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SYNTHESIS AND APPLICATION FOR THE REDUCTION OF 4-NITROPHENOL USING PALLADIUM NANOPARTICLES DECORATED GRAPHENE OXIDE

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ABSTRACT

Here, a novel and easy approach for the synthesis of Pd nanoparticles (PdNPs) decorated graphene oxide [PdNP/GO; (GO-Graphene Oxide)] in the neutral medium is proposed and employed as a heterogeneous catalyst material for transformation of 4-Nitrophenol (4-NP) into 4-Aminophenol (4-AP). The resulting materials were fully characterized by surface morphology and electroanalytical techniques. The catalyst was examined by using various microscopy techniques. FESEM analysis shows successful incorporation of Pd NPs into GO matrix and EDAX analysis also supports the presence of PdNPs in the system. It was found that the material was a successful heterogeneous catalyst material for 4-NP reduction. It was added during the conversion followed by examined with UV-Vis spectroscopy. The disappearance of 4-NP peak around 400 nm and the emergence of a new peak at 298 nm shows the entire reduction reaction and shows good conversion ability and stability towards the reaction.

Keywords: Nitrophenol, Aminophenol, Palladium, Nanoparticles, Graphene Oxide, Nanomaterials.

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INTRODUCTION

4-Aminophenol has profound use in various fields such as pharmaceuticals where it is an intermediate for the synthesis of various medicines such as paracetamol, acetanilide, phenacetin, etc., besides the applications in health care; it is highly seminal in other fields like photographic developers, corrosion inhibitors. So, there is a huge demand for the synthesis of the compound. Therefore, research is focused on the conversion of 4-NP to 4-AP. Excess amounts of reducing agents such as sodium borohydride cannot transform 4-NP to 4-AP. Therefore, research has been directed towards the development of catalyst(s) for the synthesis of 4-AP. To achieve this, various methods have been proposed such as hydrogenation of nitrobenzene[1], catalytic amination of hydroquinone[2], reduction using electrochemical methods[3] have been tried. However, those methods are associated with certain problems like pollution, side products formation like aniline, and long time consuming for the completion of the reaction, methodology involving different hazardous chemicals. During the traditional hydrogenation, iron and tin acids were used. They are associated with certain disadvantages like pollution, formation of metal oxide sludge etc.[4] Apart from these catalysts, there are reports with spinels type of materials such as $NiCo_2O_4$[5], $CuFe_2O_4$[6], Ni / Al_2O_3[7] for the production of 4-AP. Further, transition metal catalysts have been attempted for the formation of 4-AP.[8-9] Since the transition metals can exhibit different oxidation states, variable valencies and large surface area etc., they are found as an efficient catalysts in various reactions, Those reactions are found to be very useful in the fields of sensors, pharmaceuticals and catalysis etc., Further, the well-known phenomenon, high surface to volume ratio makes the metal nanoparticles as a unique one in heterogeneous catalysis. The use of metal NPs has its advantages in catalytic reduction reactions.

Hence, there are a number of reports to convert 4-NP into 4-AP using transition metal NPs such as Gold NPs[10],Silver NPs[11-12], PdNPs[13], and the combination of Au-Ag alloy NPs.[14] Though the use of noble metal nanoparticles is more often, it is evident that the use of noble metals has proved to be non-economical due to the high costs of noble metals. Keeping this in view, researchers are focusing on the catalysts like non-noble metals/combinations of noble and non-noble metals. By which, one can reduce the level of noble metals in their catalyst. In this regard, catalysts like Ag/FeO[15], Ag/TiO_2[16] and Non-noble metals such as Copper nanoparticles[17-18], Ni/Al_2O_3[15], $CuFe_2O_4$[6]were also reported.

Apart from these catalysts, carbonaceous material[19-21] and its supported metal nanoparticles have gained enormous interest. It is because of the advantages of those materials like highly abundant, low-cost, extraordinary catalytic properties etc. So, the Graphene supported noble metals such as Pd/Graphene nanocomposite[22-23], Pd/Graphene nanohybrids[24], Au/graphene[25], Au/graphene hydrogel[26] are reported for their catalytic behavior in recent days. In this regard, the present work aims to develop Pd NPs decorated graphene oxide (PdNPs/GO) for the transformation of 4-NP into 4-AP. It describes a simple procedure for PdNPs loaded on GO (PdNPs/GO) preparation and its application as a heterogeneous catalyst for the complete conversion of 4-NP. Pd nanoparticle selection as a catalyst attributes to its high resistance against CO and strong binding ability during catalytic reactions. The catalyst is found efficient towards the reaction.

