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Quasi-homogeneous carbocatalysis for one-pot selective conversion of carbohydrates to 5-hydroxymethylfurfural using sulfonated graphene quantum dots

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Abstract

Graphene quantum dot (GQD), which is the latest addition to the family of nanocarbon materials, promises a wide spectrum of novel applications. Here, we for the first time demonstrate the use of GQD and sulfonated GQDs (SGQDs) as quasi-homogenous catalysts for chemo-catalysis. Specifically, we demonstrate that SGQDs are able to selectively and effectively degrade carbohydrates (eg. fructose, glucose, and cellulose) at high concentrations into 5-hydroxymethylfurfural (5-HMF). For example, dehydration of fructose (up to 20 wt.% concentration) to 5-HMF with a yield of 51.7% and a conversion rate of 91.8%. SGQDs uniquely combine the merits of homogenous catalysts and heterogeneous catalysts, i.e., SGQDs resemble a homogenous catalyst in the reaction while they can be recycled just mimicking the heterogeneous catalysts. The high efficiency of SGQDs is attributed to their unique physicochemical and structural properties. The DFT calculations reveal that intra-molecular hydrogen bonded -OH groups and the adjacent -SO₃H groups on SGQDs play a synergistical role in their high catalytic efficiency. This study suggests the potential of SGQD as an efficient and green carbocatalyst for one-pot biomass transformation and more generally the unique potential of functionalized GQDs as novel quasi-homogeneous catalysts for various reactions.

1. Introduction

Acid catalysis is one of the most routine operations in both industrial processes and laboratorial research. The production of platform chemicals, synthetic plastics, pharmaceuticals, as well as alternative fuels from biomass is usually realized through acid catalysis. Conventionally, liquid acids (such as sulphuric acid, hydrochloric acid, and hydracids) are used as the homogeneous catalysts to ensure high efficiency because reactants and catalysts can fully interact in the same phase. Nonetheless, they are corrosive and non-recyclable. And their disposal is costly and environmental unfriendly. Therefore, much effort has been spent to develop recyclable heterogeneous acid catalysts, including cation exchange resins [1], solid superacids [2], supported metal oxides [3], zeolites [4], and natural clays [5]. But they usually suffer from poor catalytic efficiency due to limited accessible active sites and high mass transfer resistance. In addition, they are prone to deactivation due to fouling and environmental issues associated with the leakage of metal species. Carbon nanomaterials, which function as earth-abundant metal-free catalysts, hold promise to tackle the abovementioned challenges [6-12].

Qi et al reported a cellulose-derived sulfonated amorphous carbon as the catalyst for dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) [13]. The catalyst is stable and easily recoverable after reaction. However, a good yield of product was obtained only when ionic liquid was used as the reaction solvent, which is expensive and not readily available. SO₃H-functionalized carbon nanotubes were employed in the acid-catalysed transesterification of triglycerides [14]. But the synthesis method involves a complicated process for SO₃H-functionalization. Zhao et al demonstrated the use of graphene oxide (GO) sheets with diameter ranging from 2 to 10 μm for hydrolysing cellulose to glucose with a production yield of 49.9%. But as GO sheets aggregate easily, the recyclability is not satisfactory [15].

Graphene quantum dot (GQD), which is an atomically thin and nanometer wide planar carbon structure, is the latest addition to the family of nanocarbon materials. GQDs promise a wide spectrum of novel applications in sensing [16, 17], imaging [18], electro- and photocatalysis [19], energy conversion and storage [20] because of their exceptional properties, including molecular size, highly tunable physicochemical properties, high specific surface area, abundant edge sites, excellent dispersibility, high thermal and chemical stability, and easy being functionalized. For many applications, GQDs (0D graphene nanosheets) shall outperform 2D graphene counterparts because of its smaller size, higher solubility in various organic and aqueous solutions, even more abundant active sites (because of high fraction of edge, defect, and functionality sites), and even better tunability (through chemical functionalization, heteroatom doping, etc).

Herein, we employ GQD and sulfonated GQD (SGQD) in the one-pot selective conversion of carbohydrates existed in biomass to 5-HMF which is a versatile platform molecule pivotal to biorefinery engineering (Scheme 1). GQD and SGQD are discovered to act as quasi-homogeneous acid catalysts in the reaction and SGQD even show exceptionally higher catalytic activity compared with some homogeneous catalysts. After reaction, they can be readily separated for reuse. That is, SGQD is able to unify the merits of heterogeneous and homogeneous catalysts as a novel carbocatalyst. The high efficiency of SGQD is further explored by DFT calculations. This study suggests the unique potential of such emerging zero-dimensional materials as a new class of catalysts for chemical processes.

