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Waste Polyethylene terephthalate Derived Carbon Dots for Separable Production of 5-Hydroxymethylfurfural at Low Temperature

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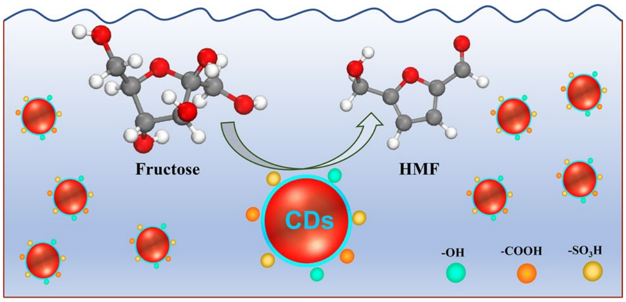
Abstract

Waste Polyethylene terephthalate plastic bottles were used as precursors to fabricate carbon dots (CDs) via air oxidation and sulfuric acid hydrothermal treatment. Owing to the nano-size effect and abundant acidic groups, CDs allowed their application as a novel solid acid for quasi-homogeneous catalytic dehydration of fructose to 5-hydroxymethylfurfural (HMF). Under the optimal condition, an ultra-high yield of HMF was 97.4% along with 100% fructose conversion at low temperature of 50 °C when [BMIM]Cl/ethanol was used as solvent. The CDs catalyst also displayed a prominent recyclability and was used for six recycles without massive loss in catalytic activity. Furthermore, 98.6% of HMF could be obtained from final products. The findings provide a novel sustainable route using recyclable plastics to synthesize carbon dots with a superior catalytic performance for conversion of biomass to important bio-based platform chemicals.

Graphic Abstract



PET CDs Catalytic conversion fructose to HMF in [BMIM]Cl/H_2O system

Keyword Carbon dots · PET · 5-Hydroxymethylfurfural · Ionic liquid · Recyclability

1 Introduction

The production of renewable fuels and chemicals from abundant biomass has attracted considerable attention in order to relieve the dependence of fossil resources towards sustainability [1]. 5-hydroxymethylfurfural (HMF) derived from lignocellulosic carbohydrates is a versatile and key platform chemical that can be converted into a broad range of value-added derivatives such as 2,5-dimethylfuran, 5-ethoxymethylfuran, 2,5-diformylfuran, and 2,5-furandicarboxylic acid with a high potential in fuel, pharmaceutical or polymer applications [2–4].

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The past several decades has seen the emergency of numerous studies for dehydration of fructose to HMF in water [5, 6], organic solvents [7, 8], ionic liquids (ILs) [9, 10], and mixed solvents [11, 12]. Water is a green solvent. Unfortunately, the reaction temperatures required in aqueous media are generally beyond 120 °C, resulting in partial degradation of HMF to undesired byproducts including levulinic and formic acid. Organic solvents can suppress the rehydration of HMF. Nevertheless, the high temperatures, typically ranging from 120 to 180 °C, are still needed, which favors the generation of humins, thereby reducing HMF yield and selectivity [13]. IL-mediated fructose conversions are mostly carried out at the temperature above 80 °C. With the aim of preventing high-temperature induced side reactions and further decreasing energy consumption, a few reports described that the fructose-to-HMF transformation in ILs could even occur at room temperature to 50 °C with appropriate catalysts. Zhang et al. demonstrated WCl_6-catalyzed conversion of fructose to HMF in butylmethyl imidazolium chloride ([BMIM]Cl), getting a HMF yield of 63% at 50 °C for 4 h [14]. Qi et al. added cosolvents such as acetone, dimethyl sulfoxide (DMSO), methanol, ethanol, and ethyl acetate (EtOAc) into [BMIM]Cl, and with strong acidic ion-exchange resin as the catalyst, the yield of obtained HMF was 78–82% with 89–95% fructose conversion at room temperature for 6 h [15]. Despite some impressive advances, the research area of low-temperature production of HMF from fructose is still in its infancy, and a number of issues remain to be resolved. One of the most crucial issues is how to increase the HMF yield in such mild conditions. Rationally design and carefully select a good catalyst may overcome the problem.

