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# Transition Metal-Free Carbon Quantum Dots for Selective Liquid Phase Oxidation of Alcohols Using Water as an Only Solvent

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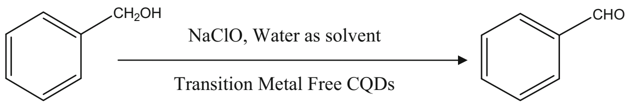
**Abstract** Transition metal-free oxidation of alcohols catalyzed by carbon quantum dots (CQDs) with NaClO oxidant using water as an only solvent was developed. High quality CQDs were synthesized via a simple one-pot electrochemistry method using cheap graphite rod as substrate materials, without the assistance of any chemicals but only pure water. The morphologies and composition of the resulting catalyst were characterized in detail. The results indicated that the CQDs catalyst showed higher activity and selectivity comparing to other carbon based transition metal-free catalyst (such as carbon nanotubes, graphene et al.) in the selective oxidation of alcohols to aldehydes. The high performance of the CQDs can be mainly attributed to its small particle size and large amounts of surface oxygen containing groups. The CQDs catalyst can be reused five times without any significant loss in their catalytic activities.

## Graphical Abstract



**Keywords** Carbon quantum dots · Selective oxidation · Alcohols · Transition metal-free · Oxidant

## 1 Introduction

Oxidation of organic compounds to their high value-added chemicals via a green route under mild condition is gathering much attention in organic chemistry. In particular, the selective conversion of alcohols to their corresponding carbonyl compounds plays a key role in organic synthesis, because the obtained products are highly valuable intermediates for pharmaceuticals and perfumery industries [1–5]. In industry, stoichiometric oxidants, such as permanganate, perchlorate et al., were widely used, leading to quantities of environmental pollutions. In order to deal with these problems, heterogeneous solid catalysts were developed. Excellent activities and selectivity have been achieved with noble metal and metal oxide based catalysts, such as Ru [6], Pd [4, 7], Ag [8], Au [5, 9], $RuO_2$ [10] and $MnO_2$ et al. [11]. However, these noble metals or metal oxides are not only relatively expensive but also they generated quantities of environmental pollutions [12].

To deal with these problems, metal free carbon based nanomaterials such as carbon nanotubes [13, 14], graphene oxides [15], graphene [16] et al., have been used to catalyze the oxidation reaction. This is owing to that carbon based nanomaterials offer unique physicochemical properties such as high specific surface areas, easy recovery, environmental acceptability, corrosion resistance, high activity, thermal stability under non-oxidative condition and readily surface modification [14–17]. For example, Su and co-workers [17] elegantly demonstrated that partially oxidized carbon nanotubes (CNTs) were able to catalytically dehydrogenate n-butane to 1-butene, albeit with modest conversion. Bielawski and co-workers showed the potential of harnessing the reactivity of graphene oxide for various synthetic reactions, demonstrating the efficient oxidation of benzyl alcohol to benzaldehyde [15]. Luo and

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coauthors [18] reported a transition metal-free carbon nanotubes catalyst system for aerobic oxidation of alcohols. Although molecular oxygen was used as a terminal oxidant, other additives such as $HNO_3$ were necessary to fulfill the reactions. However, these carbon based nanomaterials suffer from low dispersion and needing other additives. Therefore, there is continue need to develop transition metal free carbon based nanomaterials to contribute to the sustainability and efficiency of these processes.

Recently, carbon quantum dots (CQDs) has widely received attention because of their unique chemical and physical properties. Most notably, CQDs have been already proven to be attractive alternatives to conventional metal-based catalysts for several important applications, for example, photocatalytic applications [19–21], solar cells [22], bioimaging [23, 24] or fuel cell catalyst [25]. It is of particular interest to know whether it is possible to oxidize alcohols to get higher-value added product aldehydes or ketones by using cheap CQDs catalyst.

On the basis of sustainable and efficient principle, we report a facile approach to prepare CQDs and transition metal-free oxidation of alcohols catalyzed by CQDs has been developed with cheap oxidant using only water as the solvent. In comparison with alcohols oxidation using molecular oxygen oxidant in a water/1,4-dioxane mixture and using aqueous hydrogen peroxide in organic solvent, the present catalyst system presents substrate-selective performance towards alcohols oxidation and the reaction could occur entirely in water. These results provide an attractive transition metal-free alternative to noble-metal-catalyzed systems for alcohol oxidation, and push forward the research on carbon catalysis.

