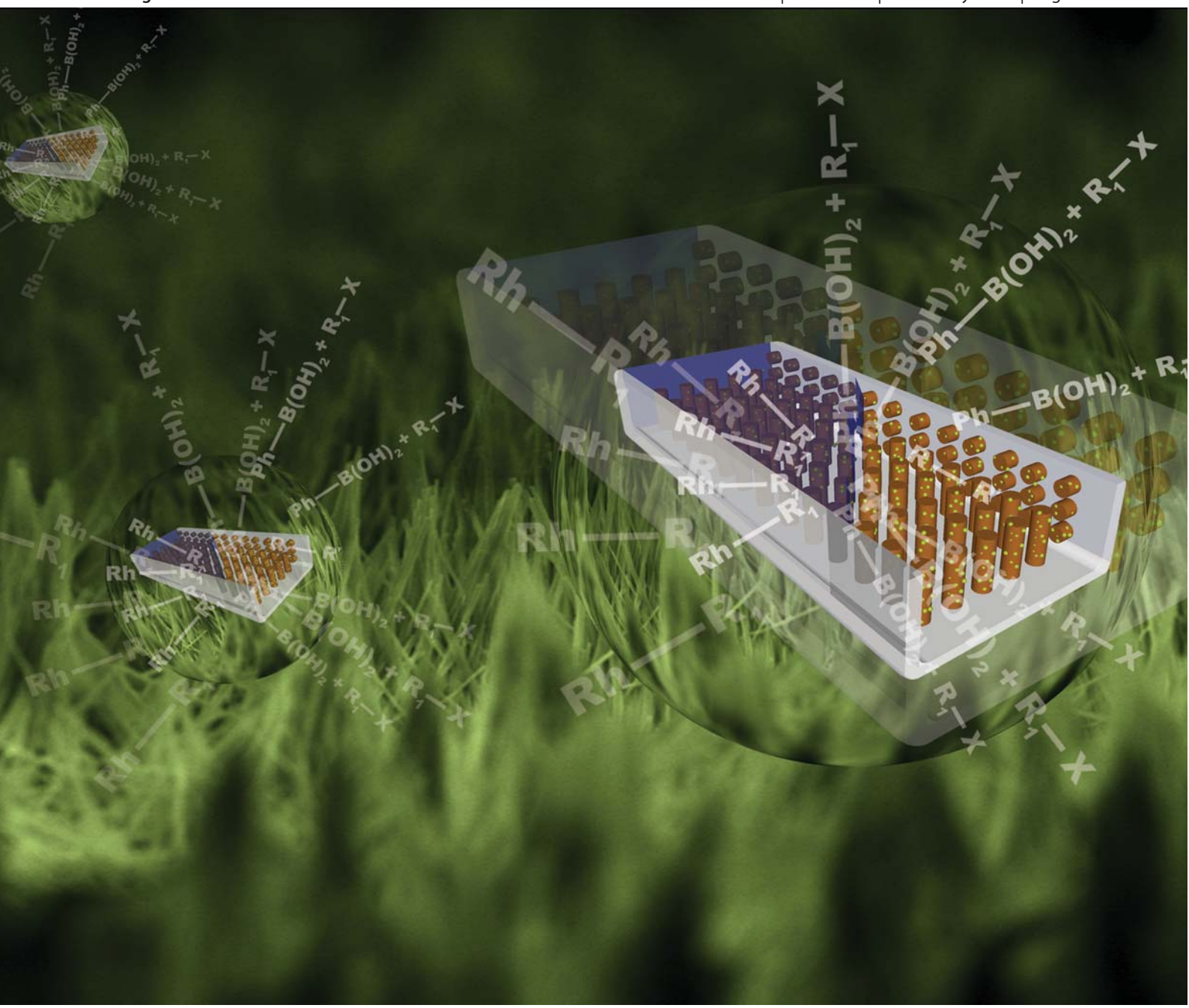
Lab on a Chip

Micro- & nano- fluidic research for chemistry, physics, biology, & bioengineering

www.rsc.org/loc

Volume 11 | Number 3 | 7 February 2011 | Pages 361–556



ISSN 1473-0197

RSC Publishing

COMMUNICATION

Park and Kim *et al.*

A microfluidic system incorporated with peptide/Pd nanowires for heterogeneous catalytic reactions

A microfluidic system incorporated with peptide/Pd nanowires for heterogeneous catalytic reactions†

Hyang-Im Ryoo,‡[a] Joon Seok Lee,‡[b] Chan Beum Park*[b] and Dong-Pyo Kim*[ac]

Received 27th September 2010, Accepted 11th November 2010
DOI: 10.1039/c0lc00448k

Highly stable diphenylalanine peptide nanowires were selectively self-assembled in the reaction zone of a microfluidic system and applied for microchemical hydrogenation and Suzuki coupling reactions through the hybridization of Pd nanoparticles.