2. Experimental

2.1. Materials and characterization

Fructose ($\geq 99\%$, Alfa Aesar), Glucose (99.5%, Sigma-Aldrich), sucrose (99%, Sigma-Aldrich), cellobiose ($\geq 98\%$, Sigma-Aldrich), xylose ($\geq 99\%$, Sigma-Aldrich), ZSM-5 (Si/Al=30, Alfa Aesar), Nafion (Sigma-Aldrich), Amberlyst-15 (hydrogen form, Sigma-Aldrich), inulin from chicory (Sigma-Aldrich), cellulose powder (Sigma-Aldrich), 5-HMF ($\geq 99\%$, Sigma-Aldrich), chlorosulfonic acid (98%, Sigma-Aldrich), methoxytrimethylsilane (99%, Sigma-Aldrich), carbon black (Cobat Corporation), carbon nanotube sheets (Sigma-Aldrich), activated carbon (Johnson Matthey, United Kingdom) and other chemicals are commercially available. All the chemicals were used without further purification. Brønsted ionic liquid was prepared according to the previous report [21].

FT-IR measurements were performed on a Bruker Tensor spectrometer. The TEM images were taken by JEOL 2100F microscope with a ZrO/W Schottky Field Emission Gun with an accelerating voltage of 200KV. Scanning TEM-energy-dispersive X-ray (STEM-EDX) spectrometry with high-angle annular dark field was used for element mapping. Atomic force microscopic (AFM) images were collected from Bruker Dimension Icon system. Raman spectroscopy (Renishaw InVia Reflex Raman) was obtained at an excitation wavelength of 633 nm.

The acidic sites on GQDs and SGQDs were determined by pyridine adsorption characterized by FTIR. In this experiment, FTIR spectra were recorded by Nicolet-6700 FT-IR spectrophotometer with a resolution of 4.0 cm^{-1} . A self-supported wafer of tested sample was placed inside a quartz IR cell equipped with CaF_2 windows. The samples were pretreated under vacuum (0.01Pa) at 350 °C for 2 h. The background spectra were recorded after cooling down to room temperature, IR spectra of adsorbed pyridine on the samples were collected after exposure of the wafer to excess pyridine vapour at room temperature for 0.5 h. Excess of pyridine was

desorbed by evacuating the samples at 150 °C and 300 °C respectively for 0.5 h. The spectra of pyridine adsorption were obtained by subtraction of the background spectrum from the sample spectrum.

The acidic strength of GQDs and SGQDs was measured by temperature programmed desorption (TPD) of ammonia on a Micromeritics AutoChem 2910 instrument. Before adsorption, the samples were pre-treated under Ar stream at 300 °C. Subsequently, they were cooled down to 100 °C at an Ar flow rate of 20 cm³/min before the ammonia adsorption started. The adsorption step was carried out by allowing small pulses of ammonia in Ar at 100 °C until saturation (normally 1 h). The samples were exposed to an Ar flow of 50 cm³/min for 2 h at 100 °C. Finally, the desorption was performed from 100 °C to 600 °C at 10 °C /min and maintained at 600 °C for 10 min under Ar stream of 50 cm³ /min. (the adsorbate was completely desorbed under this conditions)

The content of carbon, oxygen and sulfur on the surface of GQDs/SGQDs were determined by X-ray photoelectron spectroscopy (XPS, Escalab MK II spectrometer), using an Al X-ray excitation source ($K\alpha = 1487.6$ eV). The amount of the functional groups bonded to SGQDs was estimated by elemental analysis (vario EL cube, ELEMENTAL) and cation-exchange analysis[22, 23]. The density of $-\text{SO}_3\text{H}$ groups were calculated based on sulphur content obtained from element analysis. Subsequently the contents of $\text{SO}_3\text{H} + \text{COOH}$ and $\text{SO}_3\text{H} + \text{COOH} + \text{OH}$ were determined by the exchange of Na^+ in aqueous solutions of NaCl and NaOH, respectively. The proportions of each functional group were estimated based on the analysis results.

2.2. Catalyst preparation

GQDs were synthesized according to the previous procedure [24], using carbon black as raw material. To achieve sulfonation, 1 g GQDs were pretreated by calcination under N₂ at 300 °C for 1 h to form a dark solid, which is subsequently dispersed in chloroform containing 5 mL of chlorosulfonic acid. The mixture was continuously refluxed under N₂ with vigorous stirring for 24 hours at 70°C. After cooling down to room temperature, the suspension was centrifuged, diluted with DI water and neutralized with concentrated NaOH solution. The mixture was further filtered with a 0.2 µm syringe membrane followed by dialysis for 1-3 days (with 500 Da MWCO) to remove salts using a centrifugal filter with a cut-off molecular weight of 3 kDa. The catalyst powder was finally obtained after freeze drying. Other sulfonated carbon materials (e.g. sulfonated carbon nanotube, sulfonated activated carbon) are synthesized following the same procedure.

To identify the effect of –OH groups in SGQDs on the catalytic performance, methoxytrimethylsilane (MTS) was used to block the groups via condensation of –OH in SGQDs with MTS[25, 26]. In a typical procedure, 1.0 g of SGQDs was dispersed in 50 ml of toluene to form a suspension. 1.65 mmol MTS was added to the suspension and the resulting mixture was treated under refluxing at 70 °C for 12 h and then cooled to room temperature. After filtration, the solid was washed three times with anhydrous ethanol, and finally dried overnight at 100 °C. MTS-modified SGQDs (designated as SGQDs-MTS) was finally obtained.