To date, various homogeneous and heterogeneous catalysts have been utilized for conversion of fructose to HMF. Compared with homogeneous catalysts such as H_2SO_4, HCl, and organic acids which are difficult to recycle and seriously corrode the equipment [16]. Nevertheless, the heterogeneous catalysts including zeolites [17], metal oxides [18, 19], ion-exchange resins [20], and sulfonated carbonaceous materials [21, 22] share the advantages of easy separation and less corrosion. Among them, sulfonated carbonaceous materials consisting of small polycyclic aromatic carbon sheets with attached SO_3H groups have emerged as a promising class of cheap and active solid acids [23]. However, the conventional carbon materials show poor dispersion ability, which is unbeneficial for sufficient contact between active sites and reactants, limiting their catalytic performance. Moreover, the commonly use of carbon materials at high temperature may cause the leaching of sulfur-containing moieties, resulting in the loss of activity. Plastic products are widely used in our daily life, compared with its counterparts such as polyethylene, polypropylene, and polyvinyl chloride, polyethylene terephthalate (PET) was much more stable [24]. PET can theoretically be converted into carbon materials by carbonization, but it could not be turned into CDs by the classical H_2O_2-assisted hydrothermal technique even at high temperature [25]. In order to destroy the robust structure of PET, thermal oxidation method was used.

Herein, a novel nanoscale carbocatalyst of carbon dots (CDs) was synthesized by the air oxidation and sulfuric acid sulfonation of PET. The nanoparticles solid acid contained functional group of $-SO_3H$, –COOH and –OH, presented a high selectivity and activity for HMF production from fructose in green solvents [BMIM]Cl/ethanol at low temperature. The CDs catalyst displayed a prominent recyclability and was used for six recycles without massive loss in catalytic activity. Furthermore, the produced HMF could be directly extracted from the catalytic system by ethyl acetate, realizing the readily isolation, making the whole process of HMF production from fructose green and sustainable.

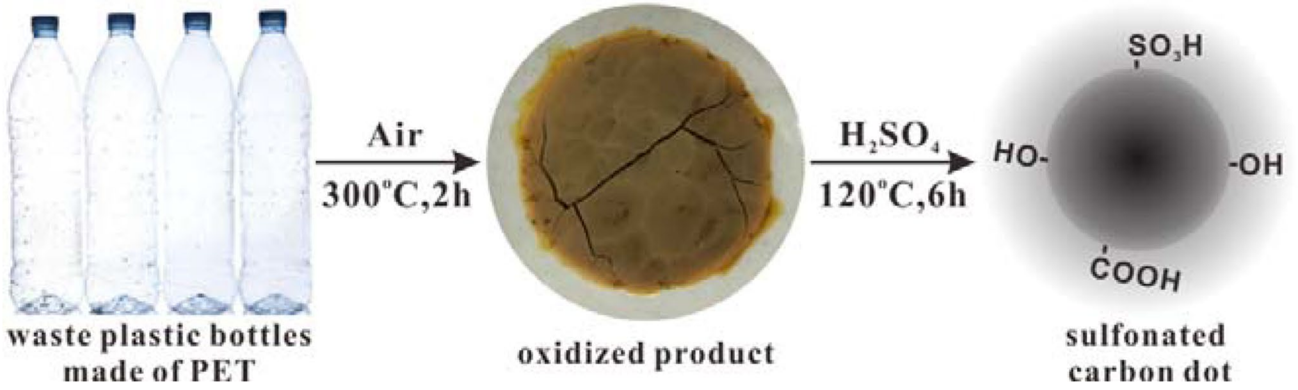
2 Experimental

2.1 Materials and Chemicals

Polyethylene terephthalate of waste Plastic bottles were obtained from Nongfu Spring Co., Ltd. (Hangzhou, China). Fructose was provided by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China). 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) was purchased from Lanzhou AoKe Chem. Co., Ltd. (Lanzhou, China). Sulfuric acid (98%), ethanol (EtOH), *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and ethyl acetate (EtOAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was used throughout the experiments.

2.2 Synthesis of Catalysts

CDs were fabricated by air oxidation of waste plastic bottles made of PET followed by the immersion in concentrated H_2SO_4 (Scheme 1). In a typical procedure, waste plastic bottles were cut into pieces, and then 3.0 g of the raw materials were put into an open ceramic crucible and heated at 300 °C for 2 h under air. The brown oxidized product was then immersed into 10 mL H_2SO_4 (98%), and heated at 120 °C for 6 h. After that, a black solution containing CDs was obtained. The solution was carefully diluted with 200 mL deionized water and filtrated through a Buchner funnel to remove the residue. Further purification of CDs was conducted through a dialysis tube (molecular weight cut off: 1000 Da) for 3 days in the dark (changed deionized water every 8 h) until sulfate ions were no longer detected. The CDs powder was obtained by freeze-drying treatment of such a purified solution.



