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# Controlled synthesis of three dimensional mesoporous $C_3N_4$ with ordered porous structure for room temperature Suzuki coupling reaction



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#### ABSTRACT

We report on the synthesis of mesoporous graphitic  $C_3N_4$  (MGCN-6) with 3D porous structure and *Ia3d* symmetry and controllable surface properties through a simple polymerization of an environmentally benign and non-toxic guanidine hydrochloride as a C and N precursor using KIT-6 with variable pore sizes as templates for Suzuki coupling reaction. The pore diameters (3.1–4.2 nm), specific surface areas (207–303 m<sup>2</sup> g<sup>-1</sup>), and the specific pore volumes (0.58–0.71 cm<sup>3</sup> g<sup>-1</sup>) of the MGCN-6 materials are finely controlled by varying the pore size of the templates used. The nano cavities of MGCN-6 with the highest specific surface area and a free amine groups are effectively utilized to chelate with Pd(OAC)<sub>2</sub> and applied the prepared catalysts for Suzuki coupling reaction between aryl halides with phenylboronic acid derivatives under very mild and sustainable reaction conditions. The Pd(OAC)<sub>2</sub>/MGCN-6 is found to be very active and stable and exhibits an excellent reactivity and selectivity for all of substrates regardless of aryl halides with electron-withdrawing and electron donating groups at room temperature. The activity of the Pd(OAC)<sub>2</sub>/MGCN-6 is much higher than that of non-porous bulk graphitic carbon nitride and 2D mesoporous carbon nitride.

#### Introduction

Immobilization of catalytically active materials on porous materials or 2D layered materials has been greatly advanced in chemical processes by means of delicate control to prevent the aggregation effectively and the efficient use of the catalytic species and porous supports [1-4]. By taking the benefit of the distinctive catalytic properties originate from the collegial effect between the porous support and active catalytic species, these nano hybrid systems offer unique prospects for the investigation of various organic transformations [5]. C<sub>3</sub>N<sub>4</sub> - carbon nitride, a 2D layered polymeric material, arguably, has received the most scrutiny from materials scientists because of their use in several applications including catalysis, CO<sub>2</sub> capture, gas storage and separation, photocatalytic hydrogen production, fuel cells, Li-ion batteries, Li-S batteries and electrocatalysts, photodynamic therapy, and sensors [6-16]. The unique and unparalleled combinations of electronic, mechanical, chemical, and physical properties including 2D layered structure, extending polymeric network, semiconducting band gap and high structural stability of these CN nanostructures make them unique for the above mentioned applications [6-16]. However, the efficient dispersion of the catalytically active materials on to the bulk  $C_3N_4$ material has been limited because of it's low specific surface area (< 10 m<sup>2</sup>g<sup>-1</sup>) due to the strong interactions between the layers and nonporous nature [14,15]. This can be overcome by introducing the porosity in  $C_3N_4$  with mesoporous structure and characteristic N-coordinating "six-fold cavities" that can be effectively utilized for the chelation and stabilization of metal nano particles by three tri-s-heptazine rings, which are not present in bulk  $C_3N_4$  carbon nitride material [17].

Construction of nanoporous  $C_3N_4$  through the templating strategies, introduction of heteroatoms, defects, special terminal group, homogeneous amorphization, has been proved to be a reliable way to improve the textural properties in  $C_3N_4$  [17,18]. Much progress has been made on the preparation of porous  $C_3N_4$  by utilizing nano hard and soft templating methods, wherein, highly ordered porous inorganic silica or metal organic framework (MOF) and pure organic based surfactant materials have been applied as the structure directing agents [11,20]. For example Vinu et al., demonstrated the preparation of mesoporous CN nano particles with different nitrogen contents and structures by using highly ordered large pore containing mesoporous silicas with

