Journal of Materials Chemistry A

COMMUNICATION



View Article Online

View Journal | View Issue

CrossMark c-fick for updates Cite this: J. Mater. Chem. A, 2014, 2, 18731

Received 15th August 2014 Accepted 25th September 2014

DOI: 10.1039/c4ta04230a

www.rsc.org/MaterialsA

Fabrication of novel hybrid nanoflowers from boron nitride nanosheets and metal—organic frameworks: a solid acid catalyst with enhanced catalytic performance[†]

Peng Wang,^a Hao Li,^b Qiang Gao,^a Pei-Zhou Li,^a Xin Yao,^a Linyi Bai,^a Kim Truc Nguyen,^a Ru-Qiang Zou^{*cd} and Yanli Zhao^{*ade}

A double solvent replacement method was employed for the synthesis of novel hybrid nanoflowers from boron nitride nanosheets (BNNSs) and the metal–organic framework (MOF) MIL-53 in aqueous solutions under hydrothermal treatments. The strong binding ability of aluminum ions onto the surface of BNNSs determines the 3D flowerlike architectures of the BNNSs/MOFs hybrid, and the BNNSs act as a structure-directing template. The BNNSs/MOFs showed an enhanced catalytic activity in the acetalization of benzaldehyde with methanol owing to the facilitated diffusion process in the hierarchical architectures.

In the past decade, two-dimensional (2D) nanomaterials have attracted significant attention in the scientific community when Novoselov, Geim and co-workers isolated graphene nanosheets and discovered their extraordinary electronic properties.¹ The significance of the development of graphene and their related materials relies on not only the potential technological applications, but also the fundamental scientific interest, which provide the inspiration for scientists to develop novel types of 2D materials, such as layered transition metal dichalcogenides including MoS₂ and WS₂, as well as hexagonal boron nitride (h-BN). These 2D materials are of importance because of their significant impact on a variety of applications in electronics, gas storage and separation, catalysis.² Among these novel materials, BN is isoelectronic to carbon-based structures including carbon nanotubes, graphite and diamond. In addition, boron nitride

^bDepartment of Chemistry, University of Texas at Austin, Austin, Texas, USA

nanosheets (BNNSs) show an isostructure to graphene, which is formed based on the B–N covalent bonds. The layers of BN can undergo a variety of noncovalent interactions forming multiple layered structures, namely h-BN, which is an isostructure to graphite.³

After h-BN and BNNSs are hybridized with other molecules or materials, the resulting hybrid materials often exhibit extraordinary properties and potential applications.⁴ For example, h-BN has already been employed as catalyst supports, mainly because of its stability with a strong mechanical strength, as well as high resistance against corrosion, high temperature and oxidation. BNNSs have also been hybridized with polymers including polymethyl methacrylate (PMMA) and poly(vinyl alcohol) (PVA). However, the materials used to integrate with h-BN or BNNSs are restricted to polymers and metal nanoparticles. Herein, we present a novel type of catalytic material by hybridizing BNNSs with metal-organic frameworks (MOFs). To the best of our knowledge, this composite material is the first example employing BNNSs as the templates to direct the MOF growth and to control the hybrid morphology. Although the investigation was inspired by MOF-graphite oxide (GO) hybrids,⁵ it is still of great importance in terms of both fundamental studies and practical applications. Unlike the GO layers, BN is relatively chemically inert without any decorated functional groups, such as hydroxyl and carboxyl units, on the surface making it more difficult to grow MOFs on the surface.6

The ability of BN to undergo hybridization relies on the lone electron pairs on their nitrogen atoms, which act as Lewis bases to coordinate with metal-based species.⁷ When multiple layered h-BN is sonicated in polar solvents, such as N,N'-dimethylformamide (DMF), single or few-layered BNNSs with retained crystallinity could be obtained. The formation and stabilization of BNNSs are attributed to the noncovalent interactions between the oxygen atoms in the carbonyl groups of DMF and the boron atoms on the BNNSs, which act as a Lewis base and acid, respectively.^{4c} However, the trials using the BNNSs obtained from DMF to template the MOF formation were unsuccessful. This result could be explained by the fact

^aDivision of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore. E-mail: zhaoyanli@ntu.edu.sg

^cDepartment of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China. E-mail: rzou@pku.edu.cn

^dSingapore Peking University Research Centre for a Sustainable Low-Carbon Future, 1 Create Way, Singapore 138602, Singapore