2.3. Catalytic reactions and analysis techniques

The catalytic reaction was performed in a 10 ml capacity flask equipped with a low-temperature condenser at 1 °C. In a typical run, fructose, catalyst and solvent were charged into the flask. The mixture was then heated to 170 °C under stirring. After 2 h, the reaction was quenched in an ice bath. The 5-HMF product predominately stays at the upper phase (organic phase) while the

catalyst and the unreacted hydrophilic reactants remained in the lower phase (aqueous phase). SGQDs are separated from the aqueous phase by dialysis using a 500 Da MWCO dialysis bag for reuse. 5-HMF in both organic phase and aqueous phase were sampled and analysed by HPLC apparatus (Agilent 1100 Series) equipped with XDB-C18 column and a UV detector at 320 nm, using a 2:8 v/v methanol: water as the mobile phase. While the sugars/sugar derivatives in both phases were analysed by the Bio-Rad Aminex HPX-87H pre-packed column (300 mm $\times$ 7.8 mm) and refractive index detectors (RID) equipped on the HPLC apparatus. 5 mM H₂SO₄ was employed as the mobile phase [27]. An external standard method was used for quantifying the products. The identities of the compounds were authenticated by comparing their retention times with those of pure compounds. The carbohydrate conversion and the molar yield of 5-HMF, as well as the molar yield of other products were calculated from the product concentration in both two phases.

2.4. Calculation methods

The optimizations were performed using density functional theory (DFT) with the popular Becke's three-parameter hybrid functional (B3LYP) method and the 6-311++G(d) basis set.

Atoms in molecule theory (AIM) analyses were performed for the optimized structures, which has been widely used for analyzing the hydrogen bond (HB) containing systems and proved to be useful and successful tools for interpreting hydrogen-bonding interactions [28]. The interaction energies refer to the energy differences between the pairs and the corresponding isolated compound. The basis set superposition errors (BSSEs) produced in the calculations was evaluated by the Boys-Bernardi counterpoise technique. In the AIM analysis, the electron density (ρ), the Laplacian of electron density ($\nabla^2 \rho$), and the energy density (H) at the bond critical point (BCP) were used to quantify the Hydrogen-bonding interaction. All the calculations were

performed using the Gaussian 09 computational package while the AIM topological analysis was performed using Multiwfn 3.3.9.

3. Results and discussion

Previously, Wang et al reported three-step sulfonation of graphene oxide microsheets involving thermal annealing (800 °C), reduction of graphene oxide by n-butyllithium and sulfonation of reduced graphene oxide by chlorosulfonic acid [29]. In contrast, we obtained sulfonated GQDs (SGQDs) by a facile synthesis which is more practical and readily engineered.

Fig. 1a shows the FTIR spectra of GQDs and SGQDs respectively. The vibrational peaks originated from epoxides (C-O-C at $\sim 1280\text{-}1330\text{ cm}^{-1}$), sp^2 -hybridized C=C (in-plane vibrations at $\sim 1580\text{ cm}^{-1}$), and edge groups such as carbonyls or carboxyls (C=O or COOH at $\sim 1650\text{-}1750\text{ cm}^{-1}$) are observed in GQDs. In comparison, the epoxide peak significantly declines in SGQDs. The appearance of vibrational bands at 1130 cm^{-1} , 1215 cm^{-1} , arisen from S=O asymmetric and symmetric stretching of $\text{-SO}_3\text{H}$, further confirms successful grafting of sulfonic groups onto SGQDs. The broadband at $2300\text{-}2700\text{ cm}^{-1}$ is assigned to an overtone (Fermi resonance) of the bending mode of $\text{-OH}\cdots\text{O=}$ originated from a strong hydrogen bond, which is often found in strong liquid Brønsted acids such as $\text{CF}_3\text{SO}_3\text{H}$ [23]. This observation implies that SO_3H groups in close proximity on SGQDs to form strong HBs.

In the Raman spectra depicted in Fig. 1b, GQDs display a D band (A_{1g} breathing mode) at 1368 cm^{-1} and a G band (E_{2g} G mode) at 1590 cm^{-1} , resulting from sp^3 carbon atoms from the defects and sp^2 carbon atoms in the graphitic hexagonal lattice, respectively [30]. In comparison, the D to G ratio is increased, suggesting disruption of graphitic structure upon introduction of SO_3H groups. In addition, a blue shift of G band is observed from SGQDs, probably due to the

formation of single-double bond alternation within the sp^2 carbon domains when two hydroxyl groups are grafted adjacently on the basal plane [31].

As seen from the X-ray photoelectron spectroscopy spectra in Fig.1c, in addition to the common C1s peak at 284.5 eV and O1s peak at 530.8 eV as observed in GQDs, additional S2s peak at 233.1 eV and S2p peak at 169.8 eV arise in SGQDs, indicative of the successful conjugation of SO_3H groups. The atom percentages of carbon, oxygen, and sulphur in SGQDs are 60.53%, 34.71%, 4.76% respectively. The sulphur content is much higher than other sulfonated carbon material [32-34], implying that SGQDs should have stronger Brønsted acidity. The total O/S atom ratio ($\sim 7:1$) of SGQD is much higher than the O/S atom ratio of $-SO_3H$ groups (3:1), suggesting that many oxygen-containing groups (e.g. $-COOH$, $-OH$) still remain after GQD being sulfonation.