Microfluidics has received much attention over the past decade in diverse fields including chemical synthesis, biological sensing, medical diagnostics, and environmental analysis.[1] For example, a microreactor that consists of a network of microscale flow channels can serve as a miniaturized system.[2] The miniaturized system reduces the time and cost of bulk chemical processes with improved safety and selectivity compared to those of conventional vessel reactors. In particular, an increased surface-to-volume ratio in a microfluidic reactor can dramatically enhance the mass transport of reactants and products with higher heat transfer coefficients.[3] Such improvements allow one to utilize the full potential of catalysts under isothermal operation. In this regard, the immobilization of catalyst within the microchannel is highly desirable; it can avoid the dispersion problem of catalysts in organic solvents as well as the filtration after chemical reaction in the microchannel. Attempts were made to create nanostructures that hold catalysts within the microchannel.[4,5] Up to date, the nanostructures such as carbon nanotubes (CNTs), Al anodic oxide nanotubes and Si nanowires were grown by gas phase techniques at extremely high temperatures over 500 °C or high-cost MEMS technology with time consuming skills. These approaches required the use of durable ceramic or metal substrates or extra steps for removing the template, and encountered poor adhesion between nanostructures and microfluidic surface.

Herein, we report on the microfluidic reactor system incorporated with vertically aligned peptide/Pd hybrid nanowires (NWs) having excellent stability applicable to soft polymeric substrates under mild conditions. Microchannels with a dimension of 500 μm (width) × 50 μm (height) × 3 cm (length) were fabricated from polyvinylsilazane through imprint lithography technique,[6] followed by *in situ* growth of peptide/Pd NW within microchannels (Fig. 1 and Scheme S1†). Firstly, a polymer microchannel with high optical transparency and strong organic solvent resistance was fabricated from polyvinylsilazane, which demonstrated reliable microchemical characteristics and stabilities for running heterogeneous catalytic synthesis reactions.[6] In the reaction zone of a microchannel, the vertically well-aligned diphenylalanine (Phe–Phe, FF) peptide NW was grown on the polymer surface at comparable conditions in a site-selective manner by covering the unwanted modified surface with aluminium tape.

The uncovered microchannel surface was coated with a mussel-inspired polydopamine (PDA) as an adhesion promoter by simply immersing in an alkaline dopamine solution.[7] Subsequently, an amorphous FF peptide film prepared by drying the FF solution under anhydrous conditions was treated with aniline vapor at 100 °C, then the FF peptide NWs were vertically grown in a self-assembled manner.[8] The morphology of FF peptide NWs could be controlled by adjusting aging time, temperature, and film thickness (data not shown). In this work, the FF peptide NWs typically grew to have 10 μm height and 300 nm diameter, and further annealed at 100 °C for 12 h to enhance the dimensional stability. Fig. 2 shows SEM images of FF peptide NWs formed in high density on the bottom and sidewalls of the polyvinylsilazane-derived microchannel.

Note that PDA exhibited a universal adhesive property owing to the presence of catechol moieties for facile covalent and coordination bonding to a variety of substrates.[7,9] Therefore, the selected bare surface of the polyvinylsilazane microchannel was initially coated with the PDA layer to strengthen the interfacial adhesion of the grown NWs to the underlying surface. Hence, the FF peptide NWs on the PDA layer were firmly adhered to the surface even under vigorous stirring or ultrasonication, while FF peptide NWs on the bare surface were easily detached at the same agitation (Fig. S1 of the ESI†). Prior to Pd nanoparticle (NP) deposition step, the FF peptide NWs were immersed in an aqueous dopamine solution for 16 h to coat *ca.* 200–400 nm thick PDA ad-layer. In addition, the hydrophobic peptide NW film exhibited a high static water contact angle ($\theta = 124°$), as reported previously.[10] But it became very hydrophilic ($\theta \leq 10°$) after the PDA coating due to polar catechol moieties

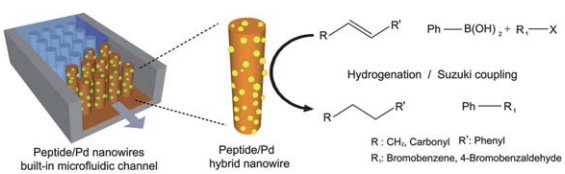


Fig. 1 Scheme for peptide/Pd nanowires built-in microfluidic system for heterogeneous catalytic hydrogenation and Suzuki coupling reactions.

