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Facile approach to the electrochemical synthesis of palladium-reduced graphene oxide and its application for Suzuki coupling reaction

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ABSTRACT

Electrochemically codeposited palladium nanoparticles (Pd NPs) and reduced graphene oxide (ERGO-Pd) were used as catalyst for Suzuki cross coupling reactions. The catalyst was characterized by various analytical techniques. The mean particle size of Pd was found to be 5.7 ± 1.8 nm. The ERGO-Pd catalyst demonstrated excellent catalytic activity and recyclability for Suzuki cross coupling reactions. The remarkable reactivity of the ERGO-Pd catalyst toward cross-coupling reactions is attributed to the high degree of the dispersion of Pd NPs on reduced graphene oxide with narrow size distribution from 3 to 9 nm.

Palladium catalyzed C–C bond formation reactions have drawn much attention in organic synthesis due to its industrial potential for the synthesis of chemicals and their intermediates.[1] Cross coupling reactions such as the Suzuki[2] and Heck[3] are widely applied for the construction of biaryl moiety as biaryls are important units in pharmaceuticals, herbicides, and natural products.[4,5]

Although homogeneous palladium catalysts exhibit higher activity and selectivity for cross coupling reactions, the uses of homogeneous Pd catalysts are restricted in large-scale reactions due to the contamination of products.[6] Tedious separation and recycling of the palladium catalyst are other major drawbacks of the homogeneous catalysts.[7] In order to address these problems, heterogeneous Pd catalysts have been employed in recent years. Palladium has been supported on materials such as activated carbon,[8] polymers,[9] glass polymer composites,[10] zeolites,[11] silica,[12] molecular sieves,[13] clays,[14] zinc ferrite,[15] carbon nano tubes,[16] graphene,[17] and sulfonated graphene.[18] Among them graphene, two-dimensional sp^2 hybridized carbon is more attractive support material for metal nanoparticles because of its extraordinary thermal, mechanical, and electrical properties.[19,20] Moreover, transparency and conductive properties of graphene give it huge prospective in the fields of electrochemical applications such as sensors,[21] electrodes,[22] transistors,[23] and fuel cells.[24]

Recently, the synthesis of metal nanoparticles by the chemical reduction of metal salts has been widely studied because of their applicability to catalysis.[25] Most of the reports demonstrate the co-reduction of metal ion and graphene oxide which involve chemical reducing agents such as hydrazine hydrate and sodium borohydrate.[26,27] However, major drawbacks of the chemical reduction method are use of toxic reducing agents which could be incorporated into nanoparticles in the form of residual contamination and rapid heat treatment at high temperature. To overcome these problems the 'green synthesis' of metal-graphene under mild conditions is desirable. Electrochemical methods are one of the promising green approaches for the synthesis of palladium-graphene composite. Mild reaction conditions, no side product, room temperature operation, and short reaction time are other merits of the electrochemical methods. A few reports are available on the electrochemical synthesis of Pd NPs and their application as catalyst for cross coupling reactions.[28] In general, graphene irrespective of its method of synthesis (chemical or electrochemical reduction) contains oxygen, so it is more appropriate to label it as 'reduced graphene oxide'.

As part of our ongoing research program on the electrochemical synthesis of metal composites and their application as catalysts for the C–C coupling reactions,[29] herein, we report the application of electrochemically prepared palladium-reduced graphene oxide (ERGO-Pd) for the promotion of Suzuki coupling reactions. To the best of our knowledge electrochemically co-deposited Pd and reduced GO (ERGO-Pd) has not been reported earlier for Suzuki

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coupling reactions. The prepared catalyst was found to be highly efficient, recyclable, and environmentally benign.

Graphene oxide was prepared by a modified Hummer's and Offenman's method.[30] The GO dispersion (1 mg/mL) in water was obtained under ultrasonication for 30 min. Electrochemical co-deposition of Pd and reduced graphene oxide was carried out with some modification of the method reported by Nagaraju and Suresh.[31] Conventional three electrode cyclic voltammetry potentiostat/galvanostat (PGSTAT302N) equipped with GPES software was used for electrodeposition of ERGO-Pd. Saturated calomel electrode, platinum rod, and glassy carbon plate (2×2.5 cm) were the reference, counter, and working electrodes, respectively (Supporting information Fig. 1). The obtained catalyst was described as ERGO-Pd.

The morphologies of the catalyst (ERGO-Pd composite) were found out by scanning electron microscopy (SEM-EDAX, Quanta −200 at 20 kV as operating voltage) and transmission electron microscopy (TEM, PHILIPS Model:CM200, Operating voltages: 20–200 kv Resolution: 2.4 Å). The composition of the catalyst was determined by X-ray diffraction (XRD, Rigaku Miniflex model by using Cu Kα = 1.54 Å with scanning range 20–80°) and energy dispersive X-ray analysis (EDAX). Thermogravimetric analyses (TGA) were performed on an STA 409 thermobalance by Netzsch under a nitrogen flow (40 mL min^{-1}) with heating rate of 20 °C min^{-1}.