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different structures and pore diameters and Fe-MIL MOF materials as structure directing templates through the sacrificial nano hard templating approach [18,19,21-28]. Most of the preparation methods of templated mesoporous C3N4 were based on the use of cyanamide as a precursor [28-31], which is an explosive, but also toxic and hazardous to the human health and environment [32]. The preparation of mesoporous C<sub>3</sub>N<sub>4</sub> with a small number of sulfur and oxygen dopants by employing ammonium thiocyanate, thiourea and urea as safe precursors alternative to harmful cyanamide was also reported [33,34]. In a recent seminal contribution. Aida et al. have serendipitously found the formation of C<sub>3</sub>N<sub>4</sub> carbon nitride polymer thin film upon calcination of guanidinium carbonate (Gdm<sub>2</sub>CO<sub>3</sub>) compound on to the glass substrate [35]. Xu et al. have successfully prepared mesostructured C<sub>3</sub>N<sub>4</sub> nanospheres by using highly safe and environmentally benign guanidine hydrochloride precursor and silica nano particles as an exotemplate [36]. By creating the C<sub>3</sub>N<sub>4</sub> nanostructures with well-ordered nanopores and 3D porous structure would offer the materials with much better structural parameters and ordered porous systems.

Among the 3D mesoporous systems, the 3D body centered bicontinuous cubic mesoporous materials with *Ia3d* symmetry and large pore diameters are the most interesting materials as they have many advantages over mesoporous materials with unidimensional mesoporous materials, as they have good protection against pore blocking and offer easy diffusion and mass transfer in the pore channels, and provide high surface to volume ratio that provides a large number of adsorption sites [26–28,37–40]. However, the preparation methods for synthesizing the 3D mesoporous  $C_3N_4$  having cubic *Ia3d* symmetry and high specific surface areas are rare and are limited to the only toxic cyanamide precursor [28,31].

In this contribution, for the first time, we have used guanidine hydrochloride as the starting compound to prepare graphitic carbon nitride with 3D mesoporous structure (MGCN-6) C<sub>3</sub>N<sub>4</sub> with different surface parameters using KIT-6 with Ia3d symmetry as a template via controlled pore filling method. Good affinity between the monomer and the template walls is extremely important for the synthesis of highly ordered mesoporous polymer structures. The functional amine groups such as -NH<sub>2</sub>/=NH present in the guanidine monomer assist for the better interaction between the silanol groups (Si-OH) existed in the KIT-6 template via hydrogen bonding which leads to better replication of the structure of template into MGCN-6 material. MGCN-6 with a specific surface area of  $303 \text{ m}^2 \text{ g}^{-1}$  and a specific pore volume of  $0.71 \text{ cm}^3 \text{g}^{-1}$  can be obtained with a fine tuning of the pore diameter of KIT-6, whereas, the previously reported Ia3d mesoporous C<sub>3</sub>N<sub>4</sub> produced from the toxic cyanamide registered the surface area of only  $208 \text{ m}^2 \text{ g}^{-1}$ , thus pointing the importance of functional amine groups present in the guanidine precursor for the replication of C<sub>3</sub>N<sub>4</sub> in the hard templating method. [28] Further, we have applied MGCN-6 to immobilize the Pd(OAC)<sub>2</sub> and has been utilized as a catalyst for the Suzuki coupling reaction of different aryl halides and aryl boronic acids. The MGCN-6/Pd(OAC)<sub>2</sub> demonstrated a superior catalytic activity even at room temperature under environmentally benign ethanol solvent.

