CHEMISTRY
AN ASIAN JOURNAL
FULL PAPER

DOI: 10.1002/asia.201402695

Tailored Synthesis of Various Nanomaterials by Using a Graphene-Oxide-Based Gel as a Nanoreactor and Nanohybrid-Catalyzed C−C Bond Formation

Abhijit Biswas and Arindam Banerjee*[a]

Abstract: New graphene oxide (GO)-based hydrogels that contain vitamin B_2/B_{12} and vitamin C (ascorbic acid) have been synthesized in water (at neutral pH value). These gel-based soft materials have been used to synthesize various metal nanoparticles, including Au, Ag, and Pd nanoparticles, as well as nanoparticle-containing reduced graphene oxide (RGO)-based nanohybrid systems. This result indicates that GO-based gels can be used as versatile reactors for the synthesis of different nanomaterials and hybrid systems on the nanoscale. Moreover, the RGO-based nanohybrid hydrogel with Pd nanoparticles was used as an efficient catalyst for C−C bond-formation reactions with good yields and showed high recyclability in Suzuki–Miyaura coupling reactions.

Keywords: cross-coupling · graphene · nanoparticles · nanoreactors · vitamins

Introduction

Supramolecular gels that are formed by trapping a large number of solvent molecules belong to an important class of soft materials that have fascinating applications in several fields, including cell cultures, tissue engineering, light harvesting, regenerating medicine, controlled drug release, oil-spill recovery, and the synthesis of metal nanoclusters.[1] Some of these gel matrices have been used to create hybrid gels that contain carbon-based nanomaterials.[2] Graphene oxide (GO), or reduced graphene oxide (RGO), is an amazing carbon-based nanomaterial that contains various reactive functional groups (including hydroxy, carboxylic acid, and epoxy groups) and can act as a wonderful building block to create different supramolecular entities, including gels.[3] Shi and co-workers synthesized a GO-based hydrogel by using a polymer and DNA.[4] Zhang and co-workers developed graphene-oxide-based hydrogels by using glucono-δ-lactone,[5a] whilst the same group also made a significant contribution to graphene-based gels.[5b,c] There have been several other reports on GO- and RGO-based nanohybrid systems,[6] although there are only a few examples of the use of micro- or nanomaterials as a nanoreactors for photocatalysis and other applications.[7] However, none of these aforementioned examples employed GO-containing-hydrogel-based nanoreactors for the tailored "green synthesis" of various nanomaterials, including metal nanoparticles (Au, Ag, and Pd) and nanohybrids with RGO and metal nanoparticles. Thus, there is a real need for the design and construction of gel-based soft materials that can act as reactors for making different nanomaterials and hybrid systems in aqueous medium.

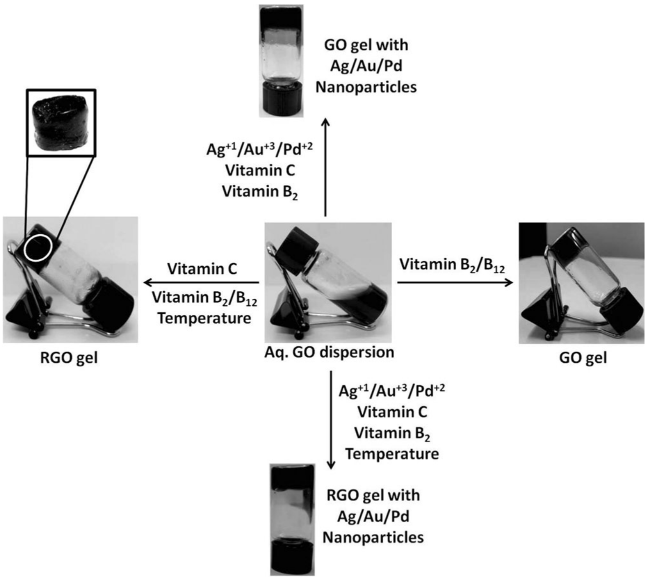
Herein, vitamin-containing (vitamin B_2/B_{12}) GO-based gel-phase materials have been found to be versatile reactors for the formation of different metal nanoparticles (Au, Ag, and Pd). Furthermore, RGO-based hydrogels were also fabricated through the in situ reduction of the corresponding metal ions and GO in the presence of another vitamin, ascorbic acid (vitamin C). The merit of this system is that judicial choice of the constituents of the gel-based material, that is, 1) water (as a medium), 2) GO and vitamin B_2/B_{12} (as gelator molecules), and 3) ascorbic acid (as the reducing agent), influence the reactivity of the gel, such that one of these vitamins (B_2 or B_{12}) promotes gelation, whereas the other vitamin (vitamin C) acts as a reducing agent to reduce GO into RGO and other metal salts into their corresponding metal nanoparticles within the hydrogel matrix. Thus, this gel system holds great promise as a nanoreactor for the formation of various nanoparticles and/or RGO-containing nanohybrid systems by using a simple "green chemical" approach (Scheme 1).

