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Carbonaceous microspheres prepared by hydrothermal carbonization of glucose for direct use in catalytic dehydration of fructose†

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A carbonaceous microsphere material was prepared by hydrothermal carbonization (HTC) of glucose, and was used directly for the catalytic dehydration of fructose into 5-HMF without any *in situ* functionalization or post-modification. The prepared material was found to be a good solid acid catalyst for the production of 5-HMF from fructose in ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), where a 5-HMF yield of 88.1% was obtained at 100 °C for 90 min reaction time, which is due to the contribution of the –COOH groups in the catalyst. It is the first time that a HTC material is reported in the efficient catalytic conversion of biomass without any *in situ* functionalization or post-modification. In addition, the catalytic system was shown to be applicable to higher fructose concentrations up to ca. 10 wt%. The HTC material catalyst exhibited constant activity for five successive reuses.

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1. Introduction

With the gradual depletion of traditional fossil resources, the search for sustainable and alternative energy sources is of great importance for a sustainable society.¹ As a renewable resource, abundant biomass resources can be a promising candidate to supplement our fuel supply and chemical demands, provided that efficient transformation pathways can be developed.² Among the possible biomass-derived value-added chemicals, 5-hydroxymethylfurfural (5-HMF) is one of the versatile intermediate products that can be used for the production of a wide variety of polymers, pharmaceuticals and biofuels.^{2,3}

In the past few years, considerable efforts have been devoted to the conversion of various biomass derivatives to 5-HMF, in which the most efficient method is catalyzed dehydration of fructose in the presence of an acid catalyst. Thus far, many types of acid catalysts have been used in the reaction, such as mineral acids,^{4,5} organic acid, H-form zeolites,^{6–8} transition metal ions,^{9–12} strong acid cation exchange resins,^{13–15} acidic ionic liquids,^{16,17} and sulfonated carbonaceous materials.^{18,19} Homogenous acids are inexpensive and effective, but they have serious drawbacks in terms of products separation, solvent recycling, and equipment corrosion. H-form zeolites and metal

phosphates can be separated and recycled easily, but they suffer from medium yields.²⁰ Strong acidic cation exchange resins are efficient for the conversion of fructose to 5-HMF,^{13,21} however, their application are restricted due to their thermal stability.²²

Recently, carbonaceous material solid acids have attracted more and more attentions in catalytic biomass conversion,^{23–26} since they not only exhibit excellent catalytic activity and recyclability, but also can be prepared from biomass itself (sugars, starch, cellulose or crude biomass). Thus far, almost all of the carbonaceous solid acid catalysts catalyze the dehydration of fructose to 5-HMF with –SO₃H as functional groups. For example, Guo *et al.*¹⁸ prepared a lignin-derived carbonaceous catalyst through the pyrolysis of lignin at 400 °C followed by sulfonation with H₂SO₄, and showed that the catalyst exhibited high activity for fructose dehydration into 5-HMF that a 5-HMF yield of 84% was obtained in dimethyl sulfoxide and 1-butyl-3-methyl-imidazolium chloride mixtures at 110 °C for 10 min reaction time. Kang *et al.*²⁷ synthesized biomass hydrochar derived sulfonated catalysts by hydrothermal carbonization of lignin, cellulose, wood meal and xylose, followed by sulfonation with H₂SO₄, and these carbonaceous material catalysts were used for the production of 5-HMF from inulin with yields of 47–65% in ionic liquid at 100 °C in 60 min. These sulfonated carbonaceous materials are commonly prepared in two steps. Firstly, a solid carbon material was prepared from the sugars, cellulose or crude biomass by pyrolysis or hydrothermal carbonization. Then, the obtained carbon material is treated with excess amount of concentrated and/or fuming sulfuric acid to introduce –SO₃H groups. This preparation method for the biomass-derived sulfonated carbon materials suffers from some problems such as toxic gases release and harsh operation conditions, and does not meet the principles of green

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chemistry.^{28,29} Thus, more environmentally benign carbonaceous solid acid catalysts are need for the sustainable biomass utilization.

