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Colloid template route for the synthesis of polyaniline-Pd nanocomposite and catalytic activity study for Suzuki-Miyaura coupling reaction in aqueous media

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Abstract

This work presents a new type of polyaniline- palladium (PANI-Pd) nanocomposite with different loading of Pd nanoparticle (0.5, 1 and 1.5 Wt.%) for catalytic reaction study that nanotechnology and green chemistry can come together for the development of green media reaction and this is the central theme of the current paper. PANI-Pd nanocatalyst was successfully synthesized using a one-pot colloid solution in water by the reaction between aniline and $PdCl_2$ with controlling the size of Pd nanoparticles inserted into the PANI matrix. The prepared PANI-Pd (1.0 Wt.%) nanocomposite as a typical sample supported by analysis techniques such as UV-Vis, Fourier transform infrared (FTIR), Powder X-ray diffraction (XRD), transmission electron microscopy (TEM). The UV-visible and FTIR revealed the strong interaction between PANI and Pd of the nanocomposite. The presence of Pd nanoparticles with a fcc crystal structure in the polymer nanocomposite confirmed with XRD. TEM analysis showed that the PANI-Pd nanocomposite has a good monodispersity of Pd nanoparticles in PANI matrix that Pd nanoparticles have spherical morphology with an average particle size of 30 nm. The catalytic behavior of the Pd–PANI nanocomposite was studied for Suzuki–Miyaura coupling reactions in the aqueous media. The excellent catalytic activity of the nanocomposite resulted in 82.5% yield in water for PANI-Pd (1.0 Wt.%) and the results revealed that the Suzuki–Miyaura reaction proceeds much faster in when potassium carbonate was used as the base.

Keywords: Nanocomposit, Polyaniline, Palladium, Suzuki-Miyaura coupling reaction, Green reaction

1. Introduction

Heterogeneous catalysis as a scientific field have developed immensely due to the advent of nanotechnology and the new nanocatalysts, especially for different organic reactions is always demanding [1,2]. A plethora of literature is available for the open challenge in Suzuki–Miyaura Carbon–carbon coupling reactions such as the need to develop nanocatalysts that are active in aqouse media [3,4]. It is expected that a novel combination of heterogeneous nanocatalysts and green reaction medi will provide a breakthrough in cutting edge catalytic technologies [5,6]. Heterogeneous nanocatalysts are the most effective catalysts and also are attractive than the traditional catalysts due to increase in surface area to volume ratio, which consequently leads to better interaction of the nanoparticles supported on a suitable support with the reactants [7,8]. Pd nanoparticles is the nanocatalyst of choice and is being widely used for Suzuki–Miyaura coupling reactions [9]. PANI is one of the conducting polymer having very good environment stability and applied for several applications such as electronics, sensors, photovoltaic cells, memory devices, protective coatings against corrosion, supercapacitors and has been also used as a catalyst support for incorporation of a variety of metals nanoparticles [10,11]. There are many preparation route to synthesis a nanoctalyst or nanocomposite [12]. It is clear that the colloid solution based on the surfactant stabilized micelles as nanoreactors have a good potential to obtain monodispersed nanoparticles [13-17].

Here we report a simple/one-pot synthesis of a series of the PANI-Pd nanocomposite with different Pd nanoparticles loading based on the colloid solution system. In this study CTAB surfactant stabilized water-in-aniline oil monomer was used to prepare Pd nanocolloid and then the polymerization was started with ammonium persulfate (APS) to form PANI-Pd nanocomposit samples at different loading of Pd nnaoparticles. The prepared nanocomposite was characterized with UV-Vis, XRD, FTIR and TEM analysis. Finally, their application as nanocatalyst for Suzuki–Miyaura C-C coupling reaction in water as reaction medium with potassium carbonate were investigated.

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2. Experimental

2.1. Materials

monomer (99.5%) was distilled under vacuum prior to use, ammonium persulfate (APS) ($(NH_4)_2S_2O_8$ (98%)), Palladium (II) chloride ($PdCl_2$) (99.0 %) were purchased from Aldrich. Iodo benzene (C_6H_5I) and phenylboronic acid ($C_6H_5B(OH)_{2)}$ (95%) were purchased from Sigma-Aldrich. Hydrazine (N_2H_4-H_2O) as a reducing agent, N-methyl pyrrolidone (NMP), and potassium carbonate (K_2CO_3), n-Octyl benzene as standard to confirm the Suzuki–Miyaura reaction production were purchased from Merck. (Ultra-pure water (18.2 MU cm) from double stage water purifier (ELGA PURELAB Option-R7) was used to prepare all solutions and also as solvent in coupling reactions.