The Suzuki–Miyaura coupling reaction is a well-established method for the creation of C−C bonds by using a palladium catalyst.[8] A number of examples of Suzuki–Miyaura C−C coupling reactions have been reported with palladium nanoparticle catalysts. Amatore and co-workers reported that Au@Pd nanoparticles acted as an efficient catalyst in Suzuki–Miyaura cross-coupling reactions.[9] Recently, it was found that GO- or RGO-supported Pd nanoparticles showed superior catalytic activity to Pd nanoparticles with-

---

[a] A. Biswas, Prof. Dr. A. Banerjee
Department of Biological Chemistry
Indian Association for the Cultivation of Science
Jadavpur, Kolkata-700032 (India)
Fax: (+91) 33-2473-2805
E-mail: bcab@iacs.res.in

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201402695.



Scheme 1. Schematic representation of the GO gel and its function as a versatile reactor for making different nanomaterials, including metal-nanoparticle-containing RGO-based nanohybrid gels.

out a GO/RGO support, owing to their high thermal and chemical stability, as well as to the large specific surface area of GO and RGO.[10] In addition, RGO was insoluble in most solvent, which enabled the effective removal of the catalyst owing to the highly hydrophobic nature of RGO. Mülhaupt and co-workers synthesized GO–Pd and CDG–Pd nanocomposite materials as air-stable catalysts and successfully applied them to the Suzuki–Miyaura coupling reaction.[11] El-Shall and co-workers prepared graphene-supported Pd nanoparticles that showed high catalytic activity in Suzuki–Miyaura coupling reactions with high turnover frequencies.[12] Gao and co-workers developed Ag–Pd@rGO bimetallic nanoparticles catalysts that exhibited high catalytic activity in Suzuki–Miyaura coupling reactions.[13] Recently, Camp et al. reported a Suzuki–Miyaura coupling reaction by using in situ generated glucose-derived palladium nanoparticles.[14] However, none of these examples included Suzuki–Miyaura reactions by using a palladium-nanoparticle-containing RGO-based hydrogel as a catalyst. A major problem associated with Pd-nanoparticle-containing catalysts is the gradual loss of their catalytic activity, owing to the need for cumbersome separation of the catalyst from the reaction mixture. To circumvent this drawback, it is necessary to use a new catalyst that is easily separable from the reaction mixture. To the best of our knowledge, herein, we report the first palladium-nanoparticle-containing RGO–vitamin B_2-based hydrogel as a catalyst for Suzuki–Miyaura coupling reactions. The use of this catalyst has several advantages: 1) it uses relatively inexpensive chemicals for the catalyst preparation in an environmentally friendly approach; 2) it employs a facile, straightforward procedure for the separation of the catalyst from the reaction mixture; and 3) the hydrogel catalyst showed excellent reusability (up to 15 times) without the significant loss of catalytic activity.

Results and Discussion

GO can form hydrogel matrixes in the presence of other molecules through π–π stacking and/or hydrogen-bonding interactions by utilizing large polyaromatic surfaces and other oxygenated functional groups (OH, COOH, and epoxy groups) under appropriate conditions. Two biologically important molecules, vitamin B_{12} and vitamin B_2, have been separately introduced as cross-linking agents into dispersions of GO in aqueous medium, which ultimately leads to the formation of stable hydrogels at room temperature (see the Supporting Information, Figure S1). Both of these vitamins (B_{12} and B_2), which contain NH_2 and OH functionalities, can form strong hydrogen bonds with the OH and COOH groups of GO sheets. Moreover, each of these vitamins contains aromatic moieties that can interact with the polyaromatic surface of GO through π–π stacking interactions. Fluorescence emission spectroscopy of vitamin-B_2-containing GO-based hydrogels has been performed to examine the π–π stacking interactions (Figure 1). Free vitamin B_2 exhibited a fluorescence emission maximum at 532 nm upon excitation at 488 nm. However, considerable quenching of the emission maximum was observed in a vitamin-B_2-containing GO-based hydrogel at the same excitation wavelength, which indicated the presence of π–π stacking interactions between the GO sheets and the molecules of vitamin B_2 in the hydrogel. The minimum gelation concentrations (MGCs) of the vitamin-B_{12}- and vitamin-B_2-containing hydrogels were 0.20% (w/v) and 0.28% (w/v), respectively, thus suggesting that each of these vitamin molecules acted as a good cross-linker between the GO sheets to form the gels. To gain an insight into the morphologies of the GO-based hydrogels, TEM analysis was performed (see the Supporting Information, Figure S2). TEM images of these hydrogels revealed the presence of large self-assembled GO nanosheets in the supramolecular hydrogel. Interestingly, the GO–vitamin B_{12}/B_2 hydrogels could be easily

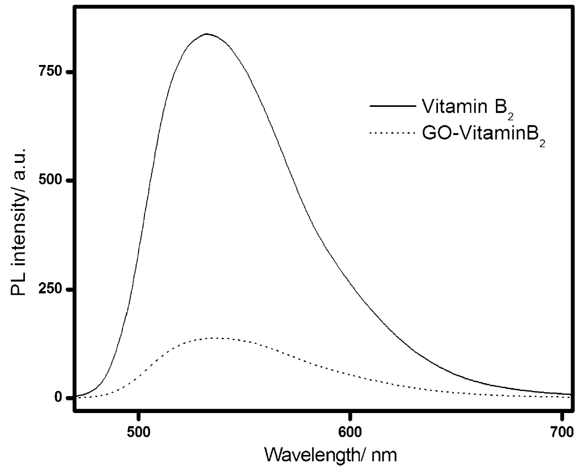


Figure 1. Fluorescence emission spectra of vitamin B_2 and GO–vitamin B_2 in water; excitation: 488 nm.