School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ta04230a

that DMF could serve as a type of competitive coordination ligand, which may also coordinate with metal ions. As a consequence, the formation of MOFs occurs in a multi-phase manner in DMF solution instead of on the surface of the h-BN (see Fig. S1 in the ESI[†]). In order to solve these problems, we employed an alternative solution, namely water, in the BNNS exfoliation and MOF formation; given that water is a relatively weaker coordinative ligand to metal ions. Even though these trials were also difficult to be realized on account of the fact that the BNNS exfoliation is often assisted by the addition of surfactants to enhance the Lewis acid-base interactions between water and BNNS layers,8 or accomplished through the hydrolysis of multiple layered h-BN.9 Thus, the surfactants, which are either acidic or basic, could coordinate with metal ions and disturb the formation of the MOF structures. On the other hand, the hydrolysis of multiple layered h-BN into BNNSs without the addition of surfactants could lead to the formation of ammonia, while the ammonia by-product could rapidly deprotonate the carboxyl groups of the organic ligands used for the MOF synthesis, as a consequence of which, the MOF formation occurs in an uncontrollable manner.10

In order to address these problems, we employed a so-called "double-solvent replacement method" to fabricate a BNNS/MOF hybrid material. In this case, we employed DMF as the solvent for the BNNS exfoliation followed by the replacement of DMF with water, such that the MOF formation on the BNNSs could take place in water. First, 1.0 g commercially available h-BN powder was sonicated in 200 mL DMF for over 24 h, and the dispersion was then centrifuged three times at 4000 rpm, for a period of 30 min each time, in order to remove the non-exfoliated BN particles. Then, the centrifugation was performed at a higher centrifuging speed (e.g., 10 000 rpm), during which the BNNSs were precipitated. After removing the DMF supernatant, the same volume of water was added into the centrifuge tube, forming an aqueous suspension of BNNSs. This aqueous mixture was vigorously sonicated by a probe sonicator at 500 W for 1 h, vielding a light blue homogeneous solution of BNNSs. This aqueous BNNS solution was placed for over 24 h until some precipitates appeared. After removing the precipitates, the aqueous supernatant was directly used for the MOF growth without further purification. Using inductively coupled plasma mass spectrometry (ICP-MS) analysis, the concentration (0.037 mg L^{-1} with regard to boron) of BNNSs in aqueous solution was determined. The absence of dissolved ammonia was confirmed by the unchanged color of the BNNS aqueous suspension after adding a few drops of Nessler's reagent (a K₂HgI₄/KOH solution) through a qualitative colorimetric test, indicating that the BNNS formation in DMF and the re-dispersion in water are a physical exfoliation process rather than a chemical hydrolysis.

The MOF MIL-53, composed of the corner-sharing $MO_4(OH)_2$ (M = Cr³⁺, Al³⁺) octahedra and benzenedicarboxylate (BDC) as the interconnection ligands, has been widely used for gas adsorption and catalysis.¹¹ Furthermore, it was demonstrated that this MOF can be successfully synthesized in water with a well-controlled size and morphology. We first tested the possibility to graft Al³⁺ onto the BNNS surface adding aluminum(m) chloride hexahydrate (AlCl₃·6H₂O) into a 20 mL BNNS aqueous

solution. We monitored the coordination process of Al³⁺ onto the BNNS surface tracing the zeta-potential of the latter. Without the Al³⁺ grafting, the zeta-potential of the original BNNS aqueous solution was determined to be +0.60 mV. After the addition of Al^{3+} , the zeta-potential increased to +16.52 mV. The increased zeta-potential value indicates that the positivelycharged Al3+ cation was successfully adsorbed onto the BNNS surface. One equivalent BDC with regard to AlCl₃·6H₂O was added to the reaction mixture containing the BNNS-Al³⁺ hybrid, followed by heating the solution at 150 °C for 24 h. Few white precipitates were observed and collected by centrifugation. Then, DMF was added into the obtained precipitates, and the suspension was refluxed at 150 °C for 8 h, during which the residual water and BDC molecules were removed from the cavities of the formed MOF. Two types of BNNS/MOF hybrids were obtained using different amounts of AlCl₃·6H₂O, namely 24 mg and 48 mg, which are denoted as BNNSs/MOF-1 and BNNSs/MOF-2, respectively. For comparison, two types of MIL-53 without BNNSs were also synthesized with different concentrations of the precursors, denoted as MIL-53-com and MIL-53-bulk (see experimental section in the ESI†). Moreover, it should be noted that if excessive aluminum ions are used (e.g. 96 mg AlCl₃ · 6H₂O for 20 mL BNNS aqueous solution) they could result in aggregation or even precipitation of the BNNS/metal ion hybrids.¹² Thus, the amounts of Al³⁺ and BNNSs should be controlled at a relatively lower ratio.