2.2. Preparation of the Pd nanocolloid in W/O microemulsion

In a typical synthesis, the two colloidal based on the microemulsion solutions were prepared by aniline monomer as oil phase, CTAB surfactant and aqueous hydrochlorhydric solutions of $PdCl_2$ (0.01, 0.02 and 0.03 M). In this procedure, 2 solution of CTAB in aniline with concentration of (0.02 M) were prepared. One of them was used to prepare a water-in-aniline (W/O) microemulsion containing Pd ion by (mole ratio of water /CTAB, W=35) and another for the preparation of W/O microemulsion containing hydrazine reducing agent was employed. After that, reducing agent based on the W/O microemulsion was slowly added to the microemulsion consist of the Pd ions under a vigorous dynamic stirring for 10 min. The obtained solution system was mixed at room temperature for 60 min. After about 45 min of reaction, as we observed change in color of the solution, a stable and brown color colloid of Pd nanoparticles based on the CTAB-stabilized microemulsion were obtained.This procedure was performed tree times for the fabrication of three types PANI-Pd nanocomposites was labeled as PANI-Pd (0.5 Wt.%), PANI-Pd (1.0 Wt.%) and PANI-Pd (1.5 Wt.%).

2.3. Preparation of the PANI-Pd nanocomposite

In this step, 40 mL of 1 $mol.L^{-1}$ HCl aqueous solutions was added to three above nanocolloid, separately. Certaein amount of APS, corresponding to an oxidizing agent-to-aniline monomer mole ratio equals to 1.5 were added to all systems. Then, the reaction colloid solutions were stirred while maintaining the temperature at 4-5°C. The colloid solutions were kept under ice cold condition for 3 h for the completion of reaction. The dark green colored precipitate product were collected by centrifugation at 10000 rpm for 15 min and repeatedly washed with water and dried in oven at 50 °C for 24 h. The dried PANI-Pd nanocomposite samples (1.0 Wt.%) was used for further characterization.

2.4. Characterization

In order to confirm the preparation of Pd nanoparticles in W/O microemulsion, and PANI-Pd nanocomposite, UV-visible absorption spectrum was recorded using using a double beam UV-vis spectrophotometer (Perkin Elmer lambda 15) spectrophotometer. To study of the PANI-Pd nanocomposite, the nanocomposite was dissolved in NMP. FTIR spectrum of the PANI-Pd nanocomposite was recorded using Galaxy series FT-IR 5000 spectrophotometer (Unicam Co.) in the frequency range from 4000 cm^{-1} to 500 cm^{-1}. For this study, a small amount of the PANI-Pd nanocomposite was mixed with KBr powder and pelletized to record the FTIR spectrum. XRD of the PANI-Pd nanocomposite was recorded using Philips PW 1800 diffractometer using Cu Ka radiation as X-ray source and Ni filter. TEM imaging of the nanocomposite was done using (Zeiss-EM10C-80kV). Prior to being loaded into TEM, the sample was dispersed in ethanol, sonicated, and dropped onto a wholly carbon-coated copper grid.

2.5. Catalytic study of the Suzuki–Miyaura reaction in aqueous medium

Typically, to a 25 ml round bottom flask containing 2 ml water, 1 mmol iodo benzene aryl halide, 1.5 mmol phenylboronic acid, 3 mmol potassium carbonate base and 0.003 g of all PANI-Pd nanocomposites was added based on the Suzuki–Miyaura coupling reaction described in the literature [18]. After that, the reaction mixture was saturated with argon gas for 15 min and sealed with Teflon rubber septum. The green Suzuki–Miyaura reaction was carried out in argon atmosphere at 90 °C with stirring for 4 h. The product was extracted in ether and pure product was collected using column chromatography. To confirm the product of the reaction, gas chromatography|(Agilent-7890B) with Capillary Column (type OV-101, Column length: 50. m; Column diameter: 0.25 mm), (N_2, 15. K/min; T_{start}: 120.01 ºC).