reduced in the presence of another vitamin, ascorbic acid (vitamin C), to form a reduced graphene oxide (RGO)-based hydrogel. The merit of using vitamin C is that the entire reduction process is environmentally friendly, because vitamin C is nontoxic and, during the reduction, no gaseous side-products are produced. In this transformation, vitamin C does not disturb the gel network. However, the gel material shrinks slightly at the time of reduction, but still contains 70 % water in the RGO–vitamin hydrogel.

The formation of RGO in the presence of ascorbic acid was examined by Raman spectroscopy, which is a powerful tool for characterizing carbon-based materials. Two fundamental vibration modes were observed in the spectrum of the RGO-based gel at 1345 and 1586 cm^{-1}, which corresponded to the D and G bands of RGO, respectively (Figure 2). The higher intensity ratio of the D/G bands for the vitamin-B_2-containing RGO-based gel suggested the formation of more sp^2 domains in RGO after the reduction of GO in the gel phase.

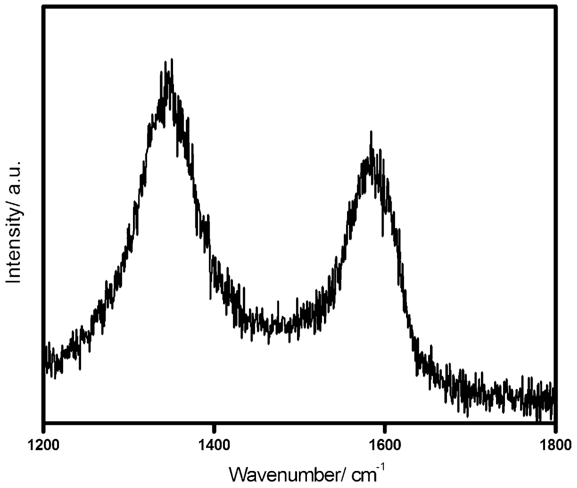


Figure 2. Raman spectrum of a dried sample of a vitamin B_2-containing RGO-based hydrogel.

The viscoelastic properties of these hydrogels were examined by measuring their rheological properties at a fixed concentration of 1.8 % (w/v; Figure 3). The storage modulus (G') and loss modulus (G'') were monitored as a function of angular frequency under a fixed strain of 0.1 %. The G' values of the vitamin-B_{12}- and vitamin-B_2-containing gels were 56.4 and 41.4 KPa, respectively, at a fixed angular strength of 103 rads^{-1}. So, the vitamin-B_{12}-containing gel was stronger than the vitamin-B_2-containing gel, because vitamin B_{12} bound more strongly with GO than vitamin B_2. Although both vitamins (B_{12} and B_2) contained NH_2 and OH functional groups and aromatic moieties for participating in hydrogen-bonding interactions and π–π interactions with GO, respectively, the number of hydrogen bonds for association and gelation was higher in the GO–vitamin B_{12} pair than in the GO–vitamin B_2 pair. In these RGO gels, the gel strength was dramatically higher than in the corresponding GO gels. The higher G' value (129 KPa) of the RGO–vitamin B_{12} gel than the RGO–vitamin B_2 gel (115 KPa) at a fixed angular strength of 103 rads^{-1} was due to a narrowing of the interlayer distance in RGO. Therefore, the stiffness of these gels followed the order: RGO–vitamin B_{12} > RGO–vitamin B_2 > GO–vitamin B_{12} > GO–vitamin B_2.

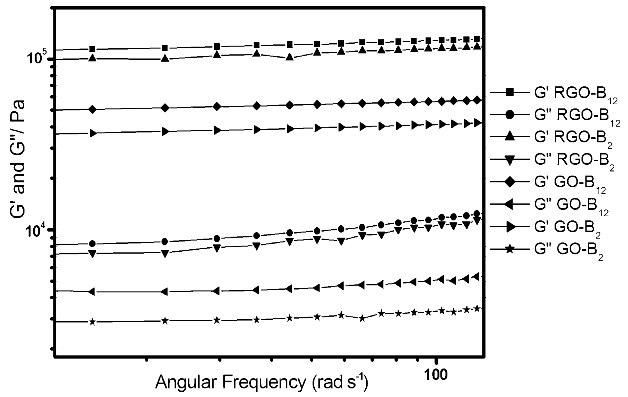


Figure 3. Frequency dependence of the dynamic storage modulus (G') and the loss modulus (G'') of GO- and RGO-based hydrogels in the presence of vitamin B_2 or vitamin B_{12}.