Scheme 1 A diagram about the synthesis of CDs from waste plastic bottles made of PET

2.3 Characterization of Catalysts

Transmission electron microscopy (TEM) analysis of CDs were taken on a JEM-2100 electron microscope operating at an accelerated voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer with Cu Ká radiation (1.54056 Å). Raman spectra of the as-prepared samples were obtained on a Renishaw in Via-reflex spectroscopy with a laser at an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed with an AXIS UL TRA DLD spectrograph with Al/Kα as the source. Fourier transformed infrared (FTIR) spectra were collected in the KBr medium on a Nicolet 6700 FTIR spectrometer.

2.4 Catalytic Procedure and Products Analysis

In a typical reaction, 50 mg fructose was dissolved in the [BMIM]Cl/ethanol solvent (1 g [BMIM]Cl mixed with 1 mL ethanol) before the addition of CDs (50 mg). The resulted suspension was stirred at 500 rpm for a certain period of time at fixed low temperatures. After the reaction reached completion, the liquor was diluted with deionized water for the product analysis by high performance liquid chromatography (HPLC).

The fructose concentration was detected on an Agilent 1260 HPLC system equipped with an Aminex HPX-87H column and a RID detector. H_2SO_4 solution (5 mM) was used as the mobile phase and the column temperature was set at 30 °C [26]. Quantitative analysis of HMF was performed by HPLC equipped with a ZORBAX SB-C18 column and a UVW detector (278 nm). Water–methanol [95:5 (v/v)] solution was used as the mobile phase. The fructose conversion (F_C) and the HMF yield (Y_{HMF}) were calculated according to the following equations:

$$F_C = \frac{Q_F^0 - Q_F^M}{Q_F^0}$$

$$Y_{HMF} = \frac{Q_{HMF}}{Q_F^0}$$

here, Q_F^0 and Q_F^M are the initial quantity of fructose (g) and the quantity of fructose (g) in the reaction solution; Q_{HMF} is the actual quantity of HMF (g) in the reaction solution.

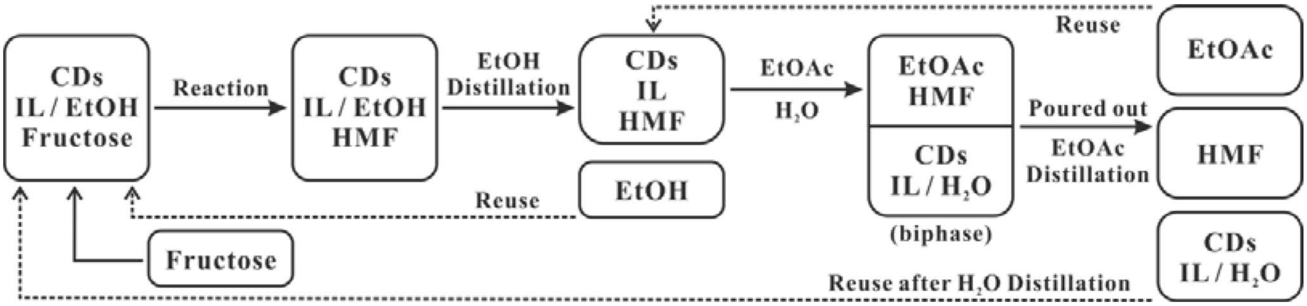
2.5 Recyclability of SCDs Catalyst

When the reaction reached completion, 5 mL EtOAc and 1 mL H_2O were added into the resultant mixture to form a biphasic solution after distillation of ethanol (Scheme 2), the HMF was effectively extracted by EtOAc under stirring at 300 rpm, while the solubilities of [BMIM]Cl and CDs in EtOAc were negligible, so they remained in the aqueous layer. The liquor was separated by separatory funnel to obtain the EtOAc/HMF and CDs/IL/H_2O components. The EtOAc/HMF liquor was distilled by reduced pressure to remove EtOAc and obtain HMF. The EtOAc can be recycled to extract HMF in this system. CDs/IL/H_2O liquor was distilled by reduced pressure to remove water and obtain CDs/IL component for reusability. Five repeated runs of extraction were carried out for sufficient HMF separation (total 25 mL EtOAc was used).