3. Results and discussion

3.1. UV-Vis

Fig. 1, presents, the UV-visible absorption spectrum of the prepared Pd nanocolloid in microemulsion system and PANI-Pd (1.0 Wt.%) nanocomposite in NMP. As can be seen, three characteristic absorption peaks at a wavelength of 290 nm (plasmon absorption of Pd nanoparticles) [19], two broad absorption bands 452 nm and 600 nm (correspond to π–π* transition within benzenoid units and transition from benzenoid to quinoid of PANI

respectively) were observed for nanocomposite. These results indicate that there is interaction between the nitrogen atom of the PANI and Pd nanoparticles [20,21].

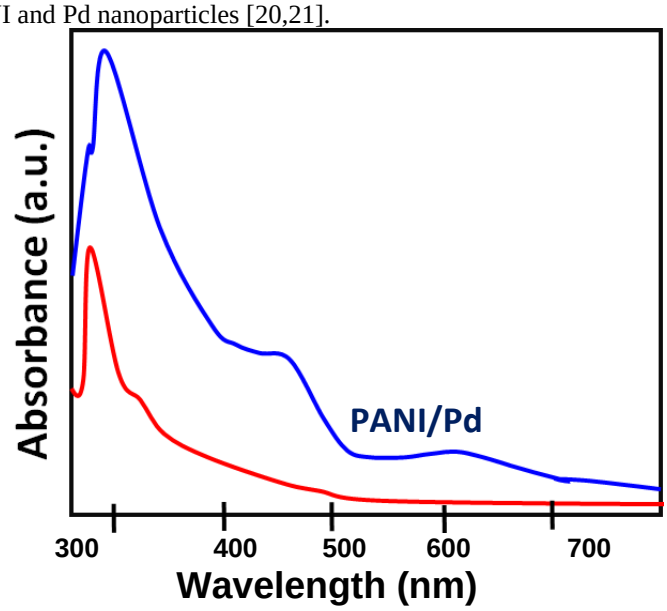

Fig. 1. The UV-visible absorption spectrum of the prepared Pd nanocolloid in microemulsion system (red line) and PANI-Pd (1.0 Wt.%) nanocomposite in NMP (blue line).

3.2. FTIR analysis

Fig. 2. shows the recorded FTIR spectrum of the resulted PANI-Pd (1.0 Wt.%) as a typical sample. The vibrational bands of PANI-Pd nanocomposite including N–H stretching, quinoid ring stretching, and benzenoid ring stretching as the most important characteristic of polymer nanocomposite were observed at 3450 cm^{-1}, 1574 cm^{-1} and 1494 cm^{-1}, respectively. The band at 1310 cm^{-1} is related to secondary C–N stretching. Two bands at 1119 cm^{-1} and 803 cm^{-1} can be assigned to the vibration band of dopant anion and para disubstituted benzene rings. The interaction between PANI and Pd was confirmed with the shifting of quinoid ring stretching, and benzenoid ring stretching AS described in the literature [22].

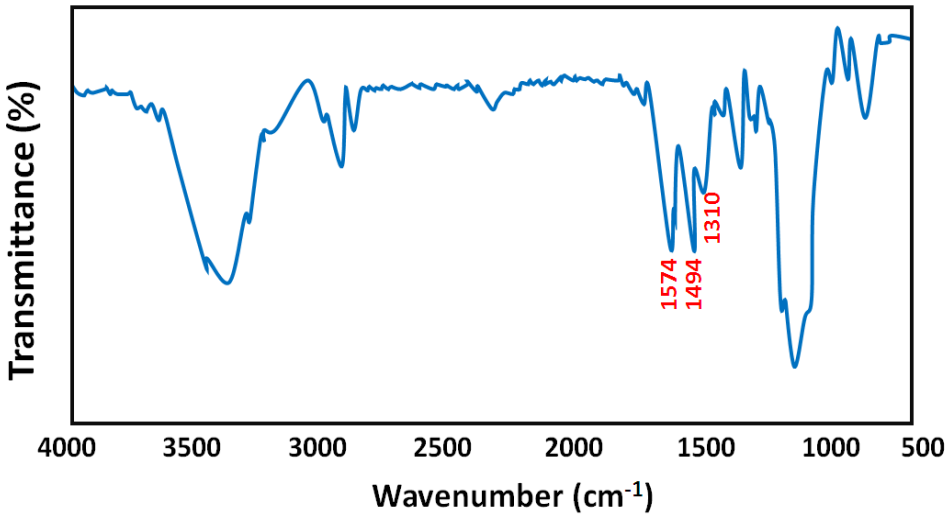

Fig. 2. FTIR spectrum of the resulted PANI-Pd (1.0 Wt.%)

