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A fluorescence active catalyst support comprising carbon quantum dots and magnesium oxide doping for stabilization of palladium nanoparticles: Application as a recoverable catalyst for Suzuki reaction in water

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ABSTRACT

Novel magnesium oxide-carbon quantum dots are synthesized and used for the formation and stabilization of palladium nanoparticles. This highly water dispersible material, Pd@MgO-CQD, has been used as an active catalyst for Suzuki coupling of aryl bromides at room temperature and aryl chlorides at 80 °C in water. Using fluorescence emission of the material, a new protocol for determining Pd loading and leaching in catalyst preparation and recycling process is developed.

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1. Introduction

Environmental problems rose up from chemical progression encouraged chemists for designing new methodologies matched with green chemistry objectives [1–7]. For instance industries have started employing green chemistry practices such as waste prevention by designing high performance heterogeneous catalysts based on naturally available materials and the use of less toxic solvents and reagents [8–11]. Palladium catalyzed cross-coupling reactions are important approaches for the formation of carbon–carbon and carbon–heteroatom bonds [12–18]. In recent years, because of high toxicity and price of palladium, growing interest has been paid to development of different heterogeneous palladium catalysts [19–22]. Magnesium oxide and clay minerals with high surface area can be found widely in nature and have been used as catalysts or as supports for stabilization of transition metal catalysts [23–27]. Rao and coworkers prepared water dis-

persible sheets of Mg-phylo(organo)silicates containing pendant amino ligands and used it for stabilization of Au, Ag, Pd, and Pt nanoparticles (NPs) [28]. We have recently reported clay composite carrying phosphinite-functionalized ionic liquid moieties (CCPIL) for palladium NPs stabilization and their applications in different cross-coupling reactions [29].

Carbon quantum dots (CQD) are nanomaterials with excellent water solubility, strong fluorescence emission, high photostability, non-toxicity, and good biocompatibility. In the past few years, CQD have been used in different applications such as biomedicine delivery systems, biosensors, dye-sensitized solar cells, organic solar cells, supercapacitors, light-emitting devices, and photocatalysts [30–32]. Recently, CQD have been used for reduction of palladium salt, formation of palladium NPs and applied as an efficient catalyst in Suzuki and Heck cross-coupling reactions [33]. Very recently, we have also reported modification of Fe₃O₄ nanoparticles with CQD and its application for the stabilization of palladium NPs in the Suzuki reaction [34]. Despite the high efficiency of our reported catalyst, quenching of fluorescence in CQD@Fe₃O₄ NPs is the drawback of this material. For instance, this problem prohibited further application of the material in fluorescence active reactions. Herein, we wish to report novel MgO-CQD as a fluorescence active composite

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for formation and stabilization of Pd NPs (referred as Pd@MgO-CQD throughout the text of this article) and its application as highly dispersible catalyst under very mild Suzuki reaction conditions for the cross-coupling of aryl bromides and chlorides with arylboronic acids in water.

2. Material and methods

2.1. Synthesis of MgO-CQD

To a stirring solution of polyethylene glycol 200 (25 mL), was added $\text{Mg}(\text{NO}_3)_2$ (9 g) and the mixture was stirred at room temperature until the salt was completely dissolved. To the resulting mixture, an aqueous solution of Na_2CO_3 (1.2 g) and urea (1.2 g) in water (8 mL) was added and the resulting mixture was sonicated for 30 min and then was heated in autoclave at 160°C for 2 h. Then, the mixture was cold down to room temperature and the obtained solid was centrifuged and dried in the oven affording 5.2g fluorescence active MgO-CQD.

2.2. Synthesis of Pd@MgO-CQD

MgO-CQD (1 g) was added to a stirring 1:1 mixture of H_2O and EtOH (5 mL). Then, sonicated solution of PdCl_2 (40 mg, 0.22 mmol) in H_2O (3 mL) was added under argon atmosphere and stirred at 60°C for 24 h. The resulting suspension was centrifuged and the solid was filtered off. After drying in the oven for 24 h at 80°C , 0.93 g of Pd@MgO-CQD containing 0.148 mmol g^{-1} palladium was obtained.

2.3. General procedure for Suzuki–Miyaura reaction

Pd@MgO-CQD catalyst (10 mg, 0.3 mol%), aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), K_2CO_3 (103 mg, 1 mmol), and distilled H_2O (2 mL) were added to a flask and the mixture was stirred at 30°C for aryl bromides and at 80°C for aryl chlorides. After completion of the reaction, which was monitored by GC, crude products were extracted by EtOAc ($2 \times 5\text{ mL}$) and purified using column chromatography.