# **Results and discussion**

To prepare the MGCN-6 with different textural parameters, a constant amount of environmentally benign and non-toxic guanidine hydrochloride precursor was introduced into the mesopores of KIT-6 silica template with tunable pore diameters via controlled pore filling method and polymerized at 500 °C under inert atmosphere. Upon removal of silica template, highly pure MGCN-6 with  $C_3N_4$  stoichiometry and various specific surface areas and pore volumes were obtained in large quantities. The structure of MGCN-6 has been verified by powder X-ray diffraction patterns. All of the samples exhibit an intense (211) peak and several higher order reflections at 20 value between 2 and 3°, similar to the XRD pattern of KIT-6 (Fig. 1A) [38]. This indicate that an excellent structural ordering with the body centered cubic mesoporous structure and *Ia3d* symmetry was presented in all of the MGCN-6 samples. The position of the (211) reflection in the XRD pattern of MGCN-6 varies significantly with increase of the pore size of the KIT-6 templates. A shift of the (211) peak towards the lower angle region with an increase in the pore diameter of the KIT-6 materials has been observed, revealing a significant increase in the *d*-spacing (Table 1). MGCN-6 samples show a broad peak at 27.0° with a *d* spacing of 0.32 nm corresponding to (002) basal plane, characteristic of interplanar graphite like stacking present in these materials, indicating that the wall structure of the MGCN-6 is made of tri-s-heptazine sheets that are arranged in a turbostatic form (Fig. 1A inset). The in-plane structural repeating motifs and interlayer structural packing motif similar to the bulk  $C_3N_4$  can also be found at 13.2° in the XRD pattern with a *d* spacing of 0.7 nm.

The textural properties including the specific surface area and pore diameter of the MGCN-6 were analyzed by  $N_2$  adsorption-desorption measurements. Fig. 1B depicts the  $N_2$  isotherms of the MGCN-6 samples prepared at different synthesis conditions. The presence of mesopores in all of the samples is clearly confirmed by the  $N_2$  adsorption isotherms as all of the materials show type IV isotherm and demonstrates characteristic capillary condensation in the mesopore region. A sharp capillary condensation and H1 hysteresis loop at a relative pressure between 0.7 to 0.9 is observed, revealing that all of the materials have a uniform channel like pores. The hysteresis loop of the KIT-6-150 template is larger than the hysteresis loop present in the MGCN-6-150 isotherm at same relative pressure ranges (Fig. S1).

The specific surface areas of the MGCN-6 obtained from the BET method was in the range of 203 to  $307 \text{ m}^2 \text{ g}^{-1}$ . The pore cavities of the realized MGCN-6 materials derived from the BJH method for the MGCN-6 display highly uniform and narrow mesopores (Fig. S2). As depicted in Fig. S1B, The BJH pore diameter of the MGCN-6-150 is almost half of the pore diameter KIT-6-150 template, revealing that pores of the template are converted into CN walls in MGCN-6 and wall thickness of the silica template converted into the pores of the carbon nitride. The specific surface area, specific pore volume and the pore size of the MGCN-6 are increased as the pore diameter of the parent KIT-6 is increased (Table 1). Among the samples studied, MGCN-6-130 shows the highest specific surface area of  $303 \text{ m}^2 \text{g}^{-1}$  with a pore size of 3.2 nm. The presence of ordered mesoporous structure in MGCN-6 samples is confirmed by TEM images. The TEM images of MGCN-6-130 are shown in Fig. 1C. The dark portions of the images correspond to pore channels and the bright lines depict to the pore wall. The TEM images of the MGCN-6-130 sample shows well-ordered mesoporous structure with a regular array of pores that are arranged in an orderly fashion. TEM image clearly displays a cubic type arrangement of the mesopores present in the MGCN-6 material [28]. Noteworthy, the pore diameter calculated from the TEM for MGCN-6 material was found to be similar to that value obtained from the N2 adsorption isotherm calculated from the mean value of BJH pore size distribution. Fig. 1D displays the electron energy-loss (EEL) spectrum of MGCN-6-130, which display energy loss ionization peaks located at 287.4, 295.8, 398.8 and, 408.2 eV, corresponding to C and N K-edges respectively. The peak at 287.4 eV is due to the  $1 \text{ s-}\pi^*$  electron transition and the other located at 295.8 eV is attributed to the 1 s- $\sigma^*$  electronic transition of the C K-edge, which is a fingerprint region of  $sp^2$ -hybridized C bonded to N present in the C3N4 heptazine core [28]. The corresponding  $\pi^*$  and  $\sigma^*$  transitions for the N K-edge show at 398.8 and 408.2 eV respectively. Similarities between C and N K edges are supportive of strong covalent bonds present between C and N atoms in the MGCN-6 wall structure composed of tri-s-heptazine based C<sub>3</sub>N<sub>4</sub>. The C/ N ratio of the sample calculated from this spectrum is found to be  $0.8 \pm 0.1$ , which perfectly matches with the C<sub>3</sub>N<sub>4</sub> stoichiometry.