Hydrothermal carbonization (HTC) of biomass is a promising method to synthesize carbonaceous materials that have potential applications in the fields such as material, adsorption and energy storage.³⁰ To enhance their performance in catalytic, adsorption or energetic applications, *in situ* functionalization or post-modification is generally required to introduce functional groups or expand their porosity and surface area.^{31,32} In this work, a carbonaceous microspheres material bearing -COOH and phenolic -OH groups was prepared by hydrothermal carbonization of glucose. The as-prepared carbonaceous microspheres was used directly without any *in situ* functionalization or post-modification and were shown to be efficient for the catalytic dehydration of fructose to 5-HMF. To our knowledge, it is the first time that the carbon material prepared from the carbonization of carbohydrates or lignocellulosic biomass is reported in the efficient catalytic conversion of biomass without any *in situ* functionalization or post-modification, indicating that the conventional two-step synthesis procedures of hydrothermal carbonization and sulfonation commonly reported in the literature to be unnecessary.

2. Experimental section

2.1 Materials

Fructose and glucose (99%) were obtained from Guangfu fine chemicals research institute (Tianjin) and were used as received. 5-Hydroxymethylfurfural (98%) was purchased from the Acros Organics Company (Geel). Ionic liquid 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl], 99%) was received from Henan Lihua pharmaceutical Co., Ltd. (Xinxiang).

2.2 Preparation of carbonaceous microspheres material

The carbonaceous microspheres material was prepared by incomplete carbonization of glucose, as depicted below. Typically, 25 g of glucose was dissolved in 50 ml of water, and the obtained glucose aqueous solution was loaded into a Teflon-lined, stainless steel autoclave (100 ml volume). Then, it was heated to 180 °C for 10 h under self-generated pressure in the closed system. Afterwards, the autoclave was cooled down to

room temperature. The resulting crude product was recovered by centrifugation and washed repeatedly with ethanol and water for ten times, and oven-dried at 80 °C for 12 h. A carbon material yield of 28.3% was achieved from 25 g of glucose.

2.3 Typical experimental procedure for 5-HMF production from fructose

In a typical reaction, 0.05 g of fructose was pre-dissolved in 1 g of [BMIM][Cl] in a 10 ml quartz tube reactor with a sealing plug, then 0.05 g catalyst was added. The reaction mixture was heated to 100 °C and maintained for a given reaction time in an oil bath. After the desired reaction time elapsed, the reactor was cooled to room temperature with cold water bath within 1 min and 0.5 g of water was added to the mixture to promote the transport of 5-HMF from the ionic liquid phase to the ethyl acetate phase in the following extraction step. The product 5-HMF was effectively extracted from the reaction mixture with ethyl acetate (10 ml × 6), since [BMIM][Cl] and fructose were insoluble in ethyl acetate and 5-HMF was the sole product in the ethyl acetate phase, as presented by Hu *et al.*³³ and Yong *et al.*³⁴ The product 5-HMF was measured with a Cary-50 Model spectrophotometer (Varian Inc.) at 284 nm using standard curve method.

2.4 Catalyst characterization

The catalysts were characterized by SEM, elemental analysis, FT-IR and Boehm Titration. The morphology/size of the samples was visualized by SEM using a JEOL JSM-6700 instrument. Elemental analysis was carried out using Elementar Vario EL cube (Germany). FT-IR spectrum was recorded over the range from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ with a MAGNA-560 apparatus with DTGS detector (NICOLET), after the catalyst was thoroughly mixed with KBr powder and compressed into pellet. The acidity distributions of the carbonaceous material was measured by the Boehm Titration method.³⁵

3. Results and discussion

3.1 Characterization of the carbonaceous material

Fig. 1 shows SEM images of the carbonaceous material obtained by hydrothermal carbonization of glucose at 180 °C for 10 h. It