2.4. Typical recycling procedure for the reaction between 4-bromobenzonitrile and phenylboronic acid

After completion of the reaction (monitored by GC), the resulting reaction mixture was extracted with ethyl acetate ($3 \times 4\text{ mL}$), the organic phase was dried and the product was purified using column chromatography. Then, the residue was subjected to centrifugation (6000 rpm) for 10 min and the solid catalyst was separated, washed with diethyl ether and dried for further use in another batch.

3. Results and discussion

In a typical preparation, Pd@MgO-CQD was prepared using reaction of $\text{Mg}(\text{NO}_3)_2$, urea and PEG 200 in an autoclave at 160°C and the obtained CQD were treated with an aqueous solution of PdCl_2 at room temperature. The synthesized Pd@MgO-CQD were characterized by fluorescence spectroscopy, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma (ICP), transmission electron microscopy (TEM), scanning electron microscopy combined with electron dispersive spectrometry and elemental mapping (SEM-EDS, SEM-map).

Loading of Pd on MgO-CQD was determined by ICP analysis to be 0.148 mmol g^{-1} . Comparing fluorescence intensity of MgO-CQD with obtained Pd@MgO-CQD showed decreasing of fluorescence

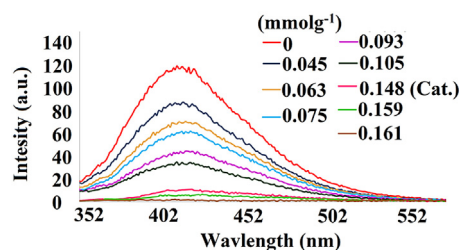


Fig. 1. Fluorescence emissions of Pd@MgO-CQD with different Pd loadings.

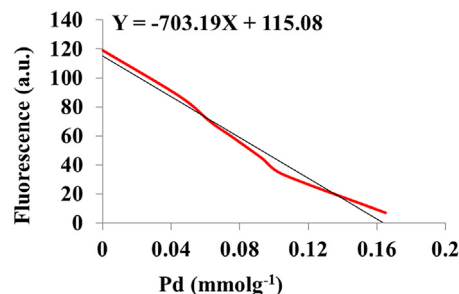


Fig. 2. A linear equation between the amount of supported Pd and the fluorescence intensity.

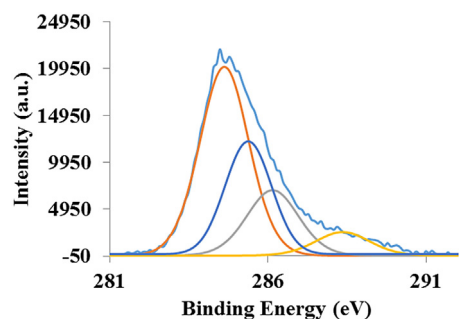


Fig. 3. XPS spectrum of Pd@MgO-CQD in the C1s region.

emission in Pd@MgO-CQD. This decreasing can be attributed to the electron transfer from the CQD to metallic ions [35,36]. In order to find an exact correlation between the amount of loaded Pd and fluorescence intensity, different Pd@MgO-CQD samples with different loading of Pd were prepared and fluorescence emissions were studied. Results of our study indicated decreasing of fluorescence intensity with increasing of palladium loading on MgO-CQD (Fig. 1). As it shown in Fig. 2, using palladium and fluorescence emission values, a linear equation between factor X (mmol of supported Pd) and factor Y (fluorescence intensity) was obtained. This equation showed good harmony between content of supported Pd and emission and it is possible to find amount of Pd on support in each stage of catalytic reaction.

Presence of carbon in the structure of Pd@MgO-CQD was confirmed by X-ray photoelectron spectroscopy (XPS) study of C1s region. Results showed related peaks to C–C or C=C, C–N, C–O–C and O–C=O forms of carbon in 284.7, 285.4, 286.1, and 288.7 eV, which are characteristic for carbon in CQDs (Fig. 3) [37,38].

Also, XPS spectrum of the region corresponding to the binding energy range of 335–342 eV related to $\text{Pd}3d_{5/2}$ and $\text{Pd}3d_{3/2}$ was studied. Results indicated the presence of two intensive doublets at 335.5 and 340.7 eV related to Pd(0) and peaks at 337 and 342.5 eV related to Pd(II) species. [39–41]. These results indicate that 46% of palladium exist in Pd(0) state confirming the reducing ability of MgO-CQD (Fig. 4).

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