The details of the morphology of the MGCN-6 were obtained by field emission scanning electron microscopy (Fig. 2A inset and Fig. S3). All of the materials show a similar morphology of KIT-6, demonstrating a well



Fig. 1. (A) Lower angle and wide angle (inset) powder XRD patterns and (B) nitrogen adsorption-desorption isotherms of MGCN-6  $C_3N_4$  materials having various textural diameters. The values of Y axis of MGCN-6-130 and MGCN-6-150 are shifted for about 50 and 100 cm<sup>3</sup> g<sup>-1</sup> respectively; (C and D) TEM image and electron energy loss spectra (EELS) of MGCN-6-130 sample.

Table 1	
Surface properties of the MGCN-6 with	different pore sizes and KIT-6 templates

Material	Unit Cell a <sub>0</sub> (nm)	$A_{\rm BET} ({ m m}^2{ m g}^{-1})$	$V_{\rm p}~({\rm cm}^3{\rm g}^{-1})$	$d_{\rm p,BJH}$ (nm)
KIT-6-100	22.5	728	0.99	8.0
KIT-6-130	23.6	625	1.32	9.9
KIT-6-150	24.0	555	1.53	11.3
MGCN-6-100	20.8	207	0.58	3.1
MGCN-6-130	21.4	303	0.68	3.2
MGCN-6-150	23.2	231	0.71	4.1

replication of structure of the template to MGCN-6 samples. Energy dispersive X-ray spectrosocopy (EDS) (Fig. 2A) of MGCN-6 samples show the peaks only for the elements of C and N. There are no other peaks observed in the EDAX spectrum. This confirms that the purity of the prepared samples is good and they are free from the impurities such as oxygen or Si. EDS spectrum also shows that the nitrogen content is more than that of the carbon content with C/N ratio of 0.8 as listed in Table S1, which is quite good agreement with the elemental analysis. EDS Elemental mappings (Fig. 2B–D) of MGCN-6 materials reveal that the uniform distribution of C and N throughout the sample, demonstrating that the elements are not agglomerated in the samples.

Typical semiconducting absorption with a band gap of 2.72 eV is observed from UV-DRS spectra for all of the MGCN-6 samples, which are shown in Fig. 3A. The structure and bonding between C and N in MGCN-6 were further verified by FTIR and XPS measurements. FTIR data of MGCN-6 materials shown in Fig. 3B confirm the existence of the condensed tri-s-heptazine in all of the samples as they show the typical out-of-plane skeletal bending and stretching modes of tri-s-heptazine at  $800 \text{ cm}^{-1}$  and between 1200-1700 cm<sup>-1</sup>, respectively. This reveals the

formation of tri-s-heptazine as predicted for the structural model of MGCN-6 (Scheme S1) [36]. X-ray photoelectron survey spectra (Fig. S4) reveal that MGCN-6-130 is mostly made of C and N with a tiny amount of O which is similar to the data obtained from EDAX. The C 1s and N 1s spectra also support the claim that the structure of the prepared materials is similar to that of C<sub>3</sub>N<sub>4</sub> structure [29,36]. The C1s peak was mainly deconvoluted (Fig. 3C) into four peaks with binding energies of 284.3 eV (3.4%), 287.6 eV (44.6%), 288.1 eV (44.6%) and 292.9 eV (4.9%). The two main peaks with equal intensities assigned to the  $sp^2$  C bonded to N atoms. The peak at 293.1 eV is assigned to the  $sp^2$  hybridized carbon in the aromatic ring with free NH<sub>2</sub> groups. A low intense peak observed at 284.6 eV is ascribed to the C-C bonding. The N 1s profile is shown in Fig. 3D and is deconvoluted into four peaks at binding energies of 398.3 eV (61.5%), 399.6 eV (13.9%), 400.6 eV (12.5%) and 403.8 eV (6.4%). The main peak was observed at 398.3 eV, which corresponds to C-N=C coordination. The peak at 399.6 eV reveals the presence of tertiary amine connected with aromatic rings and the peak at 400.6 eV is assigned to terminal amino groups (C-NH<sub>2</sub>). The sample also shows a peak at 403.8 eV which is attributed to the charging effects in triazines.