3 Results and Discussion

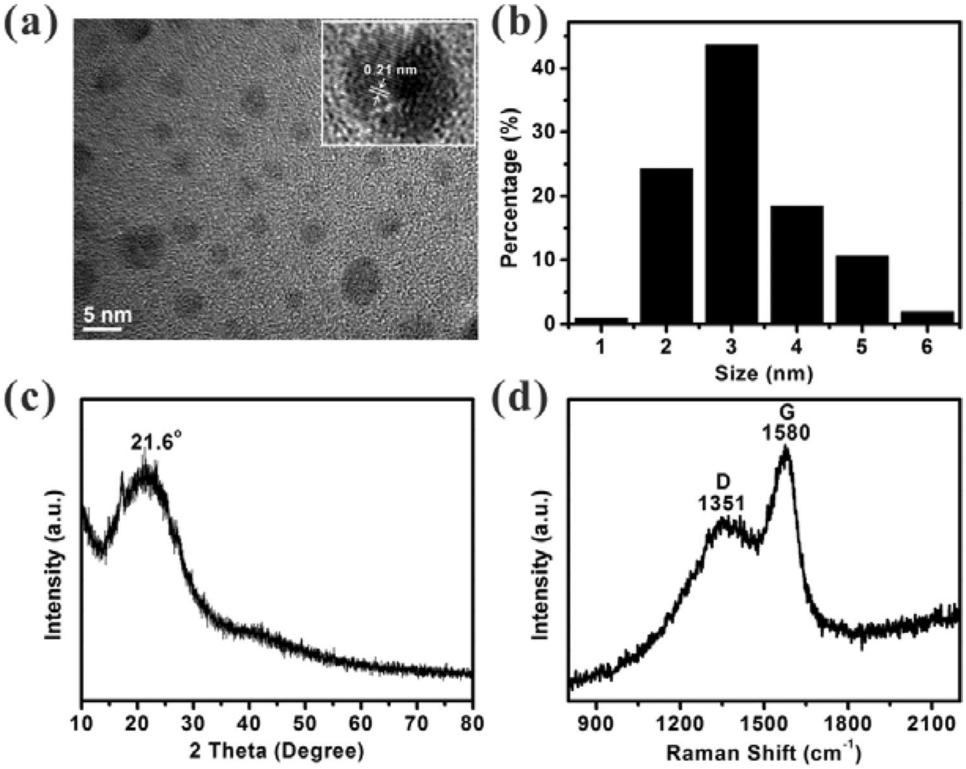
3.1 Characterization of Catalysts

The transmission electron microscopy (TEM) analysis (Fig. 1a) showed that the CDs had a circular shape and were well dispersed. Their diameters ranged from 1 to 6 nm with a



Scheme 2 A recycle process of the CDs-[BMIM]Cl/ethanol system for HMF production from fructose and the procedure of HMF separation

Fig. 1 **a** TEM image, **b** size distribution, **c** XRD pattern, and **d** Raman spectrum of CDs. Inset in **a**: high-resolution TEM image of CDs



mean size of approximately 3 nm by counting more than 200 nanoparticles (Fig. 1b). Clear Lattice fringes with a spacing of 0.21 nm were observed in the high-resolution TEM image (Fig. 1a, inset), which were corresponding to the (100) in-plane lattice of graphite, indicating the good crystallinity of CDs [27]. The X-ray diffraction (XRD) pattern (Fig. 1c) exhibited a broad peak at 2θ angle of 21.6°, being associated with the disordered graphitic structure [28]. The Raman spectrum (Fig. 1d) displayed the characteristics of *D* and *G* bands at 1351 and 1580 cm^{-1}, respectively, suggesting the coexistence of both sp^3 and sp^2 carbons inside CDs [29].

X-ray photoelectron spectroscopy (XPS) measurement was carried out to determine the elemental composition and chemical bonding of the CDs samples. The signals of C_{1s}, O_{1s}, S_{2s}, and S_{2p} peaks were found in the XPS spectrum (Fig. 2a), the elements ratio of C, O and S were 70.7% 25.7% and 3.6%, respectively, revealing the CDs mainly contained carbon and oxygen element as well as a small amount of sulfur element. The C_{1s} spectrum (Fig. 2b) could be resolved into three peaks of C–C/C=C (284.5 eV), C–O/C–S (286.1 eV), and C=O (288.8 eV) [30], indicated that the percentage of C–C/C=C was higher than the C–O/C–S and C=O, due to the air oxidation and sulfuric acid sulfonation of waste PET. In the XPS spectrum of S_{2p} (Fig. 2c), the $2p_{3/2}$ and $2p_{1/2}$ peaks of SO_3H groups were assigned to 168.5 and 169.6 eV, respectively, indicating the sulfonate was successful attached on the surface of CDs [31, 32]. The Fourier transform infrared (FTIR) spectrum of CDs was shown in Fig. 2d, the stretching vibrations of O=S=O and SO_3^- were assigned to 1232 cm^{-1} and

