to the weakening of the N-H bonds because of its coordination with the metal atom causing electron drainage from the nitrogen atom (Golcuk et al., 2003). Moreover, the overlapping of the NH_2 bending peaks at 1560-1655 cm^{-1} as a broad peak at ~1618 cm^{-1} for **6** also suggests the complexation of Pd via the nitrogen group of the EDA (Fig. 3B).

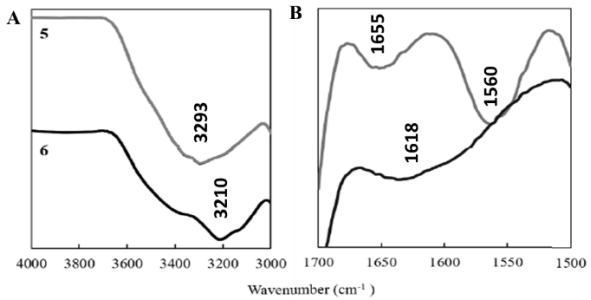


Fig. 3 Expanded FTIR spectra of bare EDA-f-PP-g-PGMA (**5**) and Pd-EDA-f-PP-g-PGMA (**6**)

XPS analysis showed the characteristic Pd-3d (334 and 340 eV) doublet prominently present confirming the formation and immobilization of PdNPs in the support (Fig. 4). Deconvolution and curve fitting of Pd peaks were done to determine the Pd components under the Pd 3d5/2 region. Three characteristic Pd components with binding energies centered at 334.4, 335.4 and 337.2 eV individually identified as the surface Pd^0, bulk Pd^0, and Pd^{+2}, respectively were identified consistent with the previously reported works by Misra et al., (2018); Chang et al., (2012), and Massard et al., (2006). The presence of Pd^{+2} in the sample may be attributed to the formation of the Pd-O bond or due to the incomplete reduction of Pd^{+2} ions. Analysis of peak area revealed that 94% of Pd^0 is formed while only 6% Pd^{+2} was obtained. The use of PP fabric support, which has a high specific area, leads to entrapment of more metal clusters either on the surface or pores (Tang et al., 2017).

SEM image of bare EDA-f-PP-g-PGMA (**5**) (Fig. 5A) showed smooth surface. In contrast, the Pd-EDA-f-PP-g-PGMA (**6**) (Fig. 5B) showed that the surface is evidently covered by PdNPs with some clusters present indicating that the functionalized PP successfully aided the formation of PdNPs.

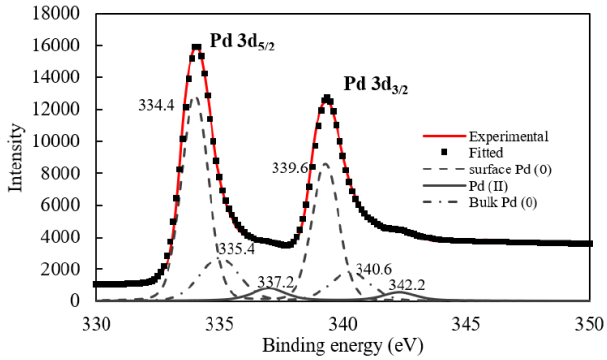


Fig. 4. HR-XPS spectra of Pd-EDA-f-PP-g-PGMA **6** irradiated at 50 kGy and 6.0 mM Pd precursor concentrations

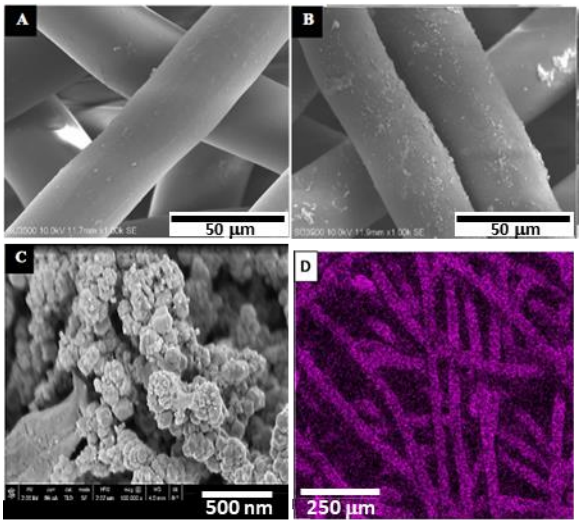


Fig. 5 SEM images of (A) EDA-f-PP-g-PGMA **5;** (B) Pd-EDA-f-PP-g-PGMA **6** with 6.0 mM initial Pd precursor concentration; (C) magnified SEM image (100K x) of **6**; and (D) Pd map surface of **6.** (Reproduced from Lopez, et al. 2020, with permission from Royal Society of Chemistry)

Closer inspection of the image (Fig. 5C) revealed noticeable variations in the clusters formed on the surface of the support. Particles with average diameter sizes of 78.12 ±30 nm were obtained on the samples prepared using 6.0 mM initial metal precursor concentration. Despite the presence of Pd clusters, it can be observed that PdNPs were successfully immobilized with full coverage on the fabric as shown by the Pd mapping of the sample (Fig. 5D).

