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# Green synthesis of carbon quantum dots from vanillin for modification of magnetite nanoparticles and formation of palladium nanoparticles: Efficient catalyst for Suzuki reaction

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ABSTRACT

In this report we prepared carbon quantum dots (CQD) from vanillin as an ecofriendly and naturally abundant compound for modification of magnetic nanoparticles (CQD@$Fe_3O_4$ NPs). This new magnetic solid has been used for complete reduction of $PdCl_2$ with formation of stabilized palladium nanoparticles (Pd@CQD@$Fe_3O_4$ NPs) and characterized by SEM, TEM, EDX, solid UV, VSM, XPS, XRD, and $N_2$ adsorption–desorption analyses. These magnetic supported Pd NPs have been used as an efficient catalyst for the Suzuki-Miyaura cross-coupling reactions of aryl bromides at room temperature in aqueous ethanol and of aryl chlorides at 120 °C in PEG200 under low catalyst loading in air. The heterogeneous catalyst can be easily recovered by an external magnet and reused for eight consecutive runs.



## 1. Introduction

Palladium catalyzed cross-coupling reactions have become a key and potent tool in organic synthesis for the formation of carbon–carbon bonds.[1] Among them, the Suzuki-Miyaura reaction, which is the coupling between aryl, vinyl or alkyl halides or pseudo-halides and organoboron reagents is one of the advanced palladium catalyzed reactions for the formation of different types of compounds.[2] Traditionally, palladium pre-catalysts in the presence of toxic phosphine[3] or nitrogen ligands[4] are often employed for coupling reactions under homogeneous conditions. However, when compared to heterogeneous catalysts, homogeneous catalysts suffer from diminished catalytic activity during the reaction, lack of catalyst reusability, and difficulty for product purification. In the case of palladium, which is toxic and costly, recycling is very important from both economic and sustainable chemistry standpoints.[5,6]

Nowadays, green chemistry objectives encourage chemists for design and preparation of new methodologies that reduce or eliminate the use or generation of hazardous substances. For this purpose, in recent years designing of new recyclable and heterogeneous catalysts with high efficiency and turnover number, low cost, and minimal leaching of toxic metals has received much attention.[7] In the past few decades, a wide range of efficient heterogeneous palladium catalysts using different solid supports have been reported for various Pd catalyzed organic reactions. However, usually separating of the heterogeneous catalyst from the reaction mixture by conventional methods such as simple filtration and centrifugation is not an easy task.[5,6] To address these challenges, many efforts have been made for using magnetic nanoparticles with unique properties such as easy isolation, high surface area and low toxicity as a promising support for palladium catalysts.[8] For this purpose, in recent years different methods and ligands have been reported for modification of magnetic nanoparticles and their relevant applications as Pd supports for various carbon-carbon bond formation reactions.[8]

Fluorescent carbon quantum dots (CQD) are an emerging class of carbon nanomaterials recently termed quasi-spherical nano carbons with sizes below 10 nm. These CQD are comprised of

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amorphous to nanocrystal line cores with predominantly graphitic or turbo static carbon ($sp^2$ carbon) or graphene and graphene oxide sheets fused by diamond-like $sp^3$ hybridized carbon insertions.[9] CQD have unique properties such as high solubility, photostability, fluorescence emission and they are considered as green, non-toxic, abundant, and inexpensive materials.[9] In recent years, different sources have been used for the preparation of CQD. However, recent emerging efforts have been paid for using inexpensive starting materials, such as chitosan,[10] orange peels[11] and cabbage[12] for the preparation of CQD. Recently, CQD obtained from clotted cream have been used for the synthesis of coated Pd nanoparticles (NPs) and used for Heck and Suzuki reactions.[13] Also, very recently, we have reported the preparation of CQD from citric acid and its using for modification of magnetic $Fe_3O_4$ nanoparticles and formation and stabilization of Pd NPs.[14]

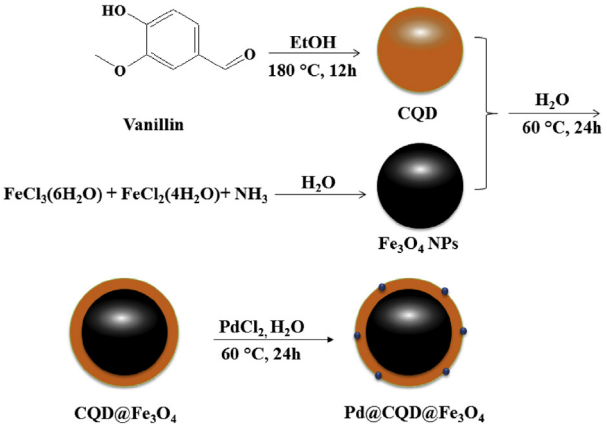
Vanillin is a highly water soluble phenolic aldehyde, which occurs widely in plants, usually as a glycoside bound to sugar or as a precursor to vanillin bound to the large lignin molecule abundant in wood. Vanillin is widely used to introduce flavors in our food and free vanillin in the environment is not considered to represent any biohazard.[15]

In continuation of our interest in CQD and magnetic supported palladium catalysts,[16] now in this work we use for the first time vanillin as a cheap and naturally abundant compound for formation of CQD and its subsequent application for the modification of $Fe_3O_4$ NPs (CQD@$Fe_3O_4$). We envisaged that CQD generated from vanillin bearing formyl groups would facilitate the reduction of Pd(II) to Pd(0) and therefore the formation of Pd NPs to be used in carbon-carbon bond forming reactions. The CQD@$Fe_3O_4$ would be further used not only for the stabilization of Pd NPs but also for the easy recovery of this heterogeneous catalyst, which is referred to as Pd@CQD@$Fe_3O_4$ throughout this manuscript.