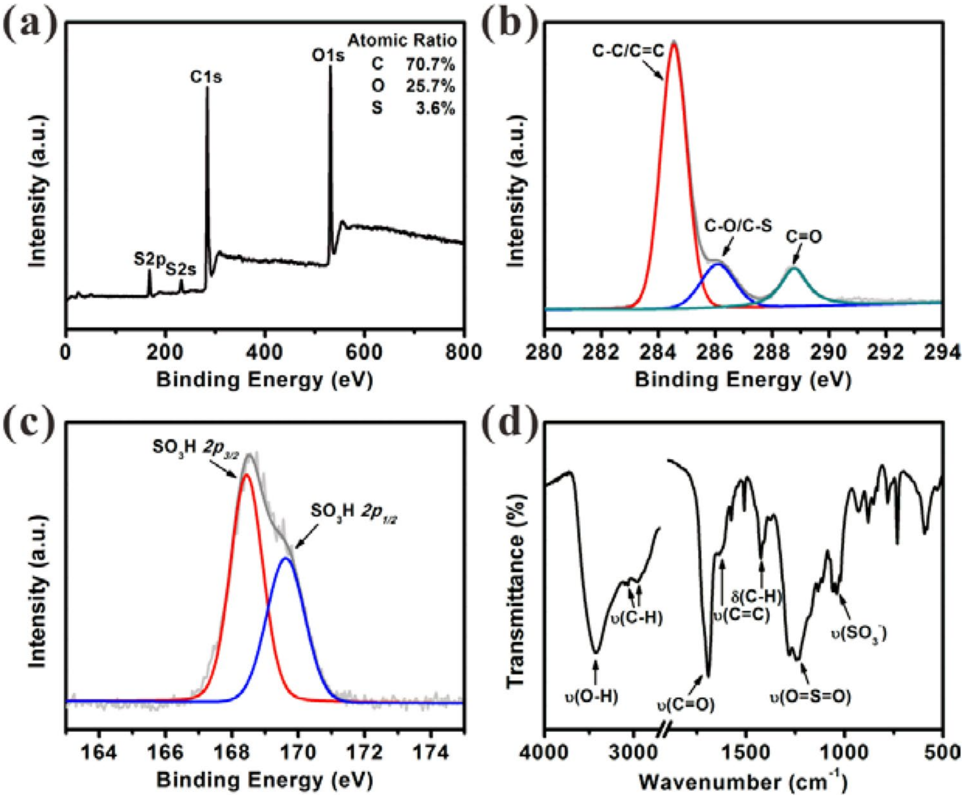


Fig. 2 **a** XPS survey, **b** C_{1s}, **c** S_{2p}, and **d** FTIR spectra of CDs

1039 cm^{-1}, respectively, demonstrating the CDs possessed SO_3H groups [33, 34]. The absorption bands of O–H, C–H, C=O, and C=C bonds were also illustrated in the FTIR spectrum. These results are consistent with the XPS analysis. As a result, it was concluded that the as-synthesized materials were carbon-rich, nanosized dots, which had graphite-like structure and bore abundant acid groups on the surface. Such a nanocarbon was then employed as a solid acid for catalytic dehydration of fructose to HMF.