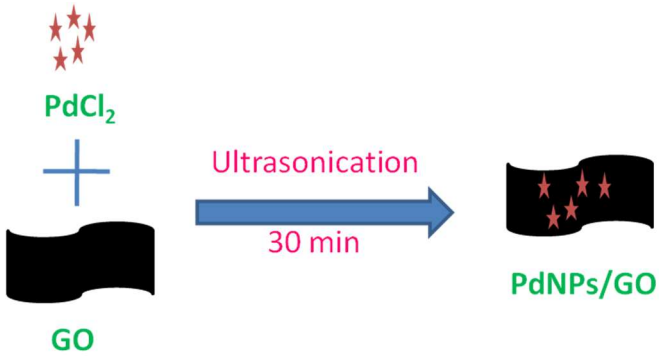
EXPERIMENTAL

Materials

All the chemicals with Analytical grade were used as received without further purification. 4-Nitrophenol, Sodium borohydride and $PdCl_2$ were purchased from Sigma Aldrich. Graphene oxide (GO) was prepared using the modified hummers technique. All the aqueous solutions were prepared using Deionized (DI) water of 18.2 MΩ resistivities from Millipore instrument.

Synthesis of Pd/GO

Synthesis of GO was done by the well-established modified Hummer's method. The synthesized GO of 1mg is dispersed in 0.5 ml of DI water and the blend was subjected for ultrasonication about 1h. Separately, 10 mmol of $PdCl_2$ has been prepared and added to GO mixture in the ratio of 10:1followed by sonicated for 30 min. Thus, resulted in PdNPs decorated GO (PdNPs/GO) mixture was used for the analysis. The catalyst preparation was shown in the Scheme-1.



Scheme-1: Schematic representation of PdNPs decoration on GO

RESULTS AND DISCUSSION

The morphological features of catalyst material are examined by different parts such as the origin of materials, conditions, modification and preparation method. Therefore, Field FE-SEM analysis was used to examine the morphological features of the synthesized PdNPs/GO catalyst. Figure-1A presents the FE-SEM image of finely dispersed PdNPs decorated GO and it confirms the presence of PdNPs on the wrinkled surface of GO. Figure-1B represents EDAX analysis of PdNP/GO. It proves the presence of Pd in the resulting catalyst. From the analysis, it is concluded that PdNps are successfully decorated on synthesized GO. Further, High-Resolution Transmission Electron Microscopic (HR-TEM) was employed to analyze the structural features of the prepared catalyst and it is shown in Fig.-2A and B. The images exhibit the fine NPs of Pd on GO and this result is in good agreement with FESEM analysis.

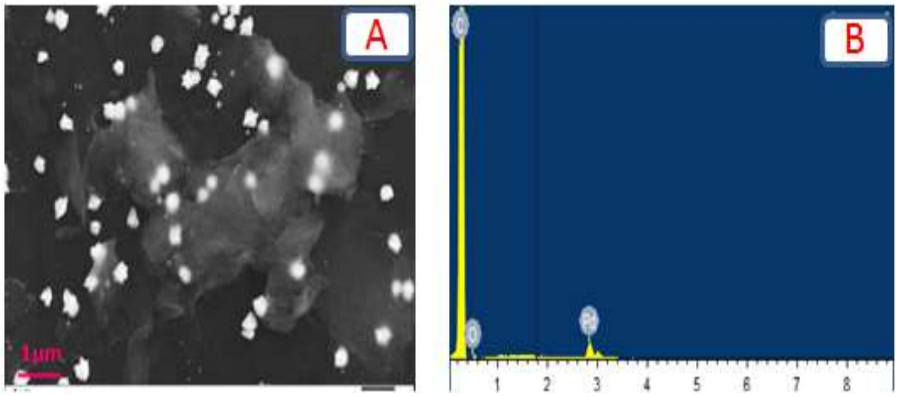


Fig.-1: (a) FE-SEM Image of PdNPs/GO (b) EDS Analysis of PdNPs/GO

The crystal lattice of PdNPs and the edges of the GO are viewed in HRTEM images are depicted in Fig.-2A with an approximate size of ~20 nm. The size of the particle was estimated from the distribution curve with an average of ~8 nm. Diffraction dots were snatched and crystallinity was evidenced by SAED image is showed in Fig.2C. The study confirms the uniform distribution of PdNPs on GO.