## 2 Experimental

### 2.1 Preparation of CQDs Catalyst

All reagents for synthesis and analysis were commercially available and used without further treatments. Carbon nanotubes were from Tsinghua University and Graphene were got from Ningbo institute of industrial technology. CQDs were prepared based on a facile one-pot electrochemistry method. In a typical process, Two graphite rods was inserted parallel into the ultrapure water as the electrode with a separation of 10 cm, Static potentials of 15–60 V were applied to the two electrodes using a direct current (DC) power supply. After 120 h continuous stirring, a dark-yellow solution appeared gradually in the reactor. The solution was filtered with slow-speed quantitative filter paper, and the resultant solution was centrifuged at 10,000 rpm for 10 min to remove the precipitated graphite particles. Finally, the obtained solution was water soluble CQDs. Bulk quantities of CQDs can be recovered by drying at 90 °C. To reduce the CQDs, the CQDs and hydrazine hydrate with mole ratio of 1:1 were put into reactor under 0 °C for 1 h.

### 2.2 Characterization of Catalyst

The morphologies and structure details of the as-synthesized samples were studied by using transmission electron microscopy (TEM, JEOL-JEM-2010F, Japan). The crystal structures of the samples were characterized by X-ray diffraction (XRD) (Bruker D8 Advance diffractometer, Germany) at a scanning rate of 4°/min (Cu Kα radiation, $\lambda = 0.154\ 18$ nm). X-ray photoelectron spectroscopy (XPS) analysis was performed with an ESCALa-b220i-XLelectronspectrometer (VG Scientific, England) using 300 W Al Kα radiation. Fourier transform infrared spectroscopy (FT-IR) experiments were conducted on a Nicolet 670 FT-IR (Thermoelectric, USA) spectrometer in the form of KBr pellets.

### 2.3 Catalytic Oxidation of Alcohols

The oxidation reactions were carried out in a 100 ml flask (with a condenser) containing 1 mmol alcohol, 0.1 g CQDs, and 25 mL deionized water as solvent. The mixture was stirred to form suspension. Then 5 mL of 10 % NaClO was slowly added. The reactions were conducted at 70 °C under ambient pressure for 6 h. When the reaction was finished, the mixture was extracted by ethyl acetate (2 × 30 mL).Then ethyl acetate was removed in vacuum. Oxygenated products were analyzed by an Agilent 7890A Gas Chromatographer (GC). Furthermore, for the test of reusability, the used catalyst was removed from the reaction by filtration and washed with deionized water and acetone, and dried in air.

## 3 Results and Discussion

### 3.1 Catalyst Characterization

The obtained CQDs catalyst was thoroughly characterized to establish its physical and chemical characteristics. Figure 1a shows the TEM image of the obtained CQDs, revealing that the average diameters of CQDs are about 4 nm. The HRTEM image (Fig. 1b) exhibits the crystal lattice spacing around 0.33 nm, showing its main $sp^2$ hybrid structure [26]. For the structure measurement, we took pristine graphite rod as the comparison. The XRD patterns of the CQDs and pristine graphite rod are shown in Fig. 2a. A detailed comparison of the CQDs samples

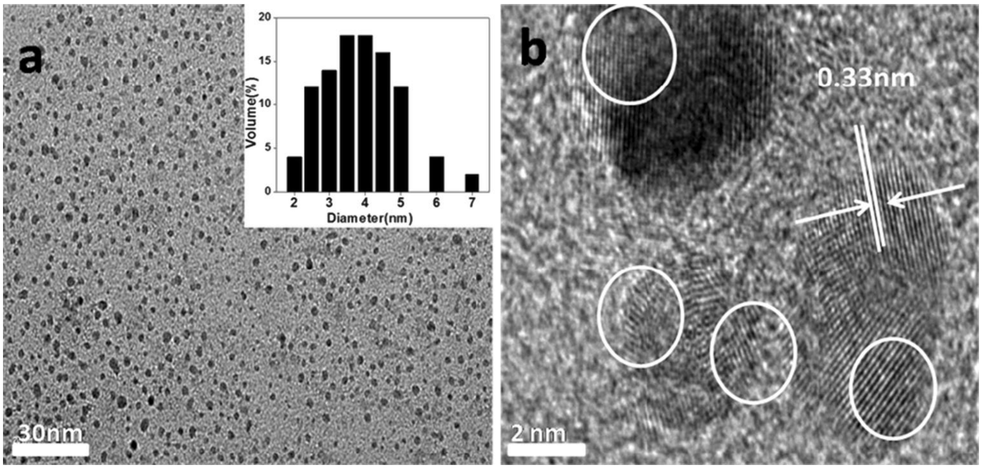


**Fig. 1** Low resolution (**a**) and high resolution (**b**) TEM images of CQDs catalyst. The insert picture in (**a**) is the size distribution of CQDs