3.2 Optimization Condition of Fructose Conversion

The CD catalysts could thoroughly distribute in the [BMIM]Cl/ethanol solution containing fructose, forming a pseudo-homogeneous state. Excitingly, the conversion of fructose to HMF proceeded smoothly at room temperature (25 °C). The yield of HMF was 13.4% after 2 h and then gradually increased to approach the plateau value of 79.4% with fructose conversion of 98% for 24 h (Fig. 3a and b, insets). Encouraged by these observations, the catalytic system was examined at temperatures ranging from 40 to 70 °C (Fig. 3a and b). Notably, an ultra-high yield of HMF was 97.4% with 100% fructose conversion when the reaction temperature and time were 50 °C and 2 h, respectively. The reaction rates increased with the increase of temperature, but the yield of HMF decreased. For example, when the temperature was 70 °C, the reaction rate increased, but the yield of HMF was 94.6%, due to the degradation of HMF and the formation of humins at elevated temperatures [21, 35]. The effect of catalyst dosage on the conversion of fructose to HMF was evaluated (Fig. 3c). The conversion of fructose was negligible and no HMF was detected when the reaction system lack of CDs. In contrast, by adding a small amount of CDs (10 mg), a satisfactory yield of HMF was 80.0% with 84.1% fructose conversion, confirming the essential catalytic role of CDs. With increasing the catalyst dosage to 50 mg, the yield of HMF reached the maximum value of 97.4%. An extra increase of catalyst dosage, however, the yield of HMF slightly decreased, implying too much acid sites provided by excess CDs favored side reactions like humin formation. Thus, the optimum conditions for converting fructose to HMF in the presence of CDs were obtained, the reaction temperature and time were 50 °C and 2 h, respectively, the catalyst dosage was 50 mg.

3.3 Reaction Kinetics and Activation Energy Analysis

Figure 4a illustrated a nice linear relationship between $-\ln(1-\text{Conversion}_{\text{fructose}})$ and time, revealing the fructose dehydration followed the first-order model of kinetics model [7, 36]. The plot of ($\ln k$) *versus* ($1/T \times 10^3$) based on the Arrhenius equation was given in Fig. 4b, reporting a low activation energy of fructose conversion to HMF

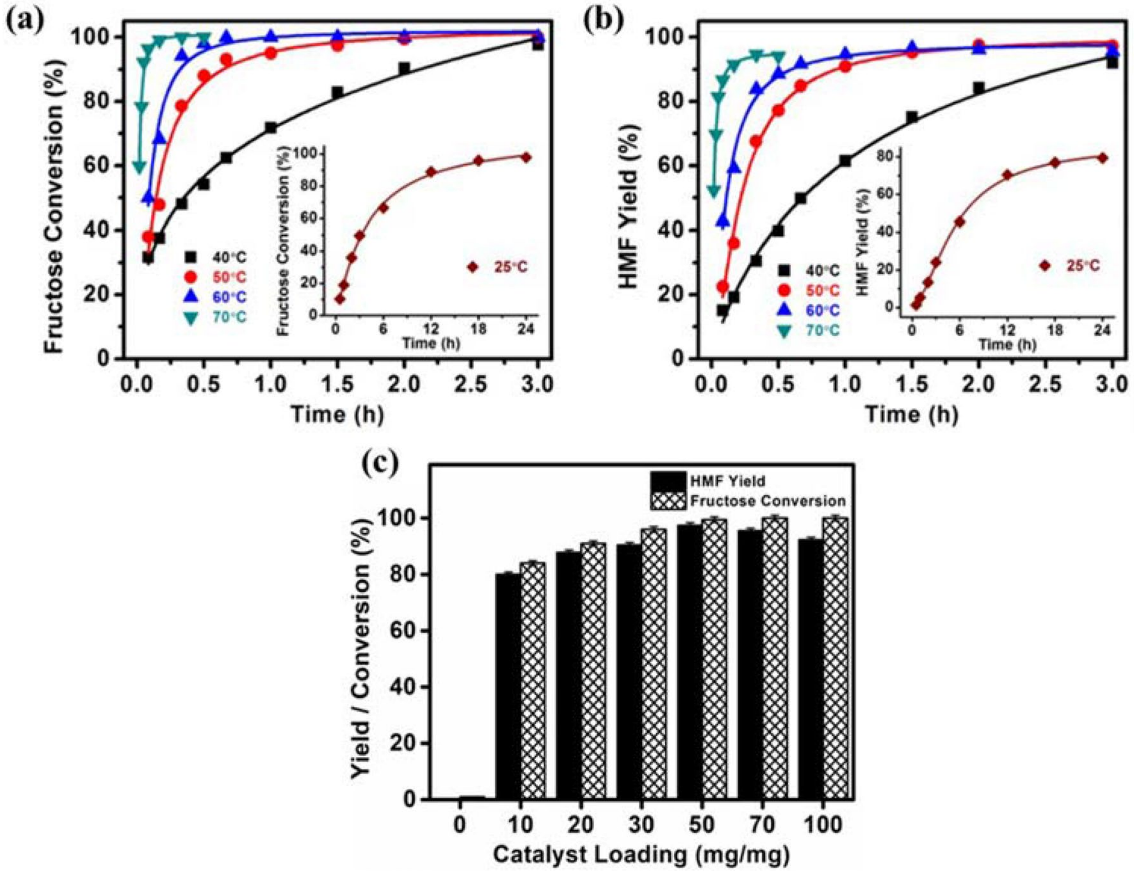
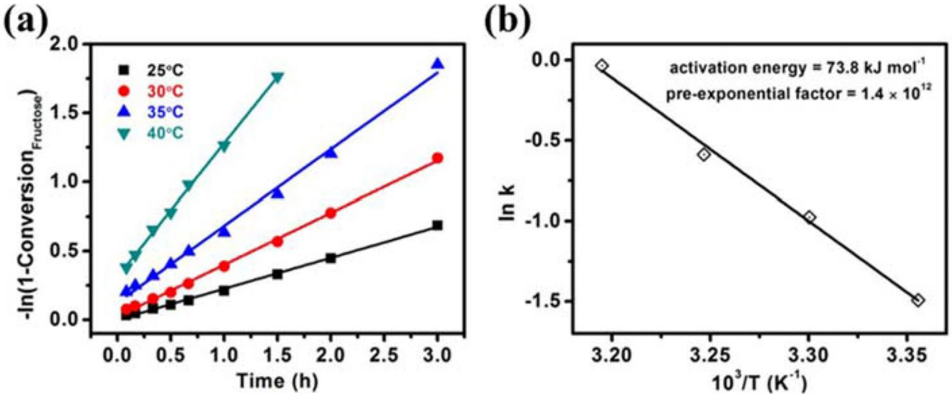