The high-resolution C1s XPS peak of original GQDs can be deconvoluted into C=C (graphitic carbon) at 284.7 eV, C-C (sp^3 -hybridized carbon) at 285.4 eV, C-O-C/C-OH (epoxy/hydroxyl) at 286.8 eV and C(=O)-OH (carboxylic group) at 289.5 eV (Fig. S1). In comparison, the 286.8 eV peak decreases in SGQDs, indicating that many epoxy groups on basal plane (which are more vulnerable to reduction as compared with hydroxyl groups) are removed after the thermal annealing [35]. This is consistent with the FTIR spectrum that the epoxy peak declines sharply in SGQDs. Taken together, the oxygen functionalities in SGQDs are mainly phenolic OH, $COOH/C=O$, and SO_3H . Similar to GQDs, SGQDs show a peak of C=C (~ 284.7 eV), suggesting that the graphitic structure is still preserved after sulfonation. GQDs and SGQDs share similar O1s spectrum whereas SGQDs display a new peak at 169.8 eV in S2p spectrum caused by SO_3H groups. Elemental analysis and cation-exchange experiment are used to confirm

the composition of SGQDs and it is determined to be $\text{CH}_{0.465}\text{O}_{0.573}\text{S}_{0.079}$. The amount of SO_3H , COOH , and phenolic OH groups are calculated to be 3.1, 1.5, and 3.5 $\text{mmol}\cdot\text{g}^{-1}$ respectively.

The acidity of GQDs and SGQDs is determined by pyridine-adsorption FTIR (Fig. 1d). After pyridine desorption at 150 °C, a small peak at 1456 cm^{-1} (indicative of Lewis acidity) and a prominent peak at 1531 cm^{-1} (indicative of Brønsted acidity) are observed in SGQDs. The Lewis acidity is probably originated from the dehydration of Brønsted acid sites or electron inductive effect of the $\text{S}=\text{O}$ bonds as demonstrated by Pravin et al [36] while Brønsted acidity are originated from $-\text{SO}_3\text{H}$ and $-\text{COOH}$ groups. When desorption temperature is increased to 300 °C, Lewis acidity peak remains unchanged while Brønsted acidity peak decreases obviously due to the loss of weak Brønsted acidity. In comparison, original GQDs show weaker Brønsted acidity and no obvious Lewis acidity. Taken together, after sulfonation, not only Brønsted acidity is significantly enhanced by addition of SO_3H groups, but also a small amount of Lewis acidity is induced onto SGQDs. The ratio of Brønsted acidity to Lewis acidity was determined to be 3.73 (Fig. 1d).

The acid strength and amount are evaluated by temperature programmed desorption of ammonia (NH_3 -TPD). 1.05 $\text{mmol}\cdot\text{g}^{-1}$ of weak acid sites (<270 °C), 2.31 $\text{mmol}\cdot\text{g}^{-1}$ of medium acid sites (270-400 °C) and 0.22 $\text{mmol}\cdot\text{g}^{-1}$ of strong acid sites (>400 °C) are found in SGQDs while 1.23 $\text{mmol}\cdot\text{g}^{-1}$ of weak acid sites and 0.35 $\text{mmol}\cdot\text{g}^{-1}$ of medium acid sites are observed in GQDs. Evidently, medium acid sites dominate in SGQDs, which is favourable to dehydration of hexoses to HMF or HMF- derivatives.[1] The acidity distribution of SGQDs is in accordance with the co-existence of weak and strong Brønsted acidity as revealed by pyridine-adsorption FTIR experiments. The observations that GQDs have no strong acidic sites and a much less

amount of medium acidic sites is also in line with the notion that GQDs only have weak Brønsted acidity.

As uncovered by transmission electron microscopy (TEM), SGQDs have a diameter about 10.4 nm ($\pm$ 3.1 nm, $n=110$) with a lattice spacing of 0.245 nm corresponding to (1120) plane of graphene (Fig. 2a and Fig. 2d). GQDs have similar morphology (Fig. S2), indicating that sulfonation doesn't cause structural changes. Energy-dispersive X-ray (EDX) spectroscopy mapping reveals that, rather than only residing at the edge sites, S element is uniformly distributed on the basal plane (presumably on both sides) of SGQD (Fig.2a). This is further confirmed by the TEM-EDS line scanning spectrum (Fig. 2b). Such homogeneous conjugation of SO₃H groups is desirable for full utilization of active catalytic sites. Furthermore, atomic force microscopy (AFM) reveals that SGQDs have an average thickness of 1.06 nm ($\pm$ 0.34 nm, $n=152$), i.e., they are mostly single or double layered (Fig. 2c and Fig. 2e).