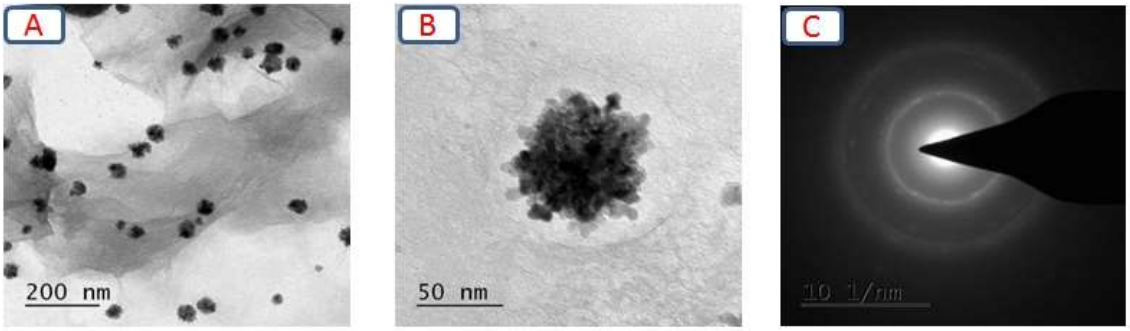


Fig.-2: (A, B) HR-TEM Micrographs and (C) SAED Design ofPdNPs/GO

The crystalline structures of synthesized GO and PdNPs/GO were investigated with XRD analysis are shown in Fig.-3. XRD pattern of GO exhibited a sharp peak at ~11° and ~42° are found as characteristics peaks for GO. They are corresponding to the diffraction patterns of 001 and 111 respectively.[27-28] Hence, it is concluded that GO is present in the system. In the case of PdNPs/GO, it displayed diffraction peaks at 28.3° and 44.2°. They were assigned to the planes, (111), (200) and (311) accredited to face-centered cubic (*fcc)* arrangement for Pd NPs/GO. From the analysis, it is confirmed that Pd NPs were successfully decorated over the GO surface.

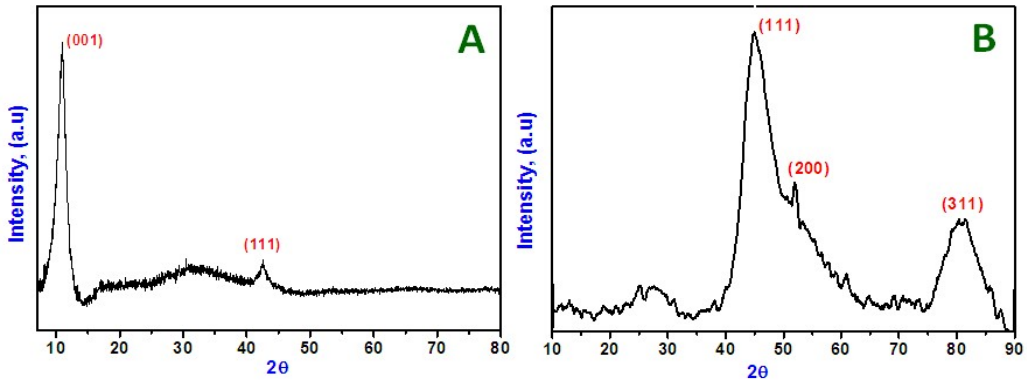


Fig.-3: XRD Pattern of (A) GO and (B) PdNPs/GO

Catalytic Reduction Studies of 4-Nitrophenol

Further, the synthesized PdNPs/GO material was used for the transformation of 4-NP. The reaction was monitored with UV-spectroscopic analysis. 4-NP usually produces the absorption band wavelength of 313 nm which is due to its resonance effect. It can be observed in Fig.-4A where a linear variation in the intensity along with analyte concentration. The concentration of the analyte ranges from 10-50 µM with a regression co-efficient value observed was 0.99. Upon addition of an excess of $NaBH_4$(1 mM), a bathochromic shift was observed at 400 nm with the color variations to dark from pale one, which strongly confirms the 4-Nitrophenolate ion[29] formation, which is depicted in Fig.-4B. Further wave intensity is increased concerning its concentration in the solution where the regression coefficient value is 0.99. From the analysis, it is proven that even in presence of excess $NaBH_4$ the reaction does not complete the reaction to yield 4-AP. Therefore, the peak observed at 400 nm remains unchanged. Hence, it arrives that $NaBH_4$ alone cannot bring 4-AP. Hence, there is a requirement for the catalyst to complete the reaction. Therefore, PdNPs/GO is employed as a heterogeneous catalyst to obtain 4-AP from 4-NP. Having added the catalyst of PdNPs/GO to the4-Nitrophenolate ion, the color was rapidly faded and finally, the solution becomes colorless. From the observation, it is concluded that the reaction moves towards the formation of 4-AP which is evidenced by the hypsochromic shift noticed at 298 nm in UV-spectrophotometric analysis which is shown in Fig.-4C.