Ascorbic acid (vitamin C) can readily reduce some metal salts into their corresponding metal nanoparticles (MNPs).[15] Thus, we anticipated that, by utilizing this reducing property of ascorbic acid, we could obtain metal-nanoparticle-fabricated RGO-based nanohybrid systems. Moreover, the free space within the 3D cross-linked network system in the hydrogels and also the in situ reduction of the metal ions provided good nucleation and growth of the nanoparticles. Herein, GO–vitamin/MNPs and RGO–vitamin/MNPs nanohybrid hydrogels were obtained by in situ reduction of the corresponding metal ions (Au, Ag, and Pd) and GO (Scheme 1). Both of these hydrogel formations (GO–vitamin/MNPs and RGO–vitamin/MNPs) were assisted by vitamin C. The formation of metal nanoparticles within the hydrogel matrix was characterized by TEM, SAED, and EDX analyses. TEM images (Figure 4) revealed that these nanoparticles were spherically shaped and uniformly distributed within the GO and RGO nanosheets. EDX analysis (see the Supporting Information, Figure S3) also showed the presence of metal nanoparticles within the hydrogels. SAED analysis (see the Supporting Information, Figure S4) showed a ring pattern that corresponded to each of these nanoparticles (Au, Ag, and Pd).

The metal-nanoparticle-anchored RGO–vitamin hydrogel was self-supported and free-standing and, hence, it could be used as a nanocatalyst. Thus, the Pd-nanoparticle-containing RGO–vitamin B_2 nanocomposite hydrogel (Pd/RGO–vitamin B_2) was tested as a nanocatalyst in Suzuki–Miyaura coupling reactions. The in situ synthesized and well-dispersed Pd nanoparticles within the graphene sheets showed good catalytic activity in Suzuki–Miyaura reactions at relatively low temperatures in an aerobic environment with good yields (Table 1). One of the most striking advantages of this catalyst is its recovery process and recyclability. The efficien-

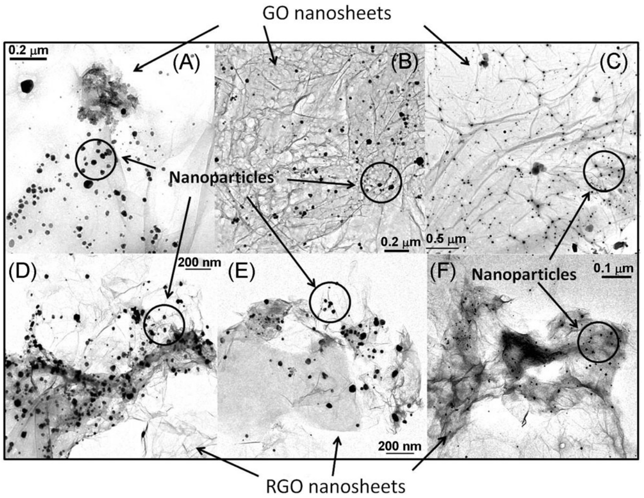


Figure 4. TEM images of A) Ag, B) Au, and C) Pd-nanoparticle-containing GO-based hydrogels and D) Ag, E) Au, and F) Pd-nanoparticle-containing RGO-based hydrogels.

cy of the catalyst is dependent on the isolation and recovery of the catalyst from the reaction mixture and, therefore, its reusability also depends on how successfully it is recovered. In most of the reported applications of such systems in heterogeneous catalysis, the catalyst has been removed through filtration or centrifugation[6g,8a,c,e] and these techniques can be attributed to some loss of catalytic activity.

Sun and co-workers recently reported the formation of a semi-heterogeneous palladium-nanoparticle-supported Fe_3O_4/sulfonated-graphene catalyst, which was efficiently removable owing to the presence of magnetic nanoparticles in the system.[16] Herein, we used the Pd-nanoparticle-containing RGO–vitamin B_2 hybrid hydrogel as a potential catalyst to test the recyclability of the catalyst. This catalyst remained in its gel form until the end of the reaction and, thus, it was easily separable from the reaction mixture by using a spatula (Figure 5). Therefore, there was no loss of catalyst for the subsequent reaction. Moreover, the catalyst contained graphene sheets. Owing to its large polyaromatic surface, the graphene sheets could promote the adsorption of reacting molecules through π–π interactions. Therefore, such adsorption provided a high effective concentration of the aryl halides and aryl boronic acids near the Pd nanoparticles. This hydrogel catalyst could be easily recycled nine times without a significant loss of yield (see the Supporting Information, Figure S6 A). After the ninth cycle, the yield of the reaction decreased slightly. This result may be due to aggregation of the nanoparticles (see the Supporting Information, Figure S7 A). However, increasing the reaction temperature to 80 °C caused a remarkable increase in the yield and the catalyst could be used 15 times efficiently without any significant loss of catalytic activity (see the Supporting Information, Figure S6B).