As MGCN-6 exhibits 3D porous structure, large surface area and uniform mesopores, and surface functionalities of free amine groups such as  $-NH_2/-NH_-/=N_-$  which are uncommon in other materials such as zeolites, mesoporous silicates and metal organic frameworks (MOFs), we have used this material for the immobilization of Pd(OAC)<sub>2</sub> [29–36]. XPS was utilized to examine the interaction between MGCN-6, C<sub>3</sub>N<sub>4</sub> support and Pd (OAC)<sub>2</sub>. Fig. S4 illustrates the XPS spectrum of the Pd supported on MGCN-6-130. As can be seen in Fig. 4S, there are two peaks with doublet of doublets at binding energies of 344.0, 341.0,



Fig. 2. (A) Energy dispersive x-ray spectroscopy (EDS) and (B-D) elemental mappings of MGCN-6 having adjustable porous properties; FESEM image (inset) of MGCN-6-130 sample.

338.0 and 336.0 eV which are in agreement with the  $Pd3d_{5/2}$  and  $Pd3d_{3/2}$  positions of Pd(II) and Pd(0), respectively [41,42]. The  $Pd3d_{3/2}$  peak at 344.0 eV and the  $Pd3d_{5/2}$  peak at 338.0 eV are assigned to Pd (0), while the  $Pd3d_{3/2}$  peak at 341.0 eV and  $Pd3d_{5/2}$  peak at 336.0 eV are attributed to Pd(II). The morphology, size and degree of dispersion of Pd nanoparticles immobilized onto the MGCN-6 after Pd(OAC)<sub>2</sub> deposition in ethanol solution were then investigated by transmission electron microscopy (TEM). As shown in Fig. 4, smaller Pd nanoparticles of size around 5.0 nm are evenly distributed on the surface of MGCN-6-130 support. The high-resolution transmission electron microscopy (HRTEM) pattern further confirmed the crystalline nature of

Pd nanoparticles with lattice spacing of 0.226 nm corresponding to (111) plane of crystalline Pd nanoparticles. These results revealed that highly uniform and discrete Pd nanoparticles can be successfully deposited on to the MGCN-6-130 support through the simple solvent assisted deposition method. Strong affinity between Pd(OAC)<sub>2</sub> and freely available amine rich functionalities with high  $\pi$  surface area of MGCN-6 could induce the self-reduction of Pd(OAC)<sub>2</sub> without using any external reducing agent and assisted the formation uniformly dispersed discrete Pd nanoparticle and then stabilize the resulted nanoparticles [43].

 $Pd(OAC)_2/MGCN-6-130$  was hound to be active catalyst for the synthesis of biaryls by Suzuki coupling reaction, an important C–C



Fig. 3. (A) UV-vis diffuse reflective spectra (DRS) and Band gap (Inset) data and (B) FTIR spectra of (a) MGCN-6-100, (b) MGCN-6-130 and (c) MGCN-6-150 samples. (C-D) C 1s and N 1s spectra of MGCN-6-130 material.



Fig. 4. (A-B) Transmission electron microscopy (TEM) images of Pd nanoparticles deposited on to MGCN-6. (C) High resolution TEM (HRTEM) image of Pd nanoparticles deposited on to MGCN-6.