Then, we examined the influence of BNNSs on the crystallization of MIL-53, as well as its morphology, given that BNNSs could potentially act as a template during the formation of MIL-53. Field emission scanning electron microscopy (FE-SEM) shows that both BNNSs/MOF-1 and BNNSs/MOF-2 were composed of separate flower-like hierarchical architectures (Fig. 1 and S3†). The magnified SEM image is shown in Fig. 1b, which reveals that these hierarchical structures contain



Fig. 1 SEM and TEM images of BNNSs/MOFs and MIL-53: (a) SEM image of BNNSs/MOF-2; (b) magnified nanosheets of (a); (c) TEM image of BNNSs/MOF-2; (d) SEM image of MIL-53-bulk.

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numerous nanoplates with a thickness from 20 to 30 nm. Furthermore, the transmission electron microscopy (TEM) image of BNNSs/MOF-2 reveals that the hybrid nanosheets appeared as a coating of MOF on the BNNSs (Fig. 1c). It is difficult to directly distinguish the BNNSs from MIL-53 under TEM, as the mass thickness contrast of the B and N elements in BNNSs is similar to that of the C atom in the MOF. As a control, we also obtained the SEM images of both the pristine h-BN and MIL-53 prepared without BNNSs as the template. These SEM images show that h-BN, BNNSs/MOF-1, and BNNSs/MOF-2 shared a similar plate-like morphology (Fig. S2[†] and 1), while MIL-53 exhibited a nanorod morphology with 200-600 nm in width and several micrometers in length (Fig. S4† for MIL-53com). These observations further support our assumption that the BNNS layers act as the template for the MOF formation. It was reported that benzoic acid-functionalized graphene could serve as a structure-directing agent in the MOF synthesis, and the number of binding sites between graphene and metal ions played a key role. The amount of carboxyl groups on modified graphene can reach up to 17.8 mmol g^{-1} .⁵⁶ BNNSs contain 40.3 mmol g^{-1} nitrogen atoms, and the nitrogen atoms on the plane act as the coordination sites. Thus, the interaction between the BNNSs and MOF units was strong enough to enable the BNNSs to be the structure-directing template. Thus, the BNNSs were used to template and control the morphology of the MOF structures in the BNNS/MOF hybrid synthesis. Recently, Rao and co-workers reported a hybrid formation from ZIF-8 and fewlayered BN.13 Furthermore, an ordinary bulky MIL-53 powder was also synthesized according to previous reports,11 and the obtained material consisted of micrometer-sized crystals (Fig. 1d for MIL-53-bulk as the contrastive material).

The phase structures of the BNNSs/MOF nanoflowers and related materials were also examined using powder X-ray diffraction (XRD), where the MIL-53-bulk and BN powder were used as the reference materials. Because MIL-53 is the major content in the hybrid materials, the predominance of the main diffraction peaks for MIL-53 was featured on the XRD pattern of the hybrids (Fig. S5–S8†). As expected, the presence of the BNNSs does not interrupt the coordination between the aluminum ion and BDC to build the small units of MIL-53. The XRD patterns combined with the zeta-potential results indicate that the interaction between the BNNSs and aluminum ions is strong enough to facilitate the dispersion of BNNSs in the matrix of MIL-53.

Fig. 2 shows nitrogen adsorption/desorption isotherms of the samples at 77 K. At a relatively low pressure (<0.4 atm), the isotherms of both MIL-53-bulk and BNNSs/MOFs showed a typical IUPAC type I behavior and no hysteresis was observed, which are consistent with the previously reported physisorption processes of microporous materials. This observation indicates that BNNSs/MOFs possess microporous regions. At relatively high pressures (>0.8 atm), the isotherms of both BNNSs/MOFs and BN powders exhibited the presence of H3-like hysteresis loops, indicating the coexistence of mesopores and macropores. These large-sized pores may be resulted from slit-shaped structures owing to the stacking of the nanoflakes.¹⁴ The pore size distribution curve (Fig. S9 in the ESI†) also indicates that



Fig. 2 Nitrogen adsorption/desorption isotherms for BN, MIL-53bulk, and BNNSs/MOFs at 77 K.

the hierarchical porous structure in BNNSs/MOFs, i.e., micropores, mesopores, and macropores coexist in the BNNSs/MOF hybrids. The porosity of the hierarchical nanoflowers could be tuned by varying the contents of BN. As shown in Table S2,† the volume of the mesopores and macropores in BNNSs/MOF-1 (0.8 wt% in boron) was 0.18 cm³ g⁻¹. When the boron content was increased to 1.6 wt% in the case of BNNSs/MOF-2, the volume increased to 0.25 cm^3 g⁻¹. In contrast, the volume of the micropores decreased upon increasing the boron content. For example, the microporous volumes were 0.30 and 0.11 $\text{cm}^3 \text{g}^{-1}$ for BNNSs/MOF-1 and BNNSs/MOF-2, respectively. These variations in the pore structures of the hybrids could be explained as follows. The BN components are mesoporous and macroporous materials with low surface areas, while the MIL-53 components are microporous materials with high surface areas. Upon increasing the contents of the BN components, the Brunauer-Emmett-Teller (BET) surface area and microporous volume decreased, while the volume of mesopores and macropores increased. Thermogravimetric analysis (TGA) and the FTIR spectra also demonstrate the integrated growth of MIL-53 onto the BNNSs and the successful formation of the hybrid materials (Fig. S10 and S11[†]). BN exhibits a characteristic Raman peak around 1366-1373 cm⁻¹ because of the E2g phonon mode. In this case, BNNSs/MOF-2 shows a Raman peak at 1368 cm^{-1} , which is about a 3 cm^{-1} shift from the Raman peak of bulk h-BN at 1365 cm^{-1} , indicating a possible reduction in the thickness of the sheets (Fig. S12[†]).