[a]*School of Applied Chemistry and Biological Engineering, Chungnam National University, 220 Kung-dong, Yusung-gu, Daejeon, 305-764, Korea. E-mail: dpkim@cnu.ac.kr; Fax: +82-42-823-6665; Tel: +82-42-821-6695*
[b]*Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 335 Science Road, Daejeon, 305-701, Korea. E-mail: parkcb@kaist.ac.kr; Fax: +82-42-350-3310; Tel: +82-42-350-3340*
[c]*Graduate School of Analytical Science and Technology, Chungnam National University, 220 Kung-dong, Yusung-gu, Daejeon, 305-764, Korea. E-mail: dpkim@cnu.ac.kr; Fax: +82-42-823-6665; Tel: +82-42-821-6695*

† Electronic supplementary information (ESI) available: Materials, fabrication of microfluidic system incorporated with peptide/Pd hybrid NWs and explanation on microchemical heterogeneous catalytic reactions. See DOI: 10.1039/c0lc00448k

‡ These authors contributed equally to this work.

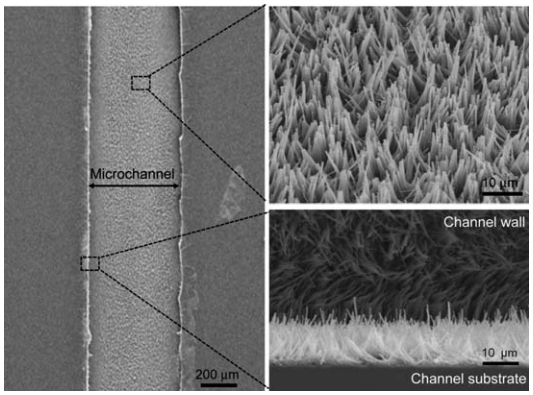


Fig. 2 SEM images of vertically aligned FF peptide NWs within the microchannel. The microchannel (500 μm width × 50 μm height × 3 cm length) was fabricated using polyvinylsilazane through soft-lithographic process, and the peptide/Pd NWs were subsequently grown on both bottom and sidewalls of the channels by self-assembly.

abundant in PDA.[7] Note that the hydrophilic modification of the FF peptide NW film with PDA facilitates efficient access of aqueous $PdCl_2$ solution to the NW surface. Finally, the FF peptide/Pd hybrid NWs were prepared by incubating the PDA-coated FF peptide NWs in Pd precursor solution that grew Pd NPs along the FF peptide NWs (Fig. 3c and d). At this step, the PDA coating not only acted as an adhesive that was strongly binding to both organic and inorganic surfaces but also as a reducing agent for the growth of Pd metal NPs with the size range 4–20 nm that was presumably attributed to the reductive capacity of the hydroxyl groups in PDA.[7] For comparison with the FF peptide NWs built-in microchannels, we immobilized Pd nanoparticles on the surface of PDA-coated, bare microchannels without FF peptide NWs (Fig. 3a and b). An aligned array of FF peptide NWs (of 300 nm in diameter and 10 μm long) would give

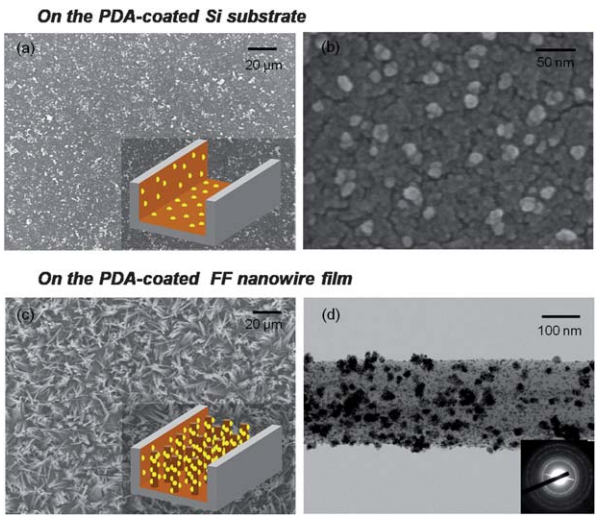


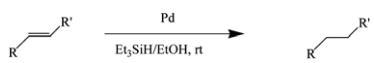
Fig. 3 (a and b) SEM images of Pd nanoparticles on PDA-coated Si substrate with different magnifications, (c) SEM and (d) TEM images of Pd nanoparticles on the PDA-coated FF peptide nanowire film. The loaded amount of Pd nanoparticles on the FF peptide NWs is much larger than that of the flat substrate due to highly increased surface area. The SAED pattern on (d) shows polycrystalline diffraction rings corresponding to fcc Pd.