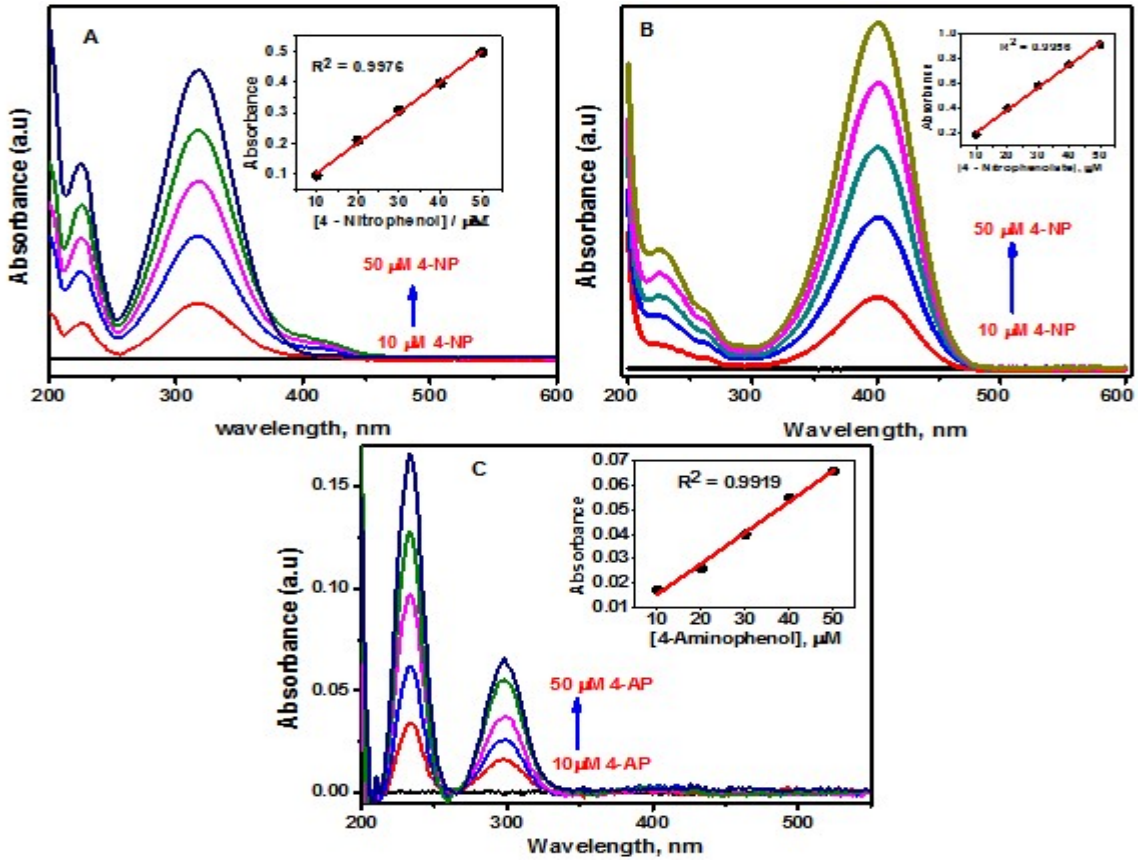
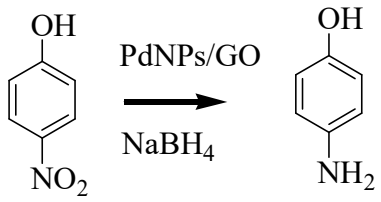


Fig. -4: (A) UV-Visible Spectrum of 4-NP in the concentration range from 10-50µM, (B) 4-NP upon the addition of 1mM of $NaBH_4$ (Formation of 4-Nitrophenolate ion) (C) Spectroscopic determination of 4-NP reduction using excess $NaBH_4$ and 20 µmol of PdNPs/GO (concentration range 10-50 µM).

It can also be observed that the intensity of the peak is directly proportional to the concentration of Aminophenol (AP) with a regression coefficient value of 0.99. Further, the yield of 4-AP is calculated from the slope and intercept values of Fig.-4C. From the calculation, it is discovered that the proposed catalyst is efficient to yield 97% of 4-AP from 4-NP. Hence, it is concluded that the proposed catalyst is found effective towards the conversion. From the experiment, it can clearly be understood that the

proposed catalyst is effective towards the transformation of the reactant (4-NP) to yield (4-AP). Because, Graphene composites are known for their excellent catalytic, optical properties etc.[30-31] further, transition metals will provide large surface area; possess different oxidation states, etc. These features made the proposed material an effective catalyst to complete the reaction. The conversion of 4-NP to 4-AP is shown in the following reaction.