**Scheme 1.** Suzuki coupling reaction between aryl halides with phenylboronic acid derivatives by using Pd(OAC)<sub>2</sub>/MGCN-6 catalyst.

formation reaction used for the manufacture of high valued compounds in the fine chemical and pharmaceutical industries [44,45]. By using Pd (OAC)<sub>2</sub>/MGCN-6-130 catalyst system, Suzuki coupling reaction between 4-bromoanisole and and phenylboronic acid proceeded with 92% of yield toards biphenyl using a low amount of catalyst loading under sustainable and environmentally benign conditions including ethanol as a solvent at room temperature (Scheme 1 and Table 2), whereas, the reaction proceeded with only ca. 20% yield upon using of lignad-less Pd (OAC)<sub>2</sub> alone as a catalyst under exactly identical conditions [46,47]. It should be noted that the previously reported Pd nanoparticles

#### Table 2

Suzuki coupling reaction	of aryl halides	and aryl	boronic	acids	catalysed	by	Pd
(OAC) <sub>2</sub> /MGCN-6.							

Entry	Aryl halide	Arylboronic Acid	Biaryl <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
a	H <sub>3</sub> CO <sup>Br</sup>	B(OH) <sub>2</sub> H <sub>3</sub> CO	$-\bigcirc -\bigcirc$	4.0	92
b	H <sub>3</sub> C	B(OH) <sub>2</sub> H <sub>3</sub> C	$-\bigcirc -\bigcirc$	4.0	90
c		B(OH) <sub>2</sub> Cl-		3.0	93
d	H <sub>3</sub> CO	B(OH) <sub>2</sub> H <sub>3</sub> CO		12.0	81
e	H <sub>3</sub> CO	NO <sub>2</sub> B(OH) <sub>2</sub> H <sub>3</sub> CO		4.0	93
f	H3CO H3	CO B(OH) <sub>2</sub> H <sub>3</sub> CO	осн	<sub>3</sub> 6.0	92
g	H <sub>3</sub> CO	B(OH) <sub>2</sub> H <sub>3</sub> CO	- С - сн3	8.0	84
h	H <sub>3</sub> C	CO B(OH) <sub>2</sub> H <sub>3</sub> C	осн	3 6.0	90
i	H <sub>3</sub> C	NO <sub>2</sub> B(OH) <sub>2</sub> H <sub>3</sub> C		4.0	94
k	CI	NO <sub>2</sub> B(OH) <sub>2</sub> CI-	$\sim$	4.0	98

<sup>a</sup>The products were characterized by <sup>1</sup>H NMR and mass spectrometry. <sup>b</sup>Yield refers to pure products after column chromatography isolation.

supported on N-free mesoporous carbon and non-porous g-C<sub>3</sub>N<sub>4</sub> supported Pd catalyst and most of the homogeneous catalysts require a high reaction temperature and environmentally toxic and hazardous solvents [48-50]. For the Suzuki-Miyaura coupling reaction, the nature of solvent is also an important factor in determining the final products yield. As can be seen in Table S2, the pure organic solvents like acetonitrile (ACN), tetrahydro-furan (THF), dimethylformamide (DMF), Nmethylpyrrolidine (NMP), dimethylsulfoxide (DMSO), and dichloromethane (DCM) exhibited lower conversions of 5-45% whereas protonated solvents of methanol (MeOH) and ethanol (EtOH) gave more than 90% conversion. The improvement of the conversion originated mainly because of the poor solubility of the products in protonated alcoholic solvents, which would drive the equilibrium in favor of the product formation. Bases used in the Suzuki-Miyaura coupling reaction also have great influence on conversion and yields, as they act as bridges to connect aryl halides and boronic acids. Table S3 depicts the effect of nature and type of bases on Suzuki-Miyaura coupling reaction using Pd(OAC)<sub>2</sub>/MGCN-6-150 as a catalyst and ethanol solvent. Na<sub>2</sub>CO<sub>3</sub> is demonstarted as the most efficient base with 97% conversion of aryl halide. Other inorganic bases such as NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH and KOH also gave the desired product inslightly less yields. Once the Pd(OAC)<sub>2</sub>/MGCN-6 is established as an excellent catalyst for the Suzuki coupling reaction, the catalytic efficiency of Pd(OAC)<sub>2</sub>/MGCN-6 was further investigated on the variety of aryl boronic acids (1.2 mmol) and aryl halides (1.0 mmol) with 1.5 mol% of Pd(OAC)<sub>2</sub>, 3.0 equivalents of Na<sub>2</sub>CO<sub>3</sub> and 20 mg of MGCN-6. The reaction was completed in 4-12 h with an excellent yield of the final products of almost 80-99% depend on the electron-withdrawing group and electron donating group present in the reaction substrates (For <sup>1</sup>H NMR data, please see Figs. S6–S14). Among the recations studied, yields for the entried d and g are slightly