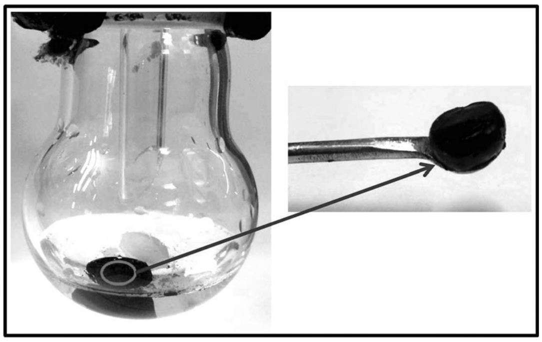
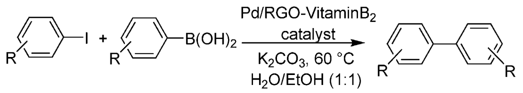
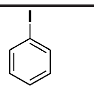
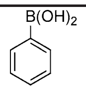
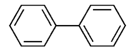
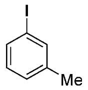
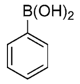
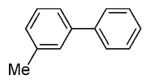
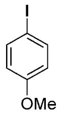
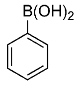
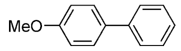
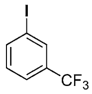
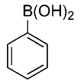
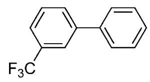
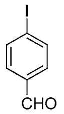
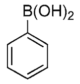
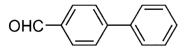
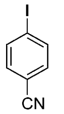
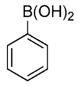
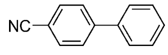
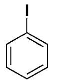
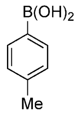
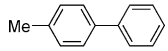
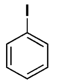
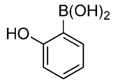
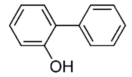
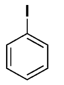
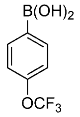
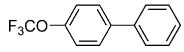


Figure 5. Photographs of the recovered catalyst. The hydrogel can be effortlessly separated from the reaction mixture by using a spatula.

Table 1. Suzuki–Miyaura coupling reactions between aryl halides and aryl boronic acids catalyzed by a Pd-nanoparticle-containing RGO–vitamin B_2 hydrogel.[a]



Entry	Aryl halide	Aryl boronic acid	Product	Yield [%][b]
1				93
2				94
3				97
4				96
5				95
6				97
7				97
8				91
9				93

[a] Reaction conditions: aryl halide (1 mmol), aryl boronic acid (1.2 mmol), K_2CO_3 (3 mmol), water/EtOH (6 mL), Pd/RGO–vitamin B_2 catalyst (0.73 g), 60 °C. [b] Yield of isolated product (as determined by ^1H and ^{13}C NMR spectroscopy).

Conclusion

A simple and elegant method for the synthesis of various nanoparticles and nanohybrid systems has been developed by using a new vitamin-containing GO-based hydrogel as a nanoreactor. An ascorbic-acid-containing GO-based gel acted as a highly efficient nanoreactor for the synthesis of RGO gels, metal-nanoparticle-containing GO gels, and metal-nanoparticle-containing RGO nanohybrid gels. One of these hybrid hydrogels (the Pd-nanoparticle-containing RGO–vitamin B_2 gel) acted as a highly efficient catalyst for Suzuki–Miyaura coupling reactions. This hydrogel catalyst offers several advantages, including: 1) the use of inexpensive and non-hazardous starting materials; 2) good stability over the course of the reaction; 3) it catalyzed Suzuki–Miyaura coupling reactions under aerobic conditions at relatively low temperatures in high yields; and 4) it could be easily separated from the reaction mixture, thereby showing remarkable recyclability. This versatile hydrogel-based reactor for the synthesis of various nanomaterials holds great promise for the creation of advanced gel-based materials for the tailored production of new functional materials for catalysis and other applications.

Experimental Section

Reagents and materials

L-Ascorbic acid, H_2SO_4, $KMnO_4$, sodium nitrate, H_2O_2, and the solvents were purchased from SRL, India. Others materials were purchased from Sigma–Aldrich.

Synthesis of graphene oxide

Graphene oxide (GO) was synthesized from graphite powder (<30 μM) by using a modified Hummers method.[17] In a typical synthesis, graphite powder (0.5 g) was added to concentrated H_2SO_4 (20 mL) and the mixture was stirred. Then, sodium nitrate ($NaNO_3$, 0.25 g) was added and the mixture was cooled to 0 °C. Under vigorous agitation, $KMnO_4$ (1.5 g) was gradually added to this mixture and the temperature was kept at less than 20 °C to prevent overheating. Then, the resulting mixture was transferred into a 35 °C water bath and stirred for 30 min, during which time a brownish gray paste was formed. Then, the mixture was diluted by the addition of water (30 mL). During the addition of the water, the temperature was raised to 90 °C and this temperature was maintained for 15 min. Then, the solution was mixed with warm water (80 mL) and 30% H_2O_2 (0.5 mL) was added to ensure the completion of the reaction. The warm solution was filtered and washed thoroughly with HCl and warm water. The solid was dispersed in distilled water (100 mL) by sonication. Then, the solution was centrifuged at 3000 rpm for 15 min. The filtrate was re-suspended by using sonication and centrifuged again at 20000 rpm. The re-suspension/centrifugation process was repeated several times. Finally, the centrifuged viscous graphene oxide was collected and freeze-dried under vacuum to afford a solid powder.