Both original GQDs and SGQDs can disperse well in aqueous solution to serve as quasi-homogenous acidic catalysts (Fig. S3). We examined SGQD's ability to dehydrate fructose into 5-HMF in different solvent systems. As shown in Fig. 3a, the production yield of 5-HMF is very low (17.1%) in pure water accompanied with a considerable amount of condensation compounds (43.5%) because water is a non-selective solvent for Brønsted acid-catalysed conversion of carbohydrates because many reaction pathways are possible [37]. Adding organic solvent can extract the produced 5-HMF and consequently avoid its further reactions in aqueous phase (e.g., condensation and rehydration) [38]. Using MIBK: butanol (v/v of 7:3) as the extracting solvent (solvent: water at w/w of 2:1) [39], conversion of fructose and yield of 5-HMF are increased to 46.1% and 22.3% respectively. Meanwhile, produced 5-HMF is extracted from aqueous phase into organic phase with high purity. Such in-situ extraction not only improves the yield but also

is desirable for convenient and high purity collection of 5-HMF. However, a large amount of condensation compounds (42.1%) is still observed. Previous work has shown that DMSO can effectively inhibit the formation of condensations such as insoluble humins [27]. As shown in Fig. 3a, with addition of DMSO in water (DMSO: water of v/v of 7:3), conversion of fructose and yield of 5-HMF are significantly enhanced to 89.5% and 41.7% while the undesired condensation compounds are obviously decreased to 38.1%. However, it is difficult to separate 5-HMF from DMSO by distillation because DMSO has a high boiling point (189 °C). Therefore, it is conceivable that combining both extraction solvent and inhibitory solvent shall be desirable. Indeed, in the biphasic system (aqueous phase containing DMSO and water with v/v of 7:3; organic phase containing MIBK and butanol with v/v of 7:3; total aqueous to organic w/w ratio of 1:2), conversion of fructose and the yield of 5-HMF are increased to 91.8% and 51.7%, while condensation is decreased to 36.5% (Fig. S4 in SI). Noteworthy, this system allows collection of 5-HMF with high purity simply by evaporation while SGQDs remain in the aqueous phase.

Also note that in the above experiments, we used a very high fructose concentration (20 wt.%). Generally, a high substrate concentration is preferable to improve the absolute production yield in a chemo-catalytic process. But the higher the initial fructose concentration the lower production yield of 5-HMF due to formation of condensation compounds (Fig. 3b). Therefore, most of current methods do not use initial fructose concentration >5 wt.% [40, 41]. Not surprisingly, when we reduce the initial fructose concentration to 5 wt.%, the yield of 5-HMF is further increased to 65.3% (Fig. 3b). The allowance of high substrate concentration by SGQD is attributable to its abundant medium acid sites which favours the dehydration of fructose to 5-HMF since strong acid sites are favourable for the formation of unwanted coking material (e.g. char, humins) [42]. Increase of fructose concentration leads to a higher conversion due to the

production of more condensation products through polymerization of fructose [43]. Therefore, 20 wt.% of fructose is chosen to balance the absolute production yield and selectivity of 5-HMF.

Various acid catalysts at the same dosage are tested for comparison (Table 1). Notably, even weakly acidic GQDs can give a 5-HMF yield of 31.2% and a fructose conversion of 54.6%, outperforming other non-SO₃H functionalized graphene oxide sheets with similar total acidity [36]. This implies that the quasi-homogeneity of GQD is desirable owing to full exposure of the active sites to the reactants in the same phase and unhindered mass transport. SGQD is much superior not only to original GQD because of its abundant medium Brønsted acidic sites but also to the common heterogeneous catalysts (Amberlyst-15, ZSM-5 and Nafion), sulfonated carbon nanotube (SCNT), and sulfonated activated carbon (SAC) with a considerably higher SO₃H density (entry 7-11, Table 1) because of the full utilization of SGQD's active sites. As shown in Fig. S5a and S5b (SI), although the SO₃H density and total acidity of SGQD are lower than some solid catalysts, it outperforms them. It suggests that the quasi-homogeneity and other properties of SGQDs also play important roles.

Remarkably, SGQD even exhibits better catalytic activity than the commonly used homogeneous catalysts (Brønsted acidic ionic liquid and H₂SO₄) which have much higher total acidity than SGQD (entry 4 and 6, Table 1). It implies that the physicochemical properties of SGQD also determine its catalytic performance. Conceivably, the chemical moieties on SGQDs may exert synergistic effects. Although HCl offers slightly higher yield than SGQD, it is corrosive, environmental unfriendly and not recoverable. Interestingly, in contrast to other heterogeneous or homogeneous catalysts, SGQD gives almost 100% carbon mass balance without apparent carbon loss to rehydration reaction and production of CO₂. It means that fructose dehydration and condensation are the two dominating reactions catalysed in parallel by

SGQD. We speculate that it may be possible to further functionalize SGQD in order to inhibit the condensation pathway whereby to improve the yield and selectivity of 5-HMF production.