3.3. XRD study

The XRD pattern of the prepared PANI-Pd (1.0 Wt.%) nanocomposite is shown in Fig. 3. The crystalline domains of PANI indicated with the broad peak centered at 25° having a shoulder at 20°. Based on the standard values (JCPDS file no. 87-0638), other distinct peaks at 2Θ 40°, 46°, 68°, 82°and 86° are corresponding to Pd

nanoparticles in the PANI matrix due to the (111), (200), (220), (113) and (222) reflection planes of metallic Pd nanoparticles with fcc lattice structure [23].

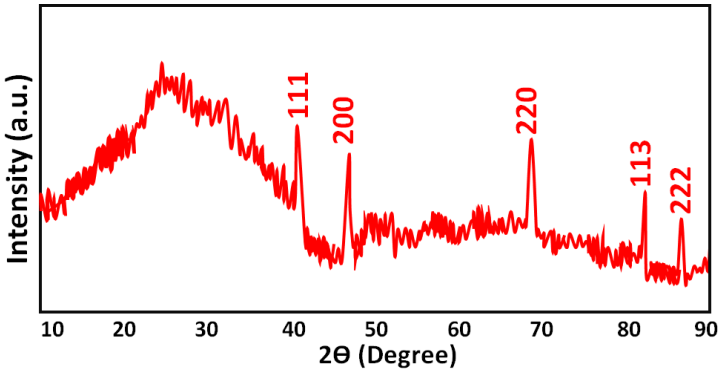

Fig. 3. XRD pattern of the resulted PANI-Pd (1.0 Wt.%) nnaocomposite

3.4. TEM imaging

The morphology of the prepared PANI-Pd (1.0 Wt.%) nanocomposite was studied using TEM imaging and the corresponding image is shown in Fig. 4. It is evident from the TEM image that the Pd nanoparticles have spherical morphology with average particle size of 30 nm. It shows that the Pd nanoparticles are present on the surface of the nanocomposite with good monodispersity due to use of microemulsion system as soft template [24-27].