Preparation of the GO/RGO-based hydrogels

Stock solutions of vitamin B_{12} and vitamin B_2 were prepared by dissolving in MiliQ water at concentrations of 1.5 and 4 mg mL^{-1}, respectively. In a typical experiment, GO was dispersed in water by sonication to make a viscous solution. Then, the vitamin solution (0.2 mL) was added to the GO dispersion (0.8 mL) to obtain a GO-based hydrogel. The GO concentrations in the GO–vitamin B_{12} and GO–vitamin B_2 hydrogels were 2.75 and 3 mg mL^{-1}, respectively. Sonication facilitated the gel formation and more time was required to form the gels without sonication. The RGO-based hydrogel was obtained by heating the GO gel in the presence of ascorbic acid at 80 °C for a few minutes.

Synthesis of metal-nanoparticle-containing RGO-based hydrogels

First, an aqueous solution (0.1 mL) of the metal salt ($HAuCl_4$/$AgNO_3$/Na_2PdCl_4; 1 mg mL^{-1}) was added to an aqueous dispersion of GO (0.6 mL, 11.8 mg mL^{-1}) and thoroughly sonicated. Then, ascorbic acid (vitamin C, 0.2 mL, 100 mg mL^{-1}) was added to the mixture, followed by vitamin B_2 (0.2 mL, 4.5 mg mL^{-1}) and the mixture was again sonicated thoroughly. Then, the mixture was heated at 80 °C for a few minutes to obtain the metal-nanoparticle-containing RGO-based hydrogels. Herein, we expect that all of the metal ions were reduced in situ by the ascorbic acid within the hydrogel matrix.

Catalyst preparation

First, an aqueous solution (0.1 mL) of a Pd^{2+} salt (8.17 mM) was added to an aqueous dispersion of GO (0.6 mL, 11.8 mg mL^{-1}) and the mixture was thoroughly sonicated. Then, ascorbic acid (vitamin C, 0.2 mL, 100 mg mL^{-1}) was added, followed by vitamin B_2 (0.2 mL, 4.5 mg mL^{-1}) and the mixture was sonicated for a few minutes. Then, the mixture was heated at 80 °C to obtain the Pd-nanoparticle-containing RGO–vitamin B_2 hydrogel catalyst.

General procedure for the Suzuki–Miyaura coupling reactions

In a Suzuki coupling reaction, an aryl halide (1 mmol), an aryl boronic acid (1.2 mmol), and K_2CO_3 (3 mmol) were dissolved in a water/EtOH mixture (1:1, 6 mL). Then, the catalyst (0.73 gm, 0.012 wt% Pd) was added and the reaction was stirred at 60 °C. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction (by TLC), the catalyst was removed by a spatula and washed thoroughly with MeOH and water. The mixture was extracted with EtOAc (3×10 mL). Evaporation of the solvent and purification by column chromatography on silica gel provided the pure product, which was characterized by ^1H and ^{13}C NMR spectroscopy.

Acknowledgements

A.B. thanks the CSIR (New Delhi, India) for financial assistance.

---

[1] a) K. Y. Lee, D. J. Mooney, *Chem. Rev.* **2001**, *101*, 1869–1879; b) A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018; *Angew. Chem.* **2008**, *120*, 8122–8139; c) S. Roy, A. Banerjee, *Soft Matter* **2011**, *7*, 5300–5308; d) X. Li, Y. Kuang, J. Shi, Y. Gao, H. C. Lin, B. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 17513–17518; e) A. M. Kloxin, M. W. Tibbitt, K. S. Anseth, *Nat. Protoc.* **2010**, *5*, 1867–1887; f) A. Chakrabarty, U. Maitra, A. D. Das, *J. Mater. Chem.* **2012**, *22*, 18268–18274; g) S. Basak, J. Nanda, A. Banerjee, *J. Mater. Chem.* **2012**, *22*, 11658–11664; h) S. Bhattacharjee, S. Dutta, S. Bhattacharya, *Chem. Eur. J.* **2013**, *19*, 16672–16681; i) S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* **2014**, *114*, 1973–2129; j) A. Baral, S. Roy, A. Dehsorkhi, I. W. Hamley, S. Mohapatra, S. Ghosh, A. Banerjee, *Langmuir* **2014**, *30*, 929–936; k) B. Adhikari, A. Banerjee, *Chem. Eur. J.* **2010**, *16*, 13698–13705; l) B. Adhikari, G. Palui, A. Banerjee, *Soft Matter* **2009**, *5*, 3452–3460; m) G. Palui, A. Garai, J. Nanda, A. K. Nandi, A. Banerjee, *J. Phys. Chem. B* **2010**, *114*, 1249–1256; n) S. Banerjee, A. K. Sahoo, A. Chattopadhyay, S. S. Ghosh, *RSC Adv.* **2013**, *3*, 14123–14131; o) J. Nanda, A. Biswas, A. Banerjee, *Soft Matter* **2013**, *9*, 4198–4208; p) J. Bachl, A. Hohenleutner, B. B. Dhar, C. Cativiela, U. Maitra, B. König, D. D. Díaz, *J. Mater. Chem. A* **2013**, *1*, 4577–4588; q) S. Banerjee, R. K. Das, U. Maitra, *J. Mater. Chem.* **2009**, *19*, 6649–6687; r) W. Edwards, D. K. Smith, *J. Am. Chem. Soc.* **2014**, *136*, 1116–1124; s) G. Cheng, V. Castelletto, R. R. Jones, C. J. Connon, I. W. Hamley, *Soft Matter* **2011**, *7*, 1326–1333; t) G. Cheng, V. Castelletto, C. M. Moulton, G. E. Newby, I. W. Hamley, *Langmuir*