SGQD was further evaluated for biomass transformation to 5-HMF using different feedstocks. As shown in Table 2, dehydrations of inulin and xylose catalysed by SGQD give 52.3% and 18.3% of 5-HMF yield respectively. Xylose is the major compound in hemi-cellulose while inulin is a fructose polymer obtainable from chicory, the successful degradation of these compounds suggests the potential of SGQD in biomass transformation. Sucrose is the most abundant disaccharide containing a glucose unit and a fructose unit. 39.2% yield of 5-HMF is obtained from sucrose. When glucose is subjected to this reaction, 19.5% yield and 45.1% conversion rate are obtained (entry4, Table 2). In contrast to fructose dehydration via cyclic furanose intermediate pathway, glucose dehydration undertakes acyclic intermediate pathway mediated by Brønsted acidic sites on SGQD [44]. Due to the stable acyclic structure of the sugar intermediates, the energy barrier for 5-HMF production is much higher from glucose than from fructose. Interestingly, the yield of 5-HMF from glucose catalysed by SGQD is considerably higher than that from commonly used SO_3H -functionalized catalysts (typically <5%) [45]. Therefore, it is conceivable that the Lewis acid sites on SGQD catalyse the isomerization of glucose into fructose with a low energy barrier and subsequently Brønsted acidic sites converts fructose into 5-HMF (scheme 1). As compared to glucose, cellobiose shows a slight decrease of 5-HMF yield (13.2%) but much higher conversion (91.2%). Surprisingly, a good 5-HMF yield of 22.2 wt% and conversion rate of 78.9% is produced from cellulose under atmospheric pressure, which is the most abundant biomass resources and whose decomposition involves a cascade of complicated reactions [46]. Likely, SGQD is able to readily catalyse cellobiose and cellulose into glucose because of abundant medium

Brønsted acid sites on SGQD (Fig.1d). These results demonstrate the unique potential of SGQD for transformation of nonedible lignocellulosic biomass.

The enhanced catalytic performance of SGQD cannot be explained only by the good dispersibility and the strong Brønsted acidity since H_2SO_4 is inferior to SGQD in fructose dehydration (Table 1). In a study using a sulfonated amorphous carbon material, Suganuma et al guessed that -OH groups can adsorb cellulose whereby facilitating the proton attack on cellulose from $-\text{SO}_3\text{H}$ groups [22]. Pravin et al also suggested that the synergistic effect of $-\text{SO}_3\text{H}$ with other functional groups such as -OH and $-\text{COOH}$ is responsible for the high catalytic performance in decomposition of glucose [29]. Nonetheless, they just provide a hypothesis rather than any mechanistic insights into this synergistic effect. Since SGQD predominately carry $-\text{COOH}$, -OH, and SO_3H groups, the synergic cooperation between the groups and the reactant can be similarly speculated. A DFT calculation is performed to investigate the hydrogen bonding interactions between fructose and the -OH group, $-\text{COOH}$ group, and $-\text{SO}_3\text{H}$ group on SGQD. Different geometries with possible interaction modes between fructose and the three groups of SGQDs are systematically optimized (Fig. S6). The most three stable geometries with lowest relative zero-point energy (ΔE_{ZPE}^*) in the three respective groups are obtained and as indicated as geometry I, geometry II and geometry III respectively (as shown in Fig. 4). The cartesian coordinates of the three geometries are shown in Table S1. The HB distribution is identified in these geometries. As seen, two inter-HBs ($\text{O}_1\text{-H}_1\text{...O}_2$ and $\text{O}_3\text{-H}_5\text{...O}_4$) and three intra-HBs ($\text{O}_4\text{-H}_3\text{...O}_1$, $\text{O}_2\text{-H}_4\text{...O}_5$ and $\text{O}_5\text{-H}_2\text{...O}_3$) are observed in the geometry I. These HBs form a loop which presumably resulting in strong affinity of SGQDs for the fructose molecule. Because a small SGQD has abundant and uniformly distributed $-\text{SO}_3\text{H}$ groups (Fig. 2a), which shall be available in the close vicinity of the interacting fructose. The proton attack from the $-\text{SO}_3\text{H}$

group of SGQDs on the O₅-H₂ group at the anomeric carbon atom in fructose will become more efficient due to their close proximity. Since the protonation of O₅-H₂ is the most thermodynamically favoured step that induces the subsequent dehydration steps to produce 5-HMF, the efficient protonation of it will result in enhanced reaction efficiency. Although similar HB distribution is also observed in geometry II and geometry III, the HB strength and interaction energy (E) of the three geometries are different. As seen in Table 3, the parameters of charge density (ρ), the Laplacians of the charge density ($\nabla^2\rho$), and the energy density (H), which are considered as the descriptors of the hydrogen-bonding strength, show that the intra-molecular HB of O₄-H₃...O₁ in geometry I presents the largest charge ρ , $\nabla^2\rho$ and H among all the HBs, implying the strongest interaction between the two neighbouring -OH groups in SGQDs. This HB is even higher than the inter-molecular HB of O₁-H₁...O₂ in geometry III which is well-known to be a strong HB. The significantly stronger HB strength of O₄-H₃...O₁ is probably due to the σ -type orbital overlap between the lone pairs of O₁ as HB acceptor and the bonding orbital of O₄-H₃ as HB donator. The participation of O₃-H₄...O₁ in the loop is believed to facilitate the stabilization of geometry I, resulting in a much lower E than that of geometry II and geometry III. Accordingly, the presence of HB resulted from the neighbouring -OH groups is predominantly responsible for the strong affinity of SGQDs with fructose *via* the HB loop while the -COOH groups and the -SO₃H groups execute Brønsted acid function as catalytic active sites. But -SO₃H is more catalytically active than -COOH. In sum, SGQD absorb fructose via the strong HB resulting from the neighbouring -OH groups on SGQD (the blue shift in the Raman spectra of SGQD indicates the presence of adjacent -OH groups) while the -COOH groups and -SO₃H groups, rather than form the HBs with fructose, release the proton to activate the fructose. Such synergy greatly enhances the catalytic efficiency.