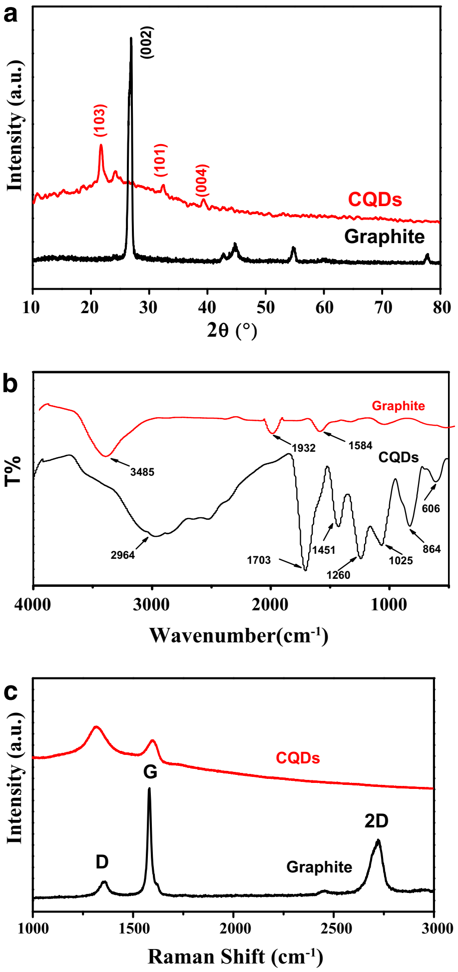


**Fig. 2** XRD patterns (**a**), FT-IR spectra (**b**) and Raman spectra ($\lambda_{ex} = 633$ nm) (**c**) of graphite and CQDs catalyst

reveals that the electrochemical oxidation process leads to weak, broadened graphite peaks compared to pristine graphite samples. The decrease in the peak intensity indicates the transformation of crystalline graphite into nano-size structure carbon, and the partial conversion of $sp^2$-hybridized C=C in the aromatic ring into $sp^3$-hybridized C=C in the CQDs [21, 27]. Figure 2b shows the FT-IR spectra of graphite rod and CQDs. Three peaks are observed in the FT-IR spectrum of graphite, while for the CQDs, seven peaks are found. The appearance of the new peaks for the CQDs correspond to the oxygen-containing groups and other new functional groups, indicating successful oxidation of graphite and the formation of hydrophilic groups, these oxygen containing groups are reported as the active center for catalytic oxidations. The Raman spectra ($\lambda$ ex = 633 nm) of the CQDs and pristine graphite are shown in Fig. 2c. The intensity ratio of the D and G band ($I_D/I_G$) is a measurement of the disorder extent, as well as the ratio of $sp^3/sp^2$ carbons [21]. In our case, the CQDs showed the $I_D/I_G$ ratios were 1.234. During the graphite oxidation, some structure defects appeared in the CQDs, such as oxygenated groups (C–O, C=O, O–C=O) in the $sp^2$ carbon site, and then vacant lattice sites and $sp^3$ carbons were produced [28], which is accordant with the results of FT-IR characterization.

To further confirm the nature of the functional groups on the surface of CQDs, we carried out XPS characterization. Figure 3a shows the XPS overall spectrum of CQDs, The surface analysis indicated that C, O elements existed on the sample surface. No other impurities were detected. Figure 3b shows the XPS spectra of C1 s, from which we can see that there were four clear peaks assigned to four types