2010, *26*, 4990 – 4998; u) F. Rodríguez-Llansola, B. Escuder, J. F. Miravet, D. Hermida-Merino, I. W. Hamley, C. J. Cardin, W. Hayes, *Chem. Commun.* **2010**, *46*, 7960 – 7962; v) A. Chakrabarty, U. Maitra, *J. Phys. Chem. B* **2013**, *117*, 8039 – 8046; w) X. Du, J. Zhou, B. Xu, *Chem. Asian J.* **2014**, *9*, 1446 – 1472; x) D. Higashi, M. Yoshida, M. Yamanaka, *Chem. Asian J.* **2013**, *8*, 2584 – 2587.

[2] a) S. Roy, A. Baral, A. Banerjee, *Chem. Eur. J.* **2013**, *19*, 14950 – 14957; b) M. Moniruzzaman, A. Sahin, K. I. Winey, *Carbon* **2009**, *47*, 645 – 650; c) S. K. Samanta, A. Pal, S. Bhattacharya, C. N. R. Rao, *J. Mater. Chem.* **2010**, *20*, 6881 – 6890; d) X. Yang, L. Qiu, C. Cheng, Y. Wu, Z. F. Ma, D. Li, *Angew. Chem. Int. Ed.* **2011**, *50*, 7325 – 7328; *Angew. Chem.* **2011**, *123*, 7463 – 7466; e) M. Mba, A. I. Jiménez, A. Moretto, *Chem. Eur. J.* **2014**, *20*, 3888 – 3893.

[3] a) Z. Tang, S. Shen, J. Zhuang, X. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 4603 – 4607; *Angew. Chem.* **2010**, *122*, 4707 – 4711; b) A. Sahu, W. I. Choi, G. Tae, *Chem. Commun.* **2012**, *48*, 5820 – 5822; c) W. Li, J. Wang, J. Ren, X. Qu, *Adv. Mater.* **2013**, *25*, 6737 – 6743; d) H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, *ACS Appl. Mater. Interfaces* **2013**, *5*, 425 – 432; e) R. Liu, S. Liang, X. Z. Tang, D. Yan, X. Li, Z. Z. Yu, *J. Mater. Chem.* **2012**, *22*, 14160 – 14167; f) Z. Y. Sui, Y. Cui, J. H. Zhu, B. H. Han, *ACS Appl. Mater. Interfaces* **2013**, *5*, 9172 – 9179; g) J. H. Lee, J. Ahn, M. Masuda, J. Jaworski, J. H. Jung, *Langmuir* **2013**, *29*, 13535 – 13541; h) C. Cha, S. R. Shin, X. Gao, N. Annabi, M. R. Dokmeci, X. Tang, A. Khademhosseini, *Small* **2014**, *10*, 514 – 523; i) D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **2010**, *39*, 228 – 240; j) F. Meng, X. Zhang, B. Xu, S. Yue, H. Guo, Y. Luo, *J. Mater. Chem.* **2011**, *21*, 18537 – 18539; k) L. Chen, X. Wang, X. Zhang, H. Zhang, *J. Mater. Chem.* **2012**, *22*, 22090 – 22096; l) H. Huang, P. Chen, X. Zhang, Y. Lu, W. Zhan, *Small* **2013**, *9*, 1397 – 1404; m) L. Chen, B. Wei, X. Zhang, C. Li, *Small* **2013**, *9*, 2331 – 2340.

[4] Y. Xu, Q. Xu, Y. Sun, H. Bai, G. Shi, *ACS Nano* **2010**, *4*, 7358 – 7362.

[5] a) H. Huang, S. Lü, X. Zhang, Z. Shao, *Soft Matter* **2012**, *8*, 4609 – 4615; b) Z. Sui, X. Zhang, Y. Lei, Y. Luo, *Carbon* **2011**, *49*, 4314 – 4321; c) Z. Sui, Q. Meng, X. Zhang, R. Ma, B. Cao, *J. Mater. Chem.* **2012**, *22*, 8767 – 8771.