To experimentally illustrate their critical roles, -OH groups on SGQD are blocked by methoxytrimethylsilane (MTS), which is confirmed by the decrease of the hydrophilicity index (HI) of SGQD-MTS from 2.86 to 2.61. As the consequence, 5-HMF yield and conversion rate obtained from SGQD-MTS is drastically reduced (yield: 29.1% vs. 51.7%; conversion: 69.8% vs. 91.8%) as compared with SGQD (Table 1). This experiment unambiguously corroborates the critical importance of -OH groups on SGQD. When -OH groups are not present, the degradation in catalytic performance is attributable to i) weakened interaction between SGQD and fructose and ii) weakened Brønsted acidity from $\text{-SO}_3\text{H}$ groups because they can form HBs with fructose.

After reaction, the biphasic reaction system undertakes phase separation without stirring. 5-HMF molecules were extracted into the organic phase while SGQDs are still homogeneously dispersed in the aqueous phase. Subsequently 5-HMF molecules can be simply collected from the organic phase by evaporation while SGQDs are separated from the aqueous phase by dialysis for reuse (Fig. 5a). As shown in Fig. 5b, even after 7 times of reuse, 36.8% of 5-HMF yield and 81.3% of fructose conversion still can be achieved. This is likely due to ~ 0.85 mol% S loss as revealed by element analyses. On the other hand, FTIR characterization shows that $\text{-SO}_3\text{H}$ groups, Brønsted acidity, and Lewis acidity are still well-preserved in SGQDs after reuses (Fig. S7). Similar to SGQD, after 5 times of reuse of GQD, its 5-HMF yield and fructose conversion rate only slightly decreased from 31.2% to 28.7% and 54.6% to 50.3% respectively. Furthermore, TEM and TEM-EDS characterizations of reused GQDs and SGQDs indicate that the morphology, size and element contents of both GQD and SGQD are well preserved (Fig. S8 in SI). Unavoidably, a small amount of insoluble humins is produced from conversion of carbohydrates to 5-HMF. Deactivation of heterogeneous catalysts is largely caused by humins. In contrast, well-dispersed

SGQDs are immune from this. Even after reuses, SGQD is still highly and stably dissolvable. Taken together, SGQDs can serve as quasi-homogeneous carbocatalysts with both good efficiency and recyclability.

4. Conclusion

A novel quasi-homogeneous catalyst, namely sulfonated graphene quantum dots (SGQD), is developed for one-pot biomass transformation to 5-HMF. SGQD unify the advantages of both homogeneous and heterogeneous catalysts. Specifically, it can achieve high efficiency as homogeneous catalysts because its excellent dispersibility and molecular size ensure full accessibility by the reactants and unhindered mass transport. On the other hand, unlike the corrosive and unrecoverable homogeneous catalysts (e.g., H_2SO_4 , HCl), SGQD is environmental friendly, and can be recycled just like heterogeneous catalysts. Although sulfidizing GQDs requires strong acid, the amount needed is several orders lower than the acid needed as the homogeneous catalyst. Furthermore, the superior catalytic ability of SGQD is also benefited from the synergistic cooperation between the Brønsted acidic sites ($-\text{SO}_3\text{H}$ groups) and hydroxyl ($-\text{OH}$) groups on a SGQD. Lastly, the large amount of medium acid sites on a SGQD enhances its catalytic performance. This study suggests the potential of SGQD as an efficient and green carbocatalyst for one-pot transformation of biomass or biomass-derivatives and more generally the unique potential of functionalized GQDs as novel quasi-homogeneous catalysts for various reactions. In principle, GQDs could be equipped with multiple catalytic properties (e.g., by doping heteroatoms, grafting of different chemical moieties, or decoration with functional nanoparticles), so that, to gain the ability of one-pot catalysis of multi-step reaction to produce complex molecules in molecular proximity.

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Appendix A. Supplementary data

The Supplementary data can be found at DOI: 10.1039/x0xx00000x

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Scheme 1 Synthesis of SGQD and its quasi-homogeneous behaviour in one-pot carbohydrate transformation to hydroxymethylfurfural

Fig. 1 a) FTIR spectrum, b) Raman spectra, c) XPS spectra, and d) acidity characterization of GQDs and SGQDs

Fig. 2 (a) TEM image of SGQDs with corresponding EDS mapping for S element. (b) TEM-EDS line scanning with a spectrum for C, O, S element distribution. (c) AFM image of SGQDs. Inset shows the height profile along the indicated line. (d) Diameter distribution of SGQDs (n = 110). (e) height distribution of SGQDs (n = 152).