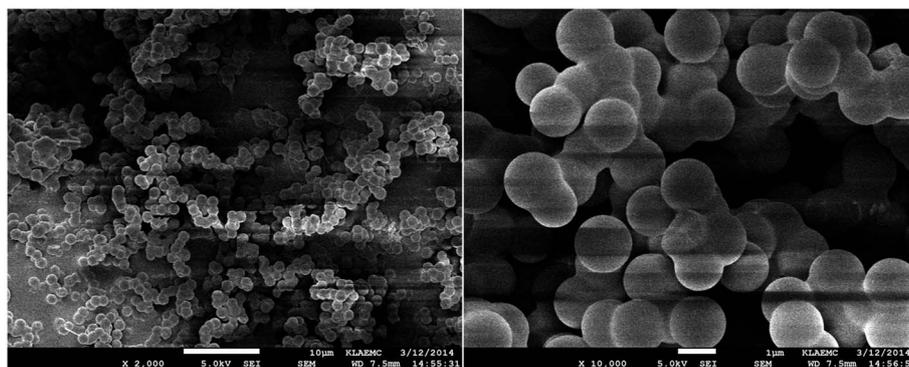


Fig. 1 SEM images of carbonaceous microspheres material prepared by hydrothermal carbonization of glucose at 180 °C for 10 h.

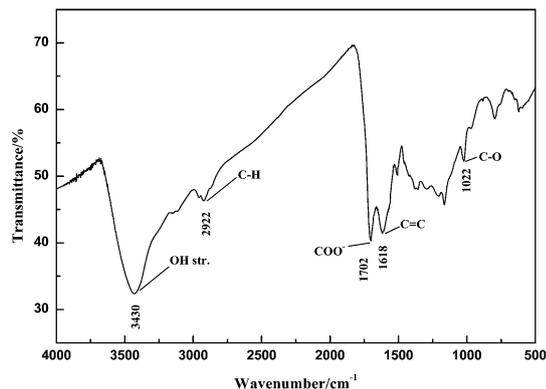


Fig. 2 FT-IR spectrum of the obtained carbonaceous material from hydrothermal carbonization of glucose at 180 °C for 10 h.

can be seen that the obtained carbonaceous material consisted mainly of aggregates of interconnected uniform carbon spheres with diameter of about 1.5 μm , which closely corresponds with the results reported by Sun *et al.*³⁶

FT-IR spectrum of the prepared carbon microspheres material is shown in Fig. 2. The band at *ca.* 3430 cm^{-1} can be assigned to O–H stretching vibration of adsorbed water molecules and surface hydroxyl groups including phenolic groups.^{36,37} The band at 2922 cm^{-1} corresponds to the stretching vibrations of aliphatic C–H and is evidence of aliphatic structures.³⁸ The absorption bands at *ca.* 1702 and 1618 cm^{-1} , are attributed to COO^- and $\text{C}=\text{C}$ stretching vibrations, respectively, demonstrating the existence of a large number of carboxylic groups in the prepared carbon material.^{38,39}

The elemental compositions (C, H and O) of the prepared carbon microspheres material are listed in Table 1, indicating it has a composition of $\text{CH}_{0.92}\text{O}_{0.34}$. The acidity distributions of the material were analyzed by the Boehm method and are also listed in Table 1, indicating a carboxylic groups concentration of 2.17 mmol g^{-1} , which verify the strong adsorption band at 1702 cm^{-1} for $-\text{COOH}$ in the FT-IR spectrum in Fig. 2.

3.2 Catalytic dehydration of fructose into 5-HMF by the prepared carbonaceous microspheres material

The prepared carbon microspheres material was tried to catalyze the dehydration of fructose into 5-HMF in an ionic liquid

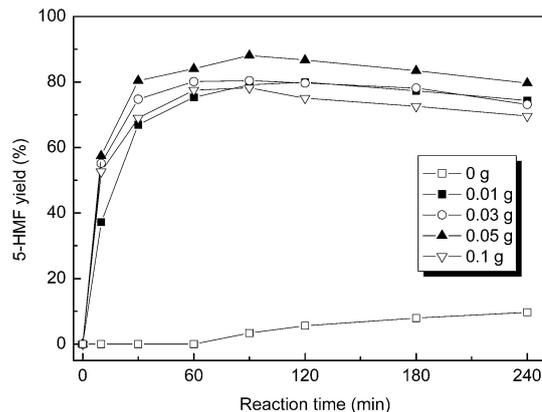


Fig. 3 Catalytic dehydration of fructose into 5-HMF by the prepared carbon microspheres material in [BMIM][Cl] (reaction conditions: 0.01 g of fructose, 1 g of [BMIM][Cl], 100 °C).