Kinetic and Stability Studies

To know the kinetics of the reaction, the UV was recorded at various intervals of time is depicted in Fig.-5A. From analysis, it arrives that the material is effective to complete the reaction in 40s. Therefore, the apparent rate constant was calculated from-$\ln(A_t/A_0)$ *vs* time and it is also shown in figure 5B. Against the measurement, the apparent rate constant (k_{app}) of reaction using catalyst was calculated as $0.091s^{-1}$. The value can be matched with the other reports.[32-34] Hence, it is claimed that the PdNPs/GO is an efficient catalyst for the reaction.

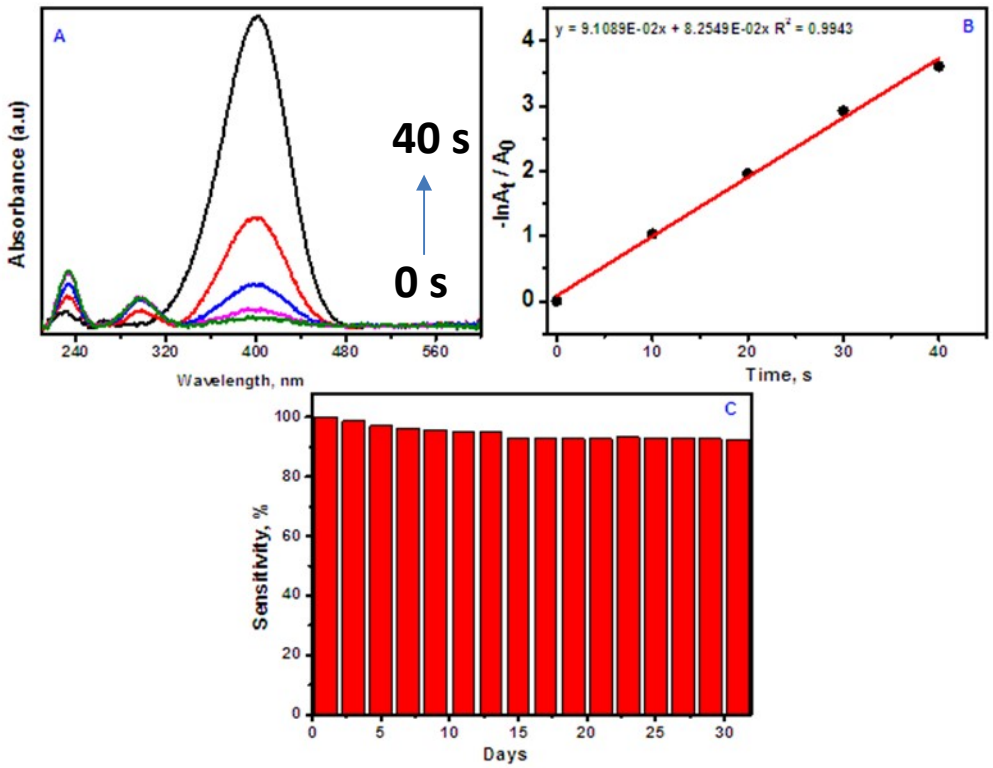


Fig.-5: (A) Time dependant spectroscopic observation 10 µM 4-NP reduction (B) corresponding correlation graph (C) Shows the stability of the PdNPs/GO catalyst material with a number of days

The synthesized catalyst was stored in the refrigerator and its catalytic properties were evaluated with respect to time. The figure shows the stability of the catalyst for a number of days. From the fig.5C, we conclude that the PdNP/GO holds its catalytic behavior without much deviation. So, we arrived that the catalyst is highly stable during the transformation of 4-NP into 4-AP.Synthesized PdNPs/GO are suitable for the reduction of 4–NP, it is due to the inherent nature of PdNPs towards adsorption/desorption of hydrogen atoms on its surface (hydrogen carrier)[35-36], the mechanism further explains that the shuttling of hydrogen atoms from $NaBH_4$ to 4-NP completed the reduction reaction.[31]

CONCLUSION

A simple and convenient one-step method has been reported for the synthesis of PdNPs/GO in an aqueous medium. The particle size of PdNPs/GO was found to be in 20-30 nm range from TEM studies. The catalytic activity of PdNPs/GO has shown controlled reaction kinetics for the reduction of 4-NP. Hence, it can conclude that PdNPs can be good catalysts for reduction reactions.

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