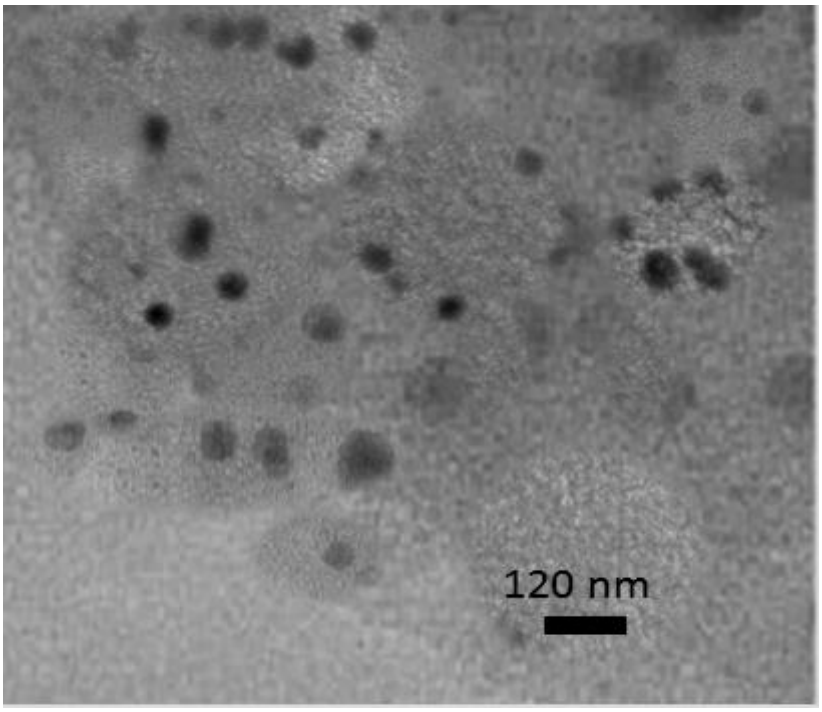

Fig. 4. TEM image of the resulted PANI-Pd (1.0 Wt.%) nanocomposite

3.5. Catalytic activity for Suzuki– Miyaura reaction

To confirm the good catalytic activity of the prepared PANI-Pd nanocomposites in green media, the Suzuki–Miyaura reaction was chosen and the reaction was almost complete in 4 h for all prepared nanocomposites and is shown in Fig.5. To separate oil and aqueous phases water and diethyl ether was added to the reaction mixture. Excellent catalytic activity and selectivity was observed for Suzuki– Miyaura reaction in water. Water and

methanol was added to the reaction mixture after completion of the reaction. The oil and aqueous phases were separated. To the oil phase excess amount of sodium sulphate was added and methanol was evaporated on rotary evaporator under reduced pressure. The formation of the product was confirmed by using gas chromatography. The yield of the Suzuki–Miyaura reaction in water was calculated of 82.5% with selectivity of 100% for n-octyl benzene production against PANI-Pd (1.0 Wt.%) nanocomposite. Dutt et al. [23] prepared Pd–PANI nanocomposite successfully using a one-pot green synthetic procedure in water by the reaction between aniline hydrochloride and potassium hexachloropalladate. The excellent catalytic activity of the nanocomposite resulted in 86 % yield in water when potassium carbonate was used as the base and n- octyl benzene and biphenyl were the reaction products.

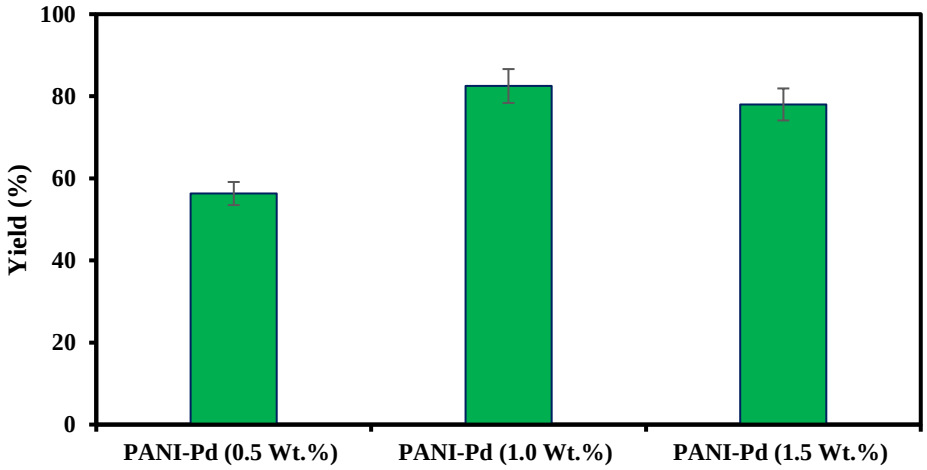

Fig. 5. Study of the effect of Pd nnaoparticles loading in PANI matrix on the yield of the Suzuki–Miyaura coupling reaction in water reaction medium

4. Conclusion

The current study described a simple route based on the microemulsion system as a soft colloid solution elaborate PANI-Pd nanocomposites. The Pd nanoparticles with different dosageS have been introduced in the PANI matrix from A W/O microemulsion solution *via* (W=35). The prepared PANI-Pd (1.0 Wt.%) nanocomposite was characterized wit UV-Vis, FTIR, XRD and TEM analysis. The presence of Pd nanoparticles with a fcc crystal structure in the PANI-based nanocomposite confirmed with XRD technique. Based on the TEM analysis, it is found that the PANI-Pd nanocomposite has a good monodispersity of Pd nanoparticles in PANI matrix that Pd nanoparticles have spherical morphology with an average particle size of 30 nm. The catalytic behavior of the Pd–PANI nanocomposite was studied for Suzuki–Miyaura coupling reactions in the aqueous media for all nanocomposite samples. The yield of the green reaction model depends greatly on the loading of Pd nanoparticles in PANI matrix. The excellent catalytic activity resulted in 82.5% yield in water for PANI-Pd (1.0 Wt.%) with potassium carbonate as the base.

Conflicts of Interest

The author declares no conflict of interest.

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