Fig. 3 Effects of time and temperature on **a** fructose conversion and **b** HMF yield of the catalytic reaction. **c** Effect of catalyst dosage on fructose conversion and HMF yield

Fig. 4 **a** Plots of − ln(1 − Conversion$_{\text{fructose}}$) *versus* time at different temperatures. **b** Plot of (ln *k*) *versus* (1/T × 10^3) for fructose dehydration



was 73.8 kJ mol^{-1} and a large pre-exponential factor was 1.4×10^{12}, which was much lower compared to the sulfuric acid (99 kJ mol^{-1}), ion-exchange resin (103.4 kJ mol^{-1}) [37], and mesoporous silica nanoparticles (80.05 kJ mol^{-1}) [38], this result accounted for the superior catalytic performance of the CD-based system.

3.4 Effect of Co-solvent and Catalyst on Fructose Conversion

The feasibilities of low-temperature HMF production from fructose in [BMIM]Cl through addition of various co-solvents were examined (Fig. 5a). Both the fructose

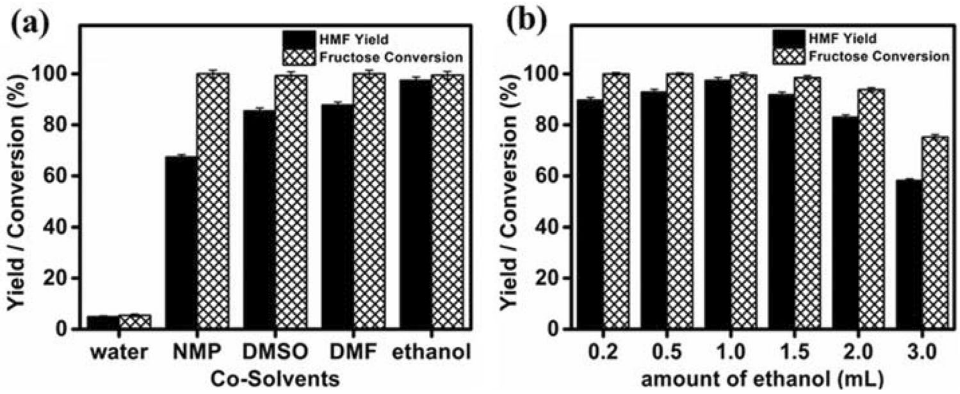


Fig. 5 **a** Effect of co-solvent on fructose conversion and HMF yield. **b** Effect of amount of ethanol on fructose conversion and HMF yield

Table 1 Comparison of the dehydration of fructose to HMF using different catalytic system at low temperatures