[6] a) X. Huang, X. Qi, F. Boey, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 666 – 686; b) C. Huang, H. Bai, C. Li, G. Shi, *Chem. Commun.* **2011**, *47*, 4962 – 4964; c) X. Huang, X. Zhou, S. Wu, Y. Wei, X. Qi, J. Zhang, F. Boey, H. Zhang, *Small* **2010**, *6*, 513 – 516; d) V. C. Tung, J. Kim, L. J. Cote, J. Huang, *J. Am. Chem. Soc.* **2011**, *133*, 9262 – 9265; e) P. V. Kamat, *J. Phys. Chem. Lett.* **2011**, *2*, 242 – 251; f) L. Huang, C. Li, W. Yuan, G. Shi, *Nanoscale* **2013**, *5*, 3780 – 3786; g) J. Nanda, A. Biswas, A. Banerjee, *Angew. Chem. Int. Ed.* **2013**, *52*, 5041 – 5045; *Angew. Chem.* **2013**, *125*, 5145 – 5149; h) S. Nardecchia, D. Carriazo, M. L. Ferrer, M. C. Gutiérrez, F. D. Monte, *Chem. Soc. Rev.* **2013**, *42*, 794 – 830; i) T. S. Sreeprasad, M. S. Maliyekkal, K. Deepti, K. Chaudhari, P. L. Xavier, T. Pradeep, *ACS Appl. Mater. Interfaces* **2011**, *3*, 2643 – 2654; j) A. Chandrasekar, T. Pradeep, *J. Phys. Chem. C* **2012**, *116*, 14057 – 14061; k) H. Chang, G. Wang, A. Yang, X. Tao, X. Liu, Y. Shen, Z. Zheng, *Adv. Funct. Mater.* **2010**, *20*, 2893 – 2902; l) H. Chang, Z. Sun, K. Y. F. Ho, X. Tao, F. Yan, W. M. Kwok, Z. Zheng, *Nanoscale* **2011**, *3*, 258 – 264; m) L. Niu, M. Li, X. Tao, Z. Xie, X. Zhou, A. P. A. Raju, R. J. Young, Z. Zheng, *Nanoscale* **2013**, *5*, 7202 – 7208.

[7] a) X. Li, J. Liu, A. F. Masters, V. K. Pareek, T. Maschmeyer, *APL Mater.* **2013**, *1*, 041101 – 041108; b) R. J. R. W. Peters, M. Marguet, S. Marais, M. W. Fraaije, J. C. M. van Hest, S. Lecommandoux, *Angew. Chem. Int. Ed.* **2014**, *53*, 146 – 150; *Angew. Chem.* **2014**, *126*, 150 – 154; c) M. C. M. van Oers, F. P. J. T. Rutjes, J. C. M. van Hest, *Curr. Opin. Biotechnol.* **2014**, *28*, 10 – 16.

[8] a) M. C. Hong, M. C. Choi, Y. W. Chang, Y. Lee, J. Kim, H. Rhee, *Adv. Synth. Catal.* **2012**, *354*, 1257 – 1263; b) E. Hariprasad, T. P. Radhakrishnan, *ACS Catal.* **2012**, *2*, 1179 – 1186; c) B. Yuan, Y. Pan, Y. Li, B, Yin, H. Jiang, *Angew. Chem. Int. Ed.* **2010**, *49*, 4054 – 4058; *Angew. Chem.* **2010**, *122*, 4148 – 4152; d) C. Deraedt, L. Salmon, J. Ruiz, D. Astruc, *Adv. Synth. Catal.* **2013**, *355*, 2992 – 3001; e) Ö. Metin, S. F. Ho, C. Alp, H. Can, M. N. Mankin, M. S. Gültekin, M. Chi, S. Sun, *Nano Res.* **2013**, *6*, 10 – 18; f) M. Shokouhimehr, J. E. Lee, S. I. Han, T. Hyeon, *Chem. Commun.* **2013**, *49*, 4779 – 4781; g) M. Shokouhimehr, J. Kim, S. W. Jun, K. Shin, Y. Jang, B. H. Kim, J. Kim, T. Hyeon, *Appl. Catal. A* **2014**, *476*, 133 – 139.

[9] P. P. Fang, A. Jutand, Z. Q. Tian, C. Amatore, *Angew. Chem. Int. Ed.* **2011**, *50*, 12184 – 12188; *Angew. Chem.* **2011**, *123*, 12392 – 12396.

[10] a) C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, *Angew. Chem. Int. Ed.* **2009**, *48*, 7752 – 7777; *Angew. Chem.* **2009**, *121*, 7890 – 7916; b) M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132 – 145; c) N. Shang, C. Feng, H. Zhang, S. Gao, R. Tang, C. Wang, Z. Wang, *Catal. Commun.* **2013**, *40*, 111 – 115.

[11] G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mülhaupt, *J. Am. Chem. Soc.* **2009**, *131*, 8262 – 8270.

[12] A. R. Siamaki, A. E. R. S. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.* **2011**, *279*, 1 – 11.

[13] M. Chem, Z. Zhang, L. Li, Y. Liu, W. Wang, J. Gao, *RSC Adv.* **2014**, *4*, 30914 – 30922.

[14] J. E. Camp, J. J. Dunsford, E. P. Cannons, W. J. Restorick, A. Gadzhieva, M. W. Fay, R. J. Smith, *ACS Sustainable Chem. Eng.* **2014**, *2*, 500 – 505.

[15] a) B. Adhikari, A. Biswas, A. Banerjee, *ACS Appl. Mater. Interfaces* **2012**, *4*, 5472 – 5482; b) J. Liu, F. He, T. M. Gunn, D. Zhao, C. B. Roberts, *Langmuir* **2009**, *25*, 7116 – 7128; c) A. Zhang, M. Liu, M. Liu, Y. Xiao, Z. Li, J. Chen, Y. Sun, J. Zhao, S. Fang, D. Jia, F. Li, *J. Mater. Chem. A* **2014**, *2*, 1369 – 1374.

[16] J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang, P. Sun, *Catal. Sci. Technol.* **2012**, *2*, 2332 – 2340.

[17] W. Hummers, Jr., R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339 – 1339.

Received: June 20, 2014