lower because of the presence of electron rich substituents on to the boronic acid derivatives. It is worth to mention that the Suzuki coupling reaction on Pd nanoparticles supported 2D mesoporous C<sub>3</sub>N<sub>4</sub> Mott-Schottky heterojunction photocatalyst showed low activity than that of Pd(OAC)<sub>2</sub>/MGCN-6 catalyst [51], pointing the importance of 3D gyroid type mesoporous structure with a high surface area in C<sub>3</sub>N<sub>4</sub>, which facilitates the easy and fast diffusion and good protection against the pore blocking of the catalytically active materials. The excellent catalytic performance of Pd(OAC)<sub>2</sub>/MGCN-6 is attributed to the stabilization of Pd(OAC)<sub>2</sub> particles into the "six-fold cavities" of the highly ordered MGCN-6 support, which provides a strong interaction with the inbuilt  $-NH_2/-NH_2 = N_2$  functional groups. In addition, the presence of nitrogen functionalities helps to avoid the agglomeration of Pd(OAC)<sub>2</sub> particles during the reaction [17]. As recyclability of a heterogenous catalyst is an eminence feature both in the economic and environmental aspects, the recyclability and reusability of the Pd(OAC)<sub>2</sub>/MGCN-6 catalysts were further studied. The Pd(OAC)<sub>2</sub>/MGCN-6 demonstrated good recyclability and could be recycled for 6 consecutive cycles without losing much activity (Fig. S5). After the reaction, the ICP result of the filtrate showed that the Pd concentration in the fil-trate is less than 0.1 ppm, which indicated that the catalyst is highly stable and there is no Pd leaching during the reaction.

# Conclusions

In summary, we have demonstrated the synthesis of MGCN-6 with 3D mesoporous structure and a high surface area using environmentally benign and non-toxic guanidine hydrochloride precursor and KIT-6 templates through the nanocasting controlled pore filling technique. The obtained MGCN-6 containing six-folded cavities has been utilized as a chelating support for stabilizing the Pd(OAC)<sub>2</sub> particles as this entire material composed with -NH<sub>2</sub>/-NH-/=N- functional groups and ordered mesoporous structure. Pd(OAC)<sub>2</sub>/MGCN-6 was found to be highly active, selective heterogeneous catalyst for the Suzuki coupling reaction of aryl boronic acids and aryl halides for the synthesis of the industrially relevant biaryls. We believe that this method is quite simple, environmental and economic benefits of the precursor, it is anticipated that the strategy can be extended for the synthesis of a series of C<sub>3</sub>N<sub>4</sub> materials with different mesoporous structure and pore properties. By modifying these nanostructures with various other organic and inorganic functionalities, the application possibilities of the materials could be extended to a wide range of field including in photocatalytic water splitting, CO<sub>2</sub> conversion, energy storage and conversion and organic transformations including continuous hydrogenations, C-X (X=C, N and O) bond forming reactions, and beyond.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110548.

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