## 2. Results and discussion

Preparations steps of Pd@CQD@$Fe_3O_4$ are summarized in Scheme 1. Firstly, $Fe_3O_4$ NPs were prepared using the Massart procedure[17] from the reaction of $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ salts (Scheme 1).

TEM image showed formation of magnetic nanoparticles in 15–20 nm average size (Fig. 1a). CQD were synthesized by heating an ethanol solution of vanillin in a Teflon autoclave at 180 °C for 12 h. Photoluminescence (PL) emission study of CQDs showed a broad emission centered at 413 nm in the emission spectrum with an excitation wavelength at 350 nm (Fig. 1, SI). Reaction of obtained CQD with magnetite NPs afforded CQD coated $Fe_3O_4$ NPs.




**Scheme 1.** The preparation steps toward the catalyst.

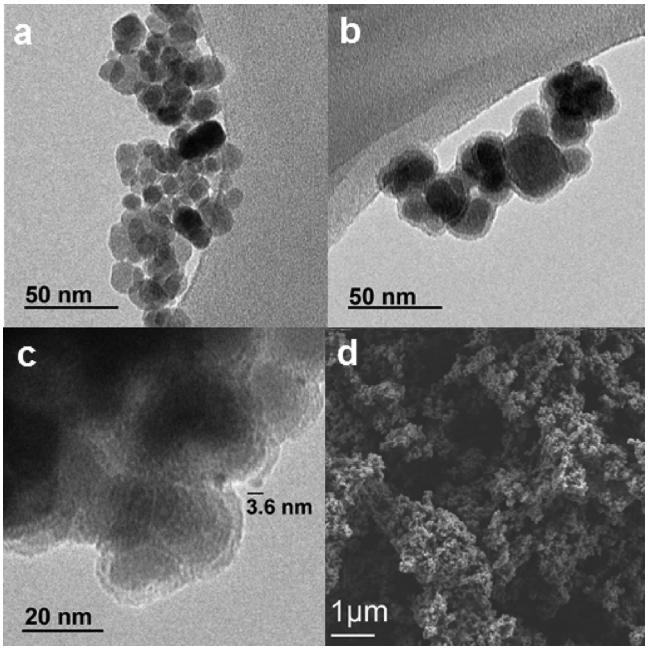



**Fig. 1.** TEM images of a) $Fe_3O_4$ NPs, b) CQD@ $Fe_3O_4$ NPs, c) Pd@CQD@ $Fe_3O_4$ NPs, and d) SEM image of Pd@CQD@ $Fe_3O_4$ NPs.

Formation of CQD@$Fe_3O_4$ was proved by TEM image showing carbon shells around the $Fe_3O_4$ nanoparticles (Fig. 1b). Finally, Pd@CQD@$Fe_3O_4$ was obtained by treating of aqueous solution of $PdCl_2$ and CQD@$Fe_3O_4$ at 80 °C for 24 h. Loading of Pd on the Pd@CQD@$Fe_3O_4$ was determined using atomic absorption spectroscopy (AAS) analysis to be 0.14 $mmolg^{-1}$. TEM images of Pd@CQD@$Fe_3O_4$ showed the presence of small Pd NPs attached on surface of CQD@$Fe_3O_4$ (Fig. 1c). Also, SEM images of the catalyst indicated the presence of dispersed and uniform particles (Fig. 1d).

In order to find information about the oxidation state of palladium in the catalyst, a solid UV spectrum of catalyst and $PdCl_2$ as a source of Pd(II) species was studied (Fig. 2). Results indicated disappearing of a peak related to Pd(II) at 280 nm which confirms the reduction of Pd(II) to Pd(0).[18]

Furthermore, oxidation state of palladium in Pd@CQD@$Fe_3O_4$ was investigated using X-ray photoelectron spectroscopy (XPS). Results showed two intensive doublet peaks at 335.6 and 340.8 eV in Pd 3d region which are assigned to the Pd(0) species (Fig. 3). These results indicated that the palladium is in reduced form, confirming the capability of CQD@$Fe_3O_4$ for efficient reduction of Pd(II) to Pd(0) nanoparticles.[3e,16a,19] This reduction only took place

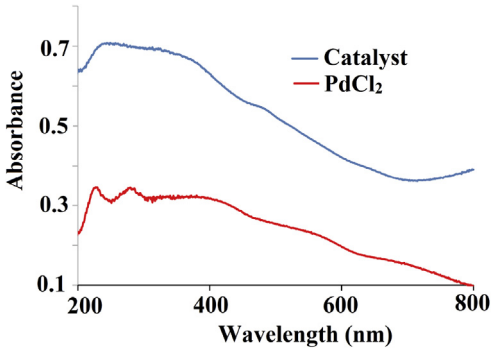



**Fig. 2.** Solid state UV–Vis spectra of the Pd@CQD@$Fe_3O_4$ NPs.