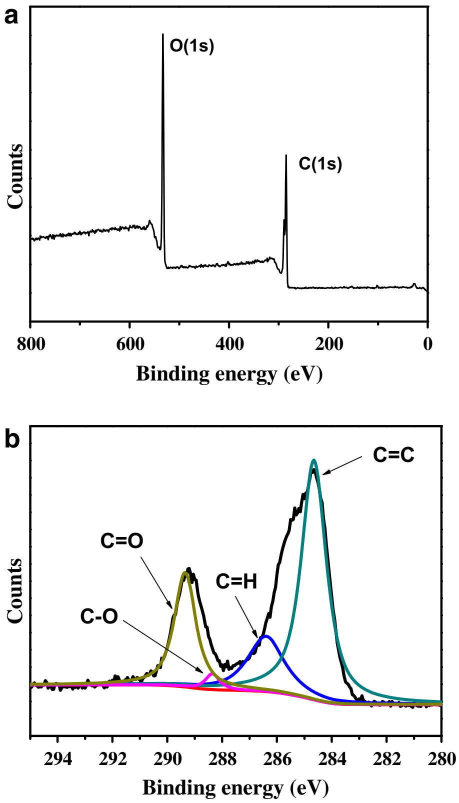


**Fig. 3** Overall (**a**) and C 1 s XPS spectra of CQDs catalyst (**b**)

of carbon with different chemical valences: non-oxygenated ring C (284.6 eV), carbon in C–O bonds (286.4 eV), carbonyl C (288.3 eV), and carboxylate carbon (O–C=O) (289.3 eV) [29], which is consistent with the results from FI-IR and Raman characterizations. On the basis of the above results, we can conclude that the oxygen functional groups are formed through the electrochemical oxidation processes, and the sp$^2$-hybridized C=C in aromatic ring in graphite are partially decomposed into oxygen functional groups in the CQDs. These functional groups may contribute to the oxidation reactions as active sites.

## 3.2 Catalytic Properties

The oxidation of alcohols was used to test the catalytic activities of the CQDs catalyst. Before discussing the effect of CQDs catalyst on the catalytic activities of the selective liquid phase oxidation of alcohols, various oxidants such as molecular oxygen, air, hydrogen peroxide and NaClO were subject to benzyl alcohol oxidation, and the result is shown in Table 1. Among the oxidants used, the addition of NaClO oxidant significantly prompted the oxidation. Then different reaction conditions including the amount of NaOCl, the amount of CQDs, oxidants and reaction temperature were investigated. As a result, 0.5 g CQDs, 10 mL of NaOCl (10 %) and 70 °C were chosen as a suitable reaction condition for oxidation of alcohols. The conversion of 75 % from benzyl alcohol to benzaldehyde could be achieved within 6 h without the formation of by-products such as benzoic acid. At the same time, in absence of catalyst, the system can only deliver a very low conversion, demonstrating that the CQDs are the active catalyst. Moreover, the carbon nanotubes and graphene have been used as catalysts for making comparison. As shown in Table 1, under the same reaction conditions, the CQDs showed highest catalytic activities. This may due to that carbon nanotubes and graphene cannot be well dispersed in the reaction system, especially in aqueous systems. On the contrary, the CQDs catalyst showed high dispersity in the aqueous system contributed by its small particle size and high surface oxygen containing groups, supported by the results from FT-IR and XPS characterizations.

**Table 1** Benzyl alcohol oxidation by various oxidants and other carbon materials

| Entry | Oxidant | Conversion (%) | Selectivity (%) |
|---|---|---|---|
| 1 | $O_2$ | 3 | >99.9 |
| 2 | 30 % $H_2O_2$ (5 mL) | 3 | >99.9 |
| 3 | 10 % NaClO (5 mL) | 75 | >99.9 |
| 4[a] | 10 % NaClO (5 mL) | 6 | >99.9 |
| 5[b] | 10 % NaClO (5 mL) | 12 | >99.9 |
| 6[c] | 10 % NaClO (5 mL) | 7 | >99.9 |

Reaction conditions: benzyl alcohol (1 mmol), CQDs (0.1 g), $H_2O$ (25 mL), 6 h, 70 °C

[a] Blank experiment, without addition of catalyst

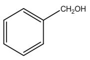
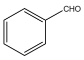
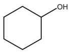
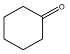
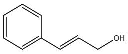
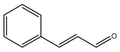
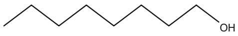
[b] Carbon nanotubes

[c] Graphene

In view of the efficient oxidation of benzyl alcohol, the oxidations for various other alcohols were investigated and the results are shown in Table 2. CQDs catalyst also displayed high activity in the oxidation of other alcohols. Cyclohexanol was significantly oxidized into cyclohexanone with 68 % conversion in 10 h. In addition, Cinnamic alcohol was oxidized into Cinnamic aldehyde with conversion of 36 % in 7 h without byproduct. N-octanol was oxidized into n-caprylic aldehyde with 100 % conversion in 6.5 h. For CQDs catalyst, its high catalytic activity benefits from its high dispersity in polar water system, which contributed by the high amounts of the oxygen containing groups. Above results demonstrated that the CQDs catalyst is an excellent material for selective liquid phase oxidation, which provide high activity for selective oxidation of alcohols.