On the basis of the structural analysis, the growth mechanism of BNNSs/MOF nanoflowers was proposed, as shown in Scheme 1. After the replacement of DMF with water, the nitrogen atoms on BNNS layers are able to coordinate with Al^{3+} cations. These Al^{3+} cations undergo nucleation reactions, forming aluminum oxide clusters on the BNNS layers. Then, the MOF growth takes place on the surface of the obtained nanosheets grafted with a number of aluminum oxide clusters, leading to the formation of the nanoflowers. This proposed mechanism is similar to that for the formation of GO/MOF hybrids, which was previously reported to investigate the structure-directing roles of graphene in the synthesis of MOF nanowires.⁵

These flower-shaped hybrids contain a number of thin nanosheets, as a consequence of which their active sites are more accessible to the substrates in catalysis and absorption on account of their relatively short diffusion pathway.¹⁵ In addition, the hierarchical porous structure of these materials is also beneficial in terms of the mass transport because of the fact that the presence of macropores and mesopores can considerably favor the diffusion of the guest molecules and make the active sites more accessible.15 In order to support this assumption, we employed a probe molecule to explore the relationship between the morphology of the hybrids and their adsorption capability. We used a relatively big-sized molecule, namely fluorescein isothiocyanate isomer I (FITC) as the probe molecule, in order to rule out the impact of micro-porosity on the adsorption. The adsorption experiments demonstrate that BNNSs/MOF-2 containing nanoflower structures could adsorb FITC faster than that of bulky MIL-53 crystals under the same experimental conditions. Within 16 min, BNNSs/MOF-2 can adsorb 34.8% of FITC from solution, while MIL-53-bulk can only adsorb 21.8% of the dye (Fig. S13 and S14[†]).

We also investigated the influence of the morphology and hierarchical structure of the BNNSs/MOF hybrids on their ability as a catalyst. We select the acetalization of benzaldehyde with methanol as the model reaction using the hybrid materials as the catalyst at room temperature, given that MIL-53 was reported to successfully catalyze this reaction.¹⁶ Under the same experimental conditions, BNNSs/MOF-2 containing a nanoflower-like structure led to 70.4% conversion of benzaldehyde (Fig. 3). In comparison, the catalytic performance of MIL-53-



Scheme 1 Proposed mechanism for the construction of BNNSs/MOF hybrids.



Fig. 3 Time-dependent conversion plots for the acetalization of benzaldehyde with and without MIL-53-bulk or BNNSs/MOF-2. Reaction conditions: benzaldehyde (100 μ L), methanol (6 mL) and catalyst (60 mg), room temperature.

bulk was significantly lower. Because the reaction cannot occur without the catalyst, these observations firmly support the assumption that the nanosheet structure in the BNNSs/MOF materials can significantly enhance the catalytic capability by providing more accessible catalytic centers.

In summary, a novel approach for the preparation of BNNSs/ MOF hybrid materials has been developed by double solvent replacement method. To the best of our knowledge, this is the first example for the use of BNNSs as the template for the formation of MOFs. The resulting hybrid materials combine the advantageous features of both the BN nanosheets and the porous MOFs, leading to nanoflower structures, which provide more accessible active sites to some reaction substrates or guest molecules. As a consequence, the hybrid materials exhibited enhanced catalytic activity. Thus, this synthetic approach of double solvent replacement may open up an opportunity for developing other hybrid materials using nanosheet materials (such as MOS_2 and WS_2) as the platforms. The obtained hybrids with a well-defined structure and morphology show a promising application potential in the areas of heterogeneous catalysts, drug/gene delivery, and biosensing.

Acknowledgements

This research is supported by the National Research Foundation (NRF), Prime Minister's Office, Singapore under its NRF Fellowship (NRF2009NRF-RF001-015) and Campus for Research Excellence and Technological Enterprise (CREATE) Programme–Singapore Peking University Research Centre for a Sustainable Low-Carbon Future, and the NTU-A*Star Centre of Excellence for Silicon Technologies (A*Star SERC No.: 112 351 0003).

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