1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]). The catalytic conversion of fructose into 5-HMF by different amount of catalyst was examined (Fig. 3). In the absence of the carbon material, only about 10% of 5-HMF yield was obtained at 100 °C for 240 min. When 0.01 g of carbon material was added, the 5-HMF yield was remarkably increased to 79.9% for 120 min reaction time, demonstrating that the prepared carbon microsphere material is a highly active catalyst for the dehydration of fructose into 5-HMF. Although the employed carbon material catalyst was prepared from the hydrothermal carbonization of glucose without any *in situ* or post functionalization, it shows to be efficient for the 5-HMF production from fructose, which should be ascribed to the $-\text{COOH}$ groups in the catalyst. A representative carboxylic acid, acetic acid was used for the catalytic dehydration of fructose to 5-HMF in the system (Fig. S1†), illustrating the good catalytic activity of $-\text{COOH}$ groups for the reaction. After the added catalyst dosage was increased to 0.03 g and 0.05 g, 5-HMF yield was improved to 80.4% and 88.1%, respectively, in 90 min reaction time. However, when the catalyst dosage was further increased to 0.1 g, the 5-HMF yield decreased to 78.2% in 90 min reaction time, which may be resulted from the excess acid-active sites that facilitate not only the dehydration of fructose to 5-HMF but also the degradation of the formed 5-HMF into other products such as humins.^{40,41} In addition, the prepared carbon material

Table 1 Elemental composition and acidity distributions of the prepared carbonaceous material by hydrothermal carbonization of glucose from the Boehm titration

Elemental composition			Acidity distributions			
C (%)	H (%)	O (%)	Total acid sites ^a (mmol g^{-1})	Carboxylic groups ^b (mmol g^{-1})	Phenolic groups ^c (mmol g^{-1})	Lactonic groups ^d (mmol g^{-1})
65.3	5.04	29.6	3.50	2.17	1.33	0.33

^a Obtained by titration with NaOH. ^b Obtained by subtracting concentration of sulfonic groups from titration results with NaHCO_3 . ^c Obtained by subtracting titration results using Na_2CO_3 from calculated values of NaOH. ^d Obtained by subtracting titration results using NaHCO_3 from calculated values of Na_2CO_3 .

was also tried for the reaction in water and dimethyl sulfoxide (DMSO) at 150 °C in 90 reaction time, and 5-HMF yield of 10.7% and 83.2% could be obtained, respectively, indicating that the catalyst is also efficient in some other solvents.

In our previous work, sulfonated carbon materials were prepared by hydrothermal carbonization of glucose or cellulose followed by sulfonation with H₂SO₄.¹⁹ These catalysts were used for the dehydration of fructose into 5-HMF, and a maximum 5-HMF yield of 83% could be obtained at 80 °C in 10 min reaction time in [BMIM][Cl].¹⁹ Thus, compared with the carbon material without any *in situ* or post modification prepared in this work, the sulfonated carbon material exhibited higher efficiency in terms of reaction temperature and reaction time, but it gave a lower maximum 5-HMF yield, which should be ascribed to the stronger acidity of the -SO₃H groups that not only favor the dehydration of fructose into 5-HMF, but also promote the decomposition of the formed 5-HMF.¹⁹

3.3 Effect of reaction temperature on the conversion of fructose into 5-HMF

The conversion of fructose catalyzed by the prepared carbon microspheres material was investigated at different reaction temperatures (Fig. 4). When the reaction was conducted at 80 °C, a 5-HMF yield of 53.5% was obtained for 30 min reaction time, and the 5-HMF yield increased to 76.2% by prolonging the reaction time to 90 min. The 5-HMF yield increased from 77.3% to 88.1% when the temperature was elevated from 90 °C to 100 °C for 90 min reaction time. With further increase of the reaction temperature to 110 °C, a maximum 5-HMF yield of 83.4% was achieved within 60 min, and then the 5-HMF yield began to decrease rapidly with increasing reaction time.