Considering the only existed oxygen containing groups on the surface of the CQDs and the water system used, the

**Table 2** Oxidation of various alcohols

| Entry | Substrate | Product | Time (h) | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|---|
| 1 |  |  | 6 | 75 | >99 |
| 2 |  |  | 10 | 68 | >99 |
| 3 |  |  | 7 | 36 | >99 |
| 4 |  |  | 6 | 100 | >99 |

Reaction conditions: substrate (1 mmol), CQDs (0.1 g), 10 % NaClO (5 mL), $H_2O$ (25 mL), 70 °C

mechanism for the oxidation of alcohols might follow the SN1 mechanism, which is similar to the β-cyclodextrin system [30]. A complex between CQDs catalyst and substrate was formed in situ first, followed by the formation of carbonium ion. This carbonium ion was then attacked by $ClO^-$ anion on carbon atom. Further elimination of HCl generates the corresponding aldehydes. It should be pointed that the existence of hydrogen bond derived from $H_2O$ obviously influenced the benzyl alcohol oxidation. In present reaction system, the addition of organic solvents gave the different reaction rate for benzyl alcohol oxidations, such as acetone (<1 % conversion) or acetonitrile (about 17 % conversion). It is found that the usage of acetone has a greater impact on the reaction rate than acetonitrile, indicating the importance of hydrogen bond. The hydrogen bond between acetone and water blocked the formation of the benzyl alcohol, $ClO^-$ and $H_2O$ complex, due to the weak hydrogen bond between benzyl alcohol and $H_2O$. The results also demonstrated that the CQDs catalyst were favorable for reaction by using water as a solvent.

In order to assess the stability of the catalysts, the catalyst was separated from the reaction mixture after each experiment by filtration and washed with deionized water and acetone, then dried in air. Figure 4 shows the reusability of the CQDs for selectivity oxidation of benzyl alcohol. No significant loss of activity and selectivity was observed after 5 runs. It can be observed that the catalyst could be reused at least five times with similar conversions of benzyl alcohol and selectivity for benzaldehyde, indicating the stability of CQDs catalyst. Thus, the results provide an attractive transition metal-free alternative catalyst to noble-metal-catalyzed systems for alcohol oxidation, and may push forward the research on carbon catalysis.

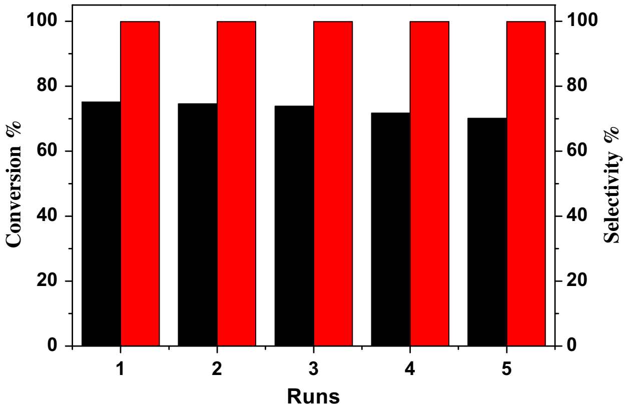


**Fig. 4** Reusability of the CQDs catalyst for the oxidation of benzyl alcohol. *Black* conversion, *Red* selectivity

## 4 Conclusions

In summary, a transition metal-free CQDs catalyst for oxidation of alcohols with cheap NaClO oxidant using water as the only solvent has been developed. The obtained CQDs catalyst showed high catalytic activities and selectivity compared to other carbon based transition metal free catalyst, such as carbon nanotubes and graphene, and it can be recovered readily without any significant loss in their catalytic activities. Its small particle size and large amounts of surface oxygen containing groups contributes to the high performance of the CQDs. Thus, the CQDs can be used as a recyclable catalyst for the oxidation of alcohols.

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