The thermal profile of Pd-EDA-f-PP-g-PGMA **6** was compared with the bare EDA-f-PP-g-PGMA **5** (Fig. 6). Both samples exhibited loss of mass at 80°C, which corresponds to the loss of water. For the bare support, the second degradation commenced at the temperature range of 100- 200°C, which parallels to the breaking down of the amine bonds (Madrid et al., 2017). On the other hand, the Pd-EDA-f-PP-g-PGMA showed majority of the decomposition occurred at the range of 200-350 °C with T_{max}= 274 °C corresponding to a weight loss of about 40%. The residual mass obtained after the analysis is 9.3 ±0.30%, which relate to the amount of immobilized Pd on the support. Results showed that the fabricated Pd-loaded material has improved thermal stability, which can be suitable for applications such as catalysis in elevated temperature.

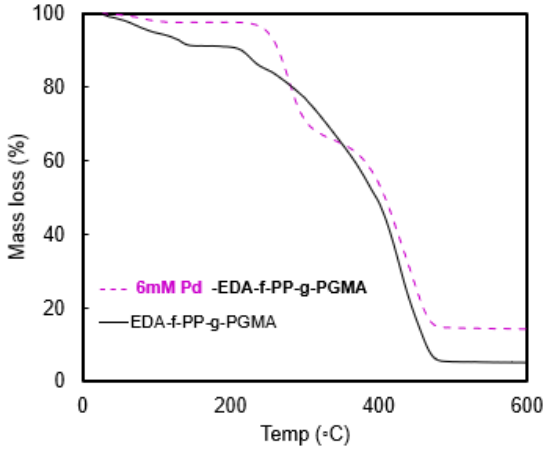


Fig. 6 Thermal profile of Pd-EDA-f-PP-g-PGMA using TGA

4. CONCLUSIONS

In conclusion, this work successfully synthesized and immobilized PdNPs on EDA-f-PP-g-PGMA using gamma irradiation. Characterization techniques such as FTIR, XPS, EDS, and SEM provided relevant information on the nature and morphology of Pd clusters present on the support.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Abedini, A., Bakar, A. A. A., Larki, F., Menon, P. S., Islam, M. S., & Shaari, S. (2016). Recent Advances in Shape-Controlled Synthesis of Noble Metal Nanoparticles by Radiolysis Route. Nanoscale Research Letters, 11(1), 1–13.

Chang, C.M., Hon, M.H., Leu, I.C. (2012). Improvement in CO sensing characteristics by decorating ZnO nanorod arrays with Pd nanoparticles and the related mechanisms. RSC Advances, 2(6), 2469-2475.

Clifford, D.C., Castano, C.E., & Rojas, J.V. (2017). Supported transition metal nanomaterials: Nanocomposites synthesized by ionizing radiation. Radiation Physics and Chemistry, 132, 52–64.

Golcuk, K., Altun, A., & Kumru, M. (2003). Thermal studies and vibrational analyses of m-methylaniline complexes of Zn(II), Cd(II) and Hg(II) bromides. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59(8), 1841–1847.

Lopez, G. E. P., Madrid, J. F., Camacho, D. H. (2020) Gamma radiation-assisted in-situ synthesis of Palladium nanoparticles supported onto ethylenediamine functionalized polypropylene fabric. New Journal of Chemistry. 44, 19337-19350.

Madrid, J.F., Lopez, G.E., Abad, L.V. (2017). Application of full-factorial design in the synthesis of polypropylene-g-poly (glycidyl methacrylate) functional material for metal ion adsorption. Radiation Physics and Chemistry, 136, 64-63.

Massard, R., Uzio, D., Thomazeau, C., Pichon, C., Rousset, J.L., Bertolini, J.C. (2006). Strained Pd overlayers on Ni nanoparticles supported on alumina and catalytic activity for buta-1,3-diene selective hydrogenation. Journal of Catalysis, 245(1), 133–143.

Misra N., Kumar V., Rawat, S., Goel NK., Shelkar A., Singhal R.K., Varshney L. (2018) Mitigation of Cr(VI) toxicity using Pd-nanoparticles immobilized catalytic reactor (Pd-NICaR) fabricated via plasma and gamma radiation. Environmental Science and Pollution Research, 25(16), 16101-16110.

Tang , B., Lin, X., Zou, F., Fan, Y., Li, D., Zhou, J., Chen, W., Wang, X. (2017). In situ synthesis of gold nanoparticles on cotton fabric for multifunctional applications Cellulose, 24(10), 4547–4560.