Therefore, it seems that higher reaction temperatures not only favored the conversion of fructose into 5-HMF, but also promoted the formation of humins that is inevitably generated in acid-catalyzed processing of carbohydrates by self-polymerization between 5-HMF molecules or cross-polymerization between 5-HMF and fructose.^{22,42,43} At present,

the humins have not been able to be quantified,^{22,42} but their generation and existence could be observed from the brown color in the reaction mixture, and the brown color remained even after yellow 5-HMF was extracted from the mixture with ethyl acetate.

3.4 Effect of initial fructose concentration on the conversion of fructose into 5-HMF catalyzed by the prepared carbon microspheres material

In acid catalytic dehydration of carbohydrates, initial loading substrate concentration normally has a remarkable effect on 5-HMF yield, since higher substrate concentration leads to an increase in the molecular collisions opportunities between the formed 5-HMF molecules or the 5-HMF and substrate molecules, and hence promotes the generation of undesirable humins. The influence of initial fructose concentration on the conversion of fructose into 5-HMF catalyzed by the prepared carbon material in [BMIM][Cl] was studied and the results are illustrated in Fig. 5. It can be seen from Fig. 5 that the 5-HMF yields decreased with increasing initial fructose concentration at the initial stage of the reaction. For example, when 0.01, 0.03, 0.05 and 0.1 g of fructose was used, respectively, the 5-HMF yield was 57, 53, 41 and 36% at 100 °C for 10 min reaction time, respectively. However, the maximum 5-HMF yields in all cases were above 75%, indicating that the prepared carbon microspheres material by the hydrothermal carbonization of glucose is applicable to higher feedstock concentrations up to *ca.* 10 wt%.

3.5 Recycling of the prepared carbon microspheres material

To examine the activity and stability of the prepared carbon material by hydrothermal carbonization of glucose for the conversion of fructose into 5-HMF in ionic liquid system, the recycle of the carbon material was studied for five times to study its stability in each run (Fig. 6). Experiments were conducted in [BMIM][Cl] at 100 °C for 90 min reaction time. After reaction, the product 5-HMF was separated from the reaction mixture by

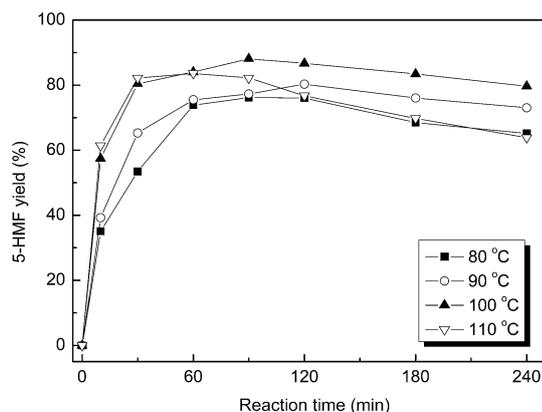


Fig. 4 Effect of reaction temperature on the conversion of fructose into 5-HMF catalyzed by the prepared carbon microspheres material in [BMIM][Cl] (reaction conditions: 0.01 g of fructose, 1 g of [BMIM][Cl], 0.05 g catalyst).

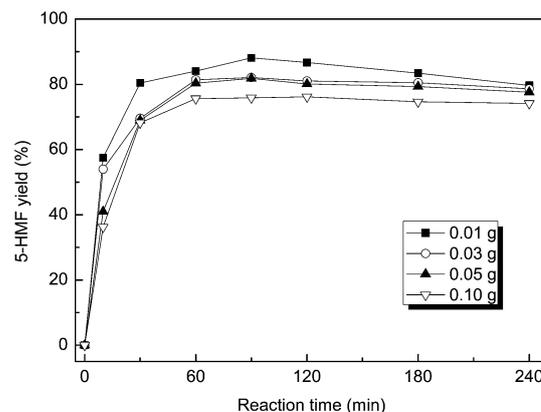


Fig. 5 Effect of fructose loading on the conversion of fructose into 5-HMF catalyzed by the prepared carbon microspheres material in [BMIM][Cl] (reaction conditions: 100 °C, 1 g of [BMIM][Cl], 0.05 g catalyst).