The SEM image (Fig. 1a) indicates formation of ERGO on glassy carbon (GC) electrode. The graphene deposition can take place on conducting surface like GC electrode.[32] The graphene oxide in contact with GC electrode surface accepts electrons and undergoes electrochemical reduction. The ERGO is very stable on GC electrode because of its poor solubility in aqueous medium. Figure 1b SEM image of ERGO-Pd shows co-deposition of Pd NPs and ERGO. Figure 1 also reveals the electrodeposition of well dispersed and uniform Pd NPs on thin sheets of electrochemically reduced graphene oxide whereas in Figure 1a, ERGO exhibit wrinkle type of morphology. Figure 1c displayed the TEM image of ERGO-Pd. The TEM image shows the presence of highly dispersed Pd nanoparticles on ERGO without agglomeration. The TEM micrograph also shows small sized monodispersed Pd NPs deposited on ERGO sheets. The smaller sized ERGO sheets can be seen in Figure 1c. The Pd NPs are in the range of 3–9 nm. The average particle size is found to be 5.7 ± 1.8 nm (Supporting information Fig. 2).

Figure 2 represents the XRD pattern of ERGO-Pd composite. The peaks at around 2θ = 40.0°, 46.6°, 68.0°, for the Pd NPs on RGO are assigned to the (1 1 1), (2 0 0), and (2 2 0), crystalline planes of the fcc structured Pd, respectively.[33] It also reveals that the Pd (1 1 1) peak has the highest intensity and thus the Pd (1 1 1) plane is supposed to be the predominant crystal facet. The lattice spacing of face-centered cubic (fcc) Pd was 0.224 nm. The EDAX analysis show elemental analysis which confirms elements C, O, and Pd in electrodeposited ERGO-Pd (Supporting information Fig. 3). The palladium content in ERGO-Pd composite was determined by means of inductively coupled plasma equipped with atomic emission spectrometry (ICP-AES) and amounted to be 32 ppm (Scheme 1).

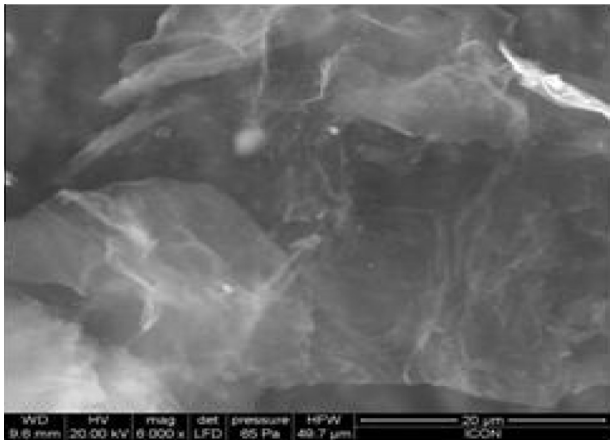

Figure 1a. SEM image of electrochemically deposited reduced graphene oxide.

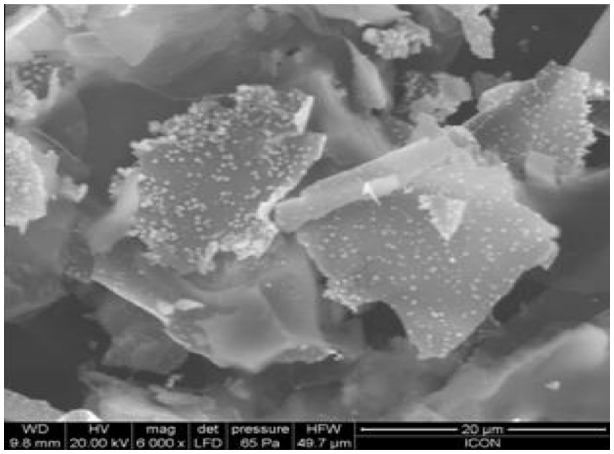

Figure 1b. SEM image of electrochemically deposited ERGO-Pd composite.

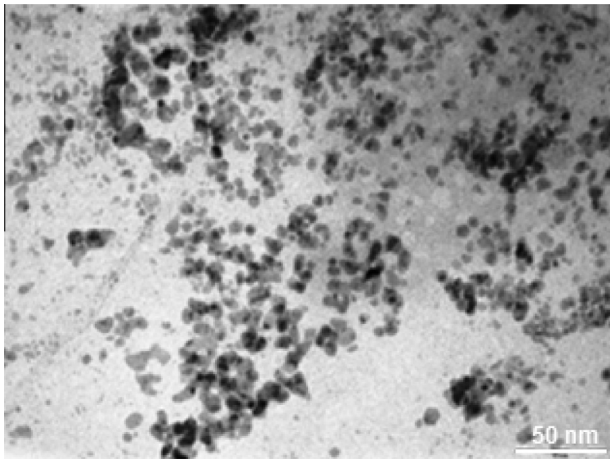

Figure 1c. TEM micrograph of electrochemically deposited ERGO-Pd composite.

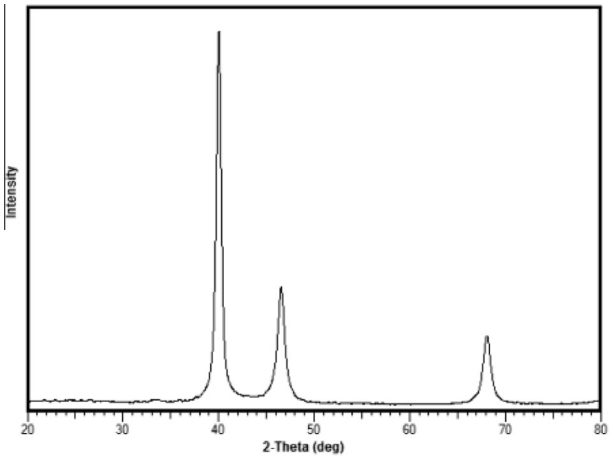

Figure 2. XRD pattern of electrochemically deposited ERGO-Pd composite.