No.	Catalyst	Solvent	T (°C)	Time (h)	Yield (%)	Ref.
1	$GeCl_4$	[BMIM]Cl/DMSO	25	12	70.0	[11]
2	WCl_6	[BMIM]Cl	50	4	63.0	[14]
3	Amberlyst 15	[BMIM]Cl/acetone	25	6	78.1	[15]
4	HCl	[BMIM]Cl	23	24	72.0	[41]
5	P_2O_5	[BMIM]Cl	50	1	81.2	[42]
6	Amberlyst 15	[BMIM]Cl/[BMIM][BF_4]	25	3	56.0	[43]
7	–	[BMIM]Cl/[HNMP][CH_3SO_3]/ethanol	25	6	89.2	[12]
8	Carbon dots	[BMIM]Cl/ethanol	50	2	97.4	This work

conversion and HMF yield were below 6% in the presence of water, indicating the water was an unsuitable co-solvent, due to the water inhibited the equilibrium shift in fructose dehydration [39]. The co-solvents of NMP, DMSO, and DMF offered complete fructose conversion, but the selectivity and yield of HMF were not high enough (67.4–87.7%), due to the generation of certain amounts of humins as by-products [40]. Clearly, ethanol was a preferred co-solvent, because of it not only gave an extra-high HMF yield (97.4%), but also was an environmentally friendly, cost-efficient, and easy-to-use reaction media. The effect of the amount of ethanol on the fructose conversion was shown in Fig. 5b. Insufficient addition of ethanol (< 1 mL) reduced the catalytic efficiency owing to the limited mass transfer in the viscous reaction mixture [11], whereas excessive ethanol addition (> 1 mL) lowered the dielectric constant of the reaction media which also brought about a negative effect [15].

Compared to the reported catalyst and solvent for conversion fructose to HMF, the highest yield of HMF was obtained when using the CDs as catalyst (Table 1). Such a good results had never been reported before under mild conditions, demonstrating the remarkable catalytic efficiency of this reaction system, which benefited from the appropriate acid strength and excellent interfacial compatibility of the CD catalysts in the [BMIM]Cl/ethanol solution.

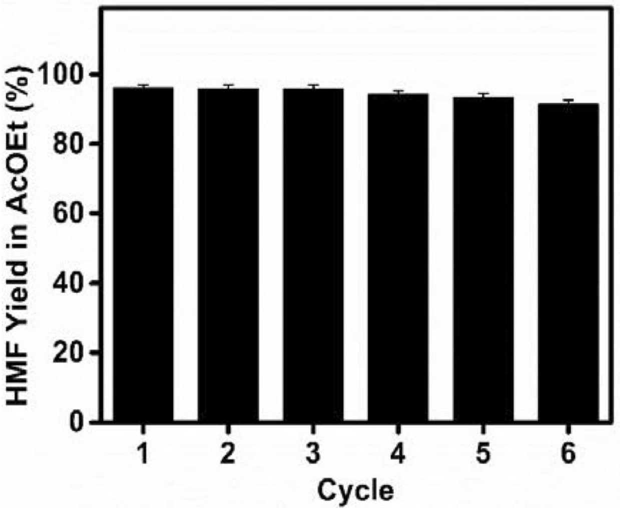


Fig. 6 Catalytic ability of the CDs catalyst recycled from [BMIM]Cl/ethanol system

3.5 Recyclability of Catalysts

This unique phase behavior was really beneficial for HMF separation without cross contamination (Scheme 2). Sufficient extraction allowed a high HMF yield of 96.1% in EtOAc with an extraction efficiency of 98.6%. [BMIM]Cl and CDs could be easily reused after removed the EtOAc and H_2O. As shown in Fig. 6, the yield of HMF still retained 91.4% in EtOAc even the six recycles of the CDs catalyst, confirming that the catalytic system was recyclable without significant deactivation of CDs.

4 Conclusions

In conclusion, nanosized CDs possessing abundant SO_3H, COOH, and OH groups were economically fabricated through air oxidation of waste plastic bottles followed by the sulfonation of H_2SO_4. Such nanomaterials as a novel solid acid could well dispersed in [BMIM]Cl/ethanol solvent to form a quasi-homogeneous catalytic state, that enabled the high-yield production of HMF from fructose at low-temperature. Easy separation of HMF was realized by EtOAc extraction, and the CDs based catalytic system was actually recyclable. This work provides new opportunities for large-scale synthesis of HMF under mild conditions for application on conversion biomass to biofuels.

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Compliance with Ethical Standards

Conflicts of interest The authors declare no competing financial interests.

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