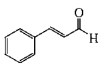
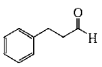
a surface area $\sim 10^2$ times larger than that of a flat surface, highly increasing the amount of immobilized Pd nanoparticles in the microchannel.

Previously reported methods for creating the nanostructures within microfluidic channels required critical conditions that limited the selection of device materials; for example, the metal catalyst-supported carbon nanotubes in the reaction zone were grown on metal-deposited alumina or stainless steel at over 500 °C causing high manufacturing costs.[4,5] In contrast, our peptide self-assembly-based approach using mussel-inspired PDA is highly versatile and simple with reliable adhesion to the substrates. Moreover, this approach is applicable to soft polymeric substrates because of its mild fabrication conditions.

We further investigated the heterogeneous catalytic performance of FF peptide/Pd hybrid NWs built-in microreactors by carrying out hydrogenation and Suzuki coupling reactions in comparison with plain microreactors without NWs. The results of hydrogenation conversions of 1-phenyl-1-cyclohexene (as a simple olefin) and cinnamaldehyde (as a bi-functioned olefin with additional C=O), respectively, are presented in Table 1. In general, the peptide NWs built-in microreactor exhibited much higher yields of conversion at both hydrogenation reactions. The conversion yields of two unsaturated olefins were dependent on the flow rate of reactants. In particular, when the flow rate became higher (*i.e.*, shorter reaction time), the catalytic performance in the FF peptide NWs built-in microreactor was dramatically enhanced by the increased surface area and catalyst loading which promote the efficient contact of the reactant with the catalyst.[4] For example, at the flow rate of 5 μl min^{-1} of 1-phenyl-1-cyclohexene, the FF peptide NWs built-in microreactor resulted in a 61.7% yield (Table 1). In contrast, no conversions were observed in the plain microreactor at the same flow rate. A similar result was observed in the case of alternative hydrogenation of unsaturated aldehyde (*i.e.*, cinnamaldehyde) to produce 3-phenylpropionaldehyde and additional by-products (*i.e.*, cinnamyl alcohol and 3-phenyl-1-propan-1-ol).[11] Similarly, the incorporated Pd catalyst on NWs greatly promoted the yields in comparison to the plain microreactor. For instance, total conversion and selective yield of 3-phenylpropionaldehyde (as a main product in the NW built-in

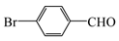
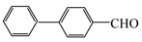
Table 1 Heterogeneous catalytic performance of FF peptide/Pd hybrid NWs built-in microfluidic reactor for hydrogenation reactions at different flow rates in comparison with the plain reactor without NWs



Substrate	Product	Flow rate/ μl min^{-1} (residence time/s)	Yields (%) Plain	Nanowire
		0.5 (90)	23.4	97.0
		1.0 (45)	5.8	95.1
		3.0 (15)	0.5	81.4
		5.0 (9)	0.0	61.7
		0.5 (90)	32.5(46.8)[a]	76.0(100)
		1.0 (45)	25.9(42.7)	69.0(94.5)
		3.0 (15)	18.2(29.8)	50.7(91.5)
		5.0 (9)	11.4(17.5)	30.7(61.4)

[a] Conversion yield including 3-phenylpropionaldehyde product and additional by-products (*i.e.*, cinnamyl alcohol and 3-phenyl-1-propan-1-ol). All reactions were carried out at room temperature (25 °C).

Table 2 Comparative catalytic performance of Suzuki coupling reactions in the FF peptide/Pd hybrid NWs built-in microfluidic reactor and plain reactor with different solvents at room temperature

Substrate	Product	Solvent	Flow rate/ μl min^{-1} (residence time/s)	Yields (%) Plain	NWs
		EtOH/ H_2O	0.5 (90)	42.9	97.2
			1.0 (45)	32.5	89.2
			3.0 (15)	17.2	84.6
			5.0 (9)	13.7	76.6
		THF/H_2O	0.5 (90)	39.4	94.3
		EtOH/ H_2O	0.5 (90)	33.6	93.1
			1.0 (45)	21.5	81.3
			3.0 (15)	11.2	63.0
			5.0 (9)	0.5	55.0
		THF/H_2O	0.5 (90)	31.9	98.0

microchannel at 5 μl min^{-1}) were 61.4% and 30.7%, respectively, which show much better performance than in the plain reactor (*i.e.*, 17.5% and 11.4%, respectively).