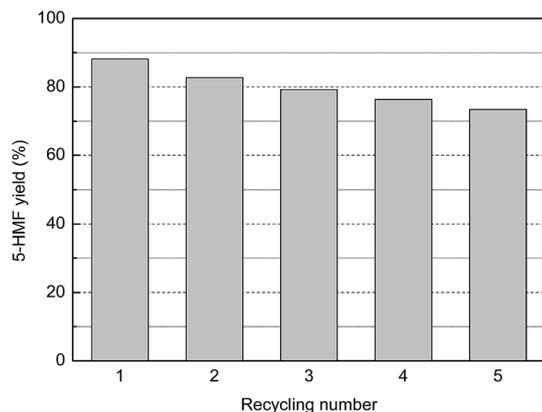


Fig. 6 Recycle of the carbon material catalyst (0.01 g of fructose, 1 g of [BMIM][Cl], 0.05 g of catalyst, 100 °C, 90 min).

extracting 6 times with 10 ml of ethyl acetate after 0.5 g of water was added, similar to that reported in the literature.^{33,34} The amount of 5-HMF in ethyl acetate represents the total amount of 5-HMF formed during the reaction. After the extraction, the reaction mixture was heated at 80 °C for 12 h in a vacuum oven to remove water and residual ethyl acetate, and then it was used directly in the next run at identical conditions after adding an equal amount of fresh fructose. It can be seen from Fig. 6 that 88.3% of 5-HMF yield was achieved for the first time use of the catalyst, and gradually decreased to 73.5% for 5-HMF yield after five successive recycles. Thus, the recycled catalyst and solvent showed a stable activity for the conversion of fructose into 5-HMF under repetitive uses, although the 5-HMF yield had a decreasing trend with the consecutive catalytic runs, which should be ascribed to the generated humins that were not removed from the system and some of them probably deposited on the catalyst.

4. Conclusions

In the present work, a carbonaceous microspheres material bearing –COOH and phenolic –OH groups was prepared by the hydrothermal carbonization of glucose, and was employed directly without any post-modification or *in situ* functionalization for the catalytic dehydration of fructose into 5-HMF in ionic liquid. The prepared carbon material was shown to be efficient for the 5-HMF formation from fructose, and a high 5-HMF yield of 88.1% could be obtained at 100 °C for 90 min reaction time, which should be ascribed to the –COOH groups in the catalyst. The catalytic system was shown to be applicable to higher fructose concentrations up to *ca.* 10 wt% with a considerable 5-HMF yield above 75.8%. The carbon material catalyst could be reused for 5 times without significant loss of activity after the product 5-HMF was separated with ethyl acetate.