Fig. 3 Effects of solvent composition (a) and initial fructose concentration (b) on product yields (left y axis) and fructose conversion rate (right y axis).

Table 1. The efficiency of different catalysts in the dehydration of fructose

Entry	Amount of fructose (mg)	Total acidity ^b (mmol/g)	SO ₃ H density (mmol/g)	Conversion (%)	Molar yield (%)		
					5-HMF	Condensation Compounds	Rehydration Compounds
1	Blank	—	—	14.7	0.6	3.0	0.15
2	GQDs	2.0	—	54.6	31.2	17.6	0.78
3	SGQDs	4.7	3.1	91.8	51.7	36.5	1.34
4	H ₂ SO ₄	20.4	—	63.7	44.2	17.5	1.29
5	HCl	27.3	—	97.6	60.1	12.8	1.86
6	Brønsted ionic liquid	13.8	—	77.5	48.4	26.5	1.29
7	ZSM-5	0.6	—	27.3	8.5	1.36	2.67
8	Amberlyst-15	4.9	4.5	62.3	36.5	5.35	0.62
9	Nafion	0.7	6.8	49.1	30.2	3.25	0.75
10	SCNT	1.8	1.5	50.2	28.1	10.2	0.32
11	SAC	3.3	2.1	55.1	33.5	8.9	1.25
12	SGQDs-MTS	4.5	3.0	69.8	29.1	7.26	1.33

^aReaction condition: The initial fructose concentration of 20 wt% with respect to aqueous phase was used in the reaction. The catalyst dosage is 40 mg. The reaction was performed at 170°C for 2 h under a biphasic solvent system (7:3 (v/v) DMSO:water and 7:3 (v/v) MIBK:butanol).

^bTotal acidity was determined by titration.

$^{\circ}\text{SO}_3\text{H}$ density was determined by element analysis.

Table 2. Production of 5-HMF from various carbohydrates catalysed by SGQDs^a

Entry	Substrate	Conversion (%)	Molar yield (%)		
			5-HMF	Condensation compounds	Rehydration compounds
1	Inulin	90.7	52.3	—	0.87
2	Xylose	41.9	18.3	14.9	7.85
3	Sucrose	79.5	39.2	—	1.68
4	Glucose	45.1	19.5	4.68	1.35
5	Cellobiose	91.2	13.2	19.4	0.11
7	Ball-milled cellulose ^b	78.9	22.2	40.7	10.2

^aReaction condition: The initial concentration of substrate is 10 wt%. The catalyst concentration is 60 mg. The reaction was performed at 170°C for 2 h under a biphasic solvent system (7:3 (v/v) DMSO:water and 7:3 (v/v) MIBK:butanol).

^bThe reaction is conducted in a 15 mL autoclave in presence of 25mg cellulose and 100mg SGQDs under hydrothermal for 2 h at 170°C. The yield of all the products in the reaction refers to weight percentage (wt%)

Geometry I : SGQDs-OH.....F

Geometry II : SGQDs-COOH.....F

Geometry III : SGQDs-SO₃H.....F

..... Intra-molecular HB Inter-molecular HB

Fig. 4 Hydrogen bonding between fructose (F) and functional groups of -OH, -COOH , and -SO₃H in SGQDs

Table 3 Charge density (ρ), Laplacian of charge density($\nabla^2\rho$), and Energy density (H) at the bond critical point of HBs by AIM study and interaction energies at B3LYP/6-311++G(d) level of theory.

Complexes	I					II				III			
	Inter-molecular HB		Intra-molecular HB			Inter-molecular HB		Intra-molecular HB		Inter-molecular HB		Intra-molecular HB	
	O ₁ -H ₁ ...O ₂	O ₃ -H ₅ ...O ₄	O ₄ -H ₃ ...O ₁	O ₂ -H ₄ ...O ₅	O ₅ -H ₂ ...O ₃	O ₁ -H ₁ ...O ₂	O ₃ -H ₂ ...O ₄	O ₆ -H ₃ ...O ₁	O ₅ -H ₄ ...O ₆	O ₁ -H ₁ ...O ₂	O ₄ -H ₂ ...O ₃	O ₂ -H ₃ ...O ₅	O ₅ -H ₄ ...O ₄
ρ (*10 ⁻²)	5.174	2.853	6.774	4.144	2.883	3.351	5.020	3.171	2.534	6.032	2.991	4.340	3.168
$\nabla^2\rho$ (*10 ⁻¹)	1.489	0.818	2.038	1.337	9.587	1.089	1.546	1.032	0.985	1.687	0.943	1.404	1.036
H(*10 ⁻⁴ a.u.)	-36.65	-17.63	-75.15	-19.04	-9.886	-5.349	-22.97	-13.04	-6.275	-54.10	-9.917	-19.71	-12.82
E ^a (kJ/mol)			14.64					33.68				36.89	

^aE is the interaction energy between the pairs and the corresponding isolated compound. All of the energies include BSSE and ZPVE corrections based on the results at the B3LYP/6-311++G(d) level of theory.

Fig. 5 a) Recycling scheme. b) The performance of recycled SGQDs in dehydration of fructose to 5-HMF. The reaction conditions are the same as that in Table 1.