This tendency was consistently observed in Suzuki coupling reactions as shown in Table 2. The coupling reaction yields of 4-bromobenzene at 5 μl min^{-1} showed 76.6% in the NWs built-in microreactor but only 13.7% in the plain reactor, and the reaction of 4-bromobenzaldehyde exhibited 55.0% and 0.5%, respectively, under EtOH/H_2O reaction media. In addition, when we tested the resistance of the microreactor system against the strong swelling solvent containing mixtures such as THF/H_2O, neither leaking of reaction media nor deteriorated performance in conversion yields was observed for more than 24 h at a steady flow rate of 5 μl min^{-1}. Alternatively, it was clearly observed in both hydrogenation and Suzuki coupling reactions that the ~100 times increased surface area of the NW built-in reactor nearly completed all reactions with 93–100% of product yields under slightly extended reaction time (90 s) at 0.5 μl min^{-1}, in contrast to 23–46% yields in the plain reactor at the same conditions. In addition, the ICP analysis of the effluent collected during Suzuki reaction showed no detection of Pd species. It indicates that the reliable physical and chemical interaction between the Pd nanoparticles and the PDA on the nanowire strongly tethered the Pd particles without leaching.[7,12]

In summary, we demonstrated the feasibility of vertically aligned FF peptide/Pd NWs for microfluidic systems fabricated under mild conditions applicable to soft polymer device materials. The FF peptide/Pd NWs within the polymer microchannel highly improved the catalytic performance of the microreactor due to the increased surface-to-volume ratio and catalyst loading. The strategy presented here provides a new and facile route for fabricating the nanostructure-embedded microchemical system that may offer new applications in the areas of heterogeneous catalytic reactions as well as biological sensing.

This study was supported by the National Research Foundation *via* National Research Laboratory (NRL) (R0A-2008-000-20041-0), Converging Research Center (2009-0082276), Engineering Research Center (2008-0062205) programs, and Creative Research Initiatives (CRI) project [20100000722] administered by the Korean Ministry of Education, Science, and Technology.

References

1 D. R. Reyes, D. Iossifidis, P.-A. Auroux and A. Manz, *Anal. Chem.*, 2002, **74**, 2623; E. Verpoorte, *Electrophoresis*, 2002, **23**, 677.
2 K. Jahnisch, V. Hessel, H. Lowe and M. Baerns, *Angew. Chem., Int. Ed.*, 2004, **43**, 406; T. Kawaguchi, H. Miyata, K. Ataka, K. Mae and J. Yoshida, *Angew. Chem., Int. Ed.*, 2005, **44**, 2413; H. R. Sahoo, J. G. Kralj and K. F. Jensen, *Angew. Chem., Int. Ed.*, 2007, **46**, 5704.
3 A. Popp and J. J. Schneider, *Angew. Chem., Int. Ed.*, 2008, **47**, 8958; G. Kolb and V. Hessel, *Chem. Eng. J.*, 2004, **98**, 1.
4 N. Ishigami, H. Ago, Y. Motoyama, M. Takasaki, M. Shinagawa, K. Takahashi, T. Ikuta and M. Tsuji, *Chem. Commun.*, 2007, 1626; A. Agiral, L. Lefferts and J. G. E. Gardeniers, *Catal. Today*, 2010, **150**, 128; A. I. Hochbaum, R. Fan, R. He and P. Yang, *Nano Lett.*, 2005, **5**, 457.
5 L. Martinex-Latprre, S. Armenise and E. Garcia-Bordeje, *Carbon*, 2010, **48**, 2047.
6 T.-H. Yoon, S.-H. Park, K.-I. Min, X. Zhang, S. J. Haswell and D.-P. Kim, *Lab Chip*, 2008, **8**, 1454; A. Asthana, Y. Asthana, I.-K. Sung and D.-P. Kim, *Lab Chip*, 2006, **6**, 1200.
7 H. Lee, S. M. Dellatore, W. M. Miller and P. B. Messersmith, *Science*, 2007, **318**, 426.
8 J. Ryu and C. B. Park, *Adv. Mater.*, 2008, **20**, 3754.
9 H. Lee, N. F. Scherer and P. B. Messersmith, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 12999; J. H. Waite and X. X. Qin, *Biochemistry*, 2001, **40**, 2887.
10 J. S. Lee, J. Ryu and C. B. Park, *Soft Matter*, 2009, **5**, 2717.
11 Y. Hu, H. Yang, Y. Zhang, Z. Hou, X. Wang, Y. qiao, H. Li, B. Feng and Q. Huang, *Catal. Commun.*, 2009, **10**, 190.
12 H. Hu, B. Yu, Q. Ye, Y. Gu and F. Zhou, *Carbon*, 2010, **48**, 2347.