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References

- 1 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
- 2 R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499–1597.
- 3 J. Lewkowski, *ARKIVOC*, 2001, **2**, 17–54.
- 4 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
- 5 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–U985.
- 6 L. Hu, Z. Wu, J. X. Xu, Y. Sun, L. Lin and S. J. Liu, *Chem. Eng. J.*, 2014, **244**, 137–144.
- 7 V. V. Ordonsky, J. van der Schaaf, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2012, **287**, 68–75.
- 8 P. Dornath and W. Fan, *Microporous Mesoporous Mater.*, 2014, **191**, 10–17.
- 9 Z. H. Zhang, B. Liu and Z. B. Zhao, *Carbohydr. Polym.*, 2012, **88**, 891–895.
- 10 Y. Yang, C. W. Hu and M. M. Abu-Omar, *Green Chem.*, 2012, **14**, 509–513.
- 11 X. H. Li, J. G. Zhao, Q. H. Li, L. F. Wang and S. C. Tsang, *Dalton Trans.*, 2007, 1875–1880.
- 12 H. Li, Q. Y. Zhang, X. F. Liu, F. Chang, D. Y. Hu, Y. P. Zhang, W. Xue and S. Yang, *RSC Adv.*, 2013, **3**, 3648–3654.
- 13 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2008, **10**, 799–805.
- 14 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *ChemSusChem*, 2009, **2**, 944–946.
- 15 S. P. Teong, G. S. Yi, X. Q. Cao and Y. G. Zhang, *ChemSusChem*, 2014, **7**, 2120–2124.
- 16 J. C. Shi, H. Y. Gao, Y. M. Xia, W. Li, H. J. Wang and C. G. Zheng, *RSC Adv.*, 2013, **3**, 7782–7790.
- 17 L. L. Zhou, R. J. Liang, Z. W. Ma, T. H. Wu and Y. Wu, *Bioresour. Technol.*, 2013, **129**, 450–455.
- 18 F. Guo, Z. Fang and T. J. Zhou, *Bioresour. Technol.*, 2012, **112**, 313–318.
- 19 X. H. Qi, H. X. Guo, L. Y. Li and R. L. Smith, *ChemSusChem*, 2012, **5**, 2215–2220.
- 20 C. Carlini, P. Patrono, A. M. R. Galletti and G. Sbrana, *Appl. Catal., A*, 2004, **275**, 111–118.
- 21 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Ind. Eng. Chem. Res.*, 2008, **47**, 9234–9239.
- 22 B. F. M. Kuster, *Starch*, 1990, **42**, 314–321.
- 23 Y. Y. Bai, L. P. Xiao and R. C. Sun, *Cellulose*, 2014, **21**, 2327–2336.
- 24 M. Liu, S. G. Jia, Y. Y. Gong, C. S. Song and X. W. Guo, *Ind. Eng. Chem. Res.*, 2013, **52**, 8167–8173.
- 25 S. G. Shen, B. Cai, C. Y. Wang, H. M. Li, G. Dai and H. F. Qin, *Appl. Catal., A*, 2014, **473**, 70–74.
- 26 H. Guo, Y. Lian, L. Yan, X. Qi and R. L. Smith, *Green Chem.*, 2013, **15**, 2167–2174.

- 27 S. M. Kang, J. Ye, Y. Zhang and J. Chang, *RSC Adv.*, 2013, **3**, 7360–7366.
- 28 S. Y. Tang, R. A. Bourne, M. Poliakoff and R. L. Smith, *Green Chem.*, 2008, **10**, 276–277.
- 29 P. T. Anastas and J. B. Zimmerman, *Environ. Sci. Technol.*, 2003, **37**, 94A–101A.
- 30 M. M. Titirici, R. J. White, C. Falco and M. Sevilla, *Energy Environ. Sci.*, 2012, **5**, 6796–6822.
- 31 X. H. Qi, L. Y. Li, Y. Wang, N. Liu and R. L. Smith, *Chem. Eng. J.*, 2014, **256**, 407–414.
- 32 S. Paul, S. Ghosh, P. Bhattacharyya and A. R. Das, *RSC Adv.*, 2013, **3**, 14254–14262.
- 33 S. Q. Hu, Z. F. Zhang, Y. X. Zhou, B. X. Han, H. L. Fan, W. J. Li, J. L. Song and Y. Xie, *Green Chem.*, 2008, **10**, 1280–1283.
- 34 G. Yong, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2008, **47**, 9345–9348.
- 35 F. Adib, A. Bagreev and T. J. Bandosz, *Environ. Sci. Technol.*, 2000, **34**, 686–692.
- 36 X. M. Sun and Y. D. Li, *Angew. Chem., Int. Ed.*, 2004, **43**, 597–601.
- 37 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787–12793.
- 38 M. Sevilla and A. B. Fuertes, *Carbon*, 2009, **47**, 2281–2289.
- 39 R. Demir-Cakan, N. Baccile, M. Antonietti and M. M. Titirici, *Chem. Mater.*, 2009, **21**, 484–490.
- 40 X. H. Qi, M. Watanabe, T. M. Aida and R. L. Smith, *Green Chem.*, 2009, **11**, 1327–1331.
- 41 S. K. R. Patil and C. R. F. Lund, *Energy Fuels*, 2011, **25**, 4745–4755.
- 42 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2007, **46**, 7703–7710.
- 43 J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, **9**, 342–350.