# Pt-$Co_3O_4$-CDs electrocatalyst with enhanced electrocatalytic performance and resistance to CO poisoning achieved by carbon dots and $Co_3O_4$ for direct methanol fuel cell

## Supporting Information

**Quantification of the hydroxyls and carboxylic groups on CDs.**

10 mg CDs was dissolved in 200 mL deionized water with sonication. After that, 5 mL 0.05M NaOH was added into the above solution. The solution was standing for 24 h at room temperature, then 0.05 M HCl was used as titrant to carry out back titration. According to the consumption of HCl (mL), the total quantity of both hydroxyls and carboxylic acid was estimated through the following calculation formula:

$$n(\text{carboxyl and hydroxyl}) = (5 - V)\ \text{mL} \times 0.05\ \text{mol L}^{-1}$$

The total quantity of both hydroxyls and carboxylic acid are listed in Table S2. To qualify the relative content ratio of carboxyl versus hydroxyl, conductometric titration was performed by using a DDS-11A conductance titrator. Dried CDs (100 mg), 40 mL of solvent (pyridine/acetone = 1/4), 1 mL of distilled water and 1 mL of ethanol were mixed in a 50 mL triangular flask. The mixture was thoroughly stirred at 150 rpm and 25 ºC for 10 min. Then, we prepared 0.005 mol $L^{-1}$ KOH-isopropyl alcohol standard solution as titrant. The data were recorded by the conductance titrator. The conductivity-titrant amount curve was shown in Figure S6b. Here, a and b represent the equivalence points for hydroxyl and carboxyl groups, respectively. The contents of carboxyl and hydroxyl groups were estimated as follows:

$$n(\text{carboxyl}) = V_a \times c$$

$$n(\text{hydroxyl}) = (V_b - V_a) \times c$$

$$\text{COOH/OH} = n(\text{carboxyl})/n(\text{hydroxyl}) = (V_a \times c)/[(V_b - V_a) \times c] = V_a/(V_b - V_a)$$

The relative content ratios of carboxyl and hydroxyl content of CDs-1 and CDs-2 were also gained with the same method.

**CO stripping.**

Highly pure CO was bubbled into 0.5M H2SO4 for 30 min while the working electrode was held at 0.2V vs SCE. Then N2 was purged into the system for 20 min to remove the non-adsorbed CO before the measurement was made. The CO stripping voltammetry was performed in the potential of -0.2-0.8 V at a scan rate of 50 mV s-1.

**DMFC performance evaluation.**

The single-cell performance of the as-synthesized catalysts for MOR was evaluated by fabricating membrane electrode assemblies (MEA). The proton exchange membrane used in the experiments was Nafion 117 (DuPont). The active cell area of MEA was 4 $cm^2$, which was fabricated using a spraying technology to apply the

catalyst layer. The catalyst ink was prepared by dispersing the catalysts into calculated amount of the dispersion liquid (produced by Hesen) and 5 wt% Nafion solution. For all MEAs in this study, the cathode consisted of Pt/C nanoparticles (20 wt%, Alfa Aesar) at a standard loading of 4.0 mg $cm^{-2}$. The anode catalyst loading of our as-synthesized composite materials was also 4.0 mg $cm^{-2}$ including the mass of the carbon supports. MEAs were obtained by sandwiching the Nafion-117 membrane between the anode and cathode followed by hot compaction under a pressure of 4 MPa at 150 °C for 3 min. The MEA was fitted between two graphite plates with a parallel serpentine flow bed. The polarization curves were obtained by a fuel cell test system (GEFC-10), high purity $O_2$ (99.99 %) is applied at 200 mL $min^{-1}$ as the cathode atmosphere and 2 M methanol as the reactant feed at the anode side at 2 mL $min^{-1}$. The polarization data were collected point by point. All MEAs were evaluated in DMFCs under atmospheric pressure.

## Supplementary tables.

**Table S1** - ICP results of various Pt-$Co_3O_4$-CDs/C electrocatalysts.

| element | Pt-$Co_3O_4$-CDs/C (mg/kg) | Pt-$Co_3O_4$/C (mg/kg) | Pt-CDs/C (mg/kg) | Pt-$Co_3O_4$-CDs-1/C (mg/kg) | Pt-$Co_3O_4$-CDs-2/C (mg/kg) |
|---|---|---|---|---|---|
| Pt | $1.24\times10^5$ | $1.2\times10^5$ | $1.21\times10^5$ | $1.32\times10^5$ | $1.27\times10^5$ |
| Co | $9.92\times10^4$ | $1.0\times10^5$ | — | $9.80\times10^4$ | $1.01\times10^5$ |

**Table S2** - The quantification of the hydroxyls and carboxylic groups on CDs.

| sample | Concentration (mg/L) | Carboxyl & Hydroxyl (mol/L) | Hydroxyl (mol) | carboxylic acid (mol) | Ratio (OH/COOH) |
|---|---|---|---|---|---|
| CDs | $0.5\times10^3$ | $2.95\times10^{-4}$ | $1.92\times10^{-4}$ | $0.64\times10^{-4}$ | 1.99:1 |
| CDs-1 | $0.5\times10^3$ | $1.74\times10^{-4}$ | $1.48\times10^{-4}$ | $0.40\times10^{-4}$ | 2.73:1 |
| CDs-2 | $0.5\times10^3$ | $1.03\times10^{-4}$ | $0.66\times10^{-4}$ | $0.28\times10^{-4}$ | 1.38:1 |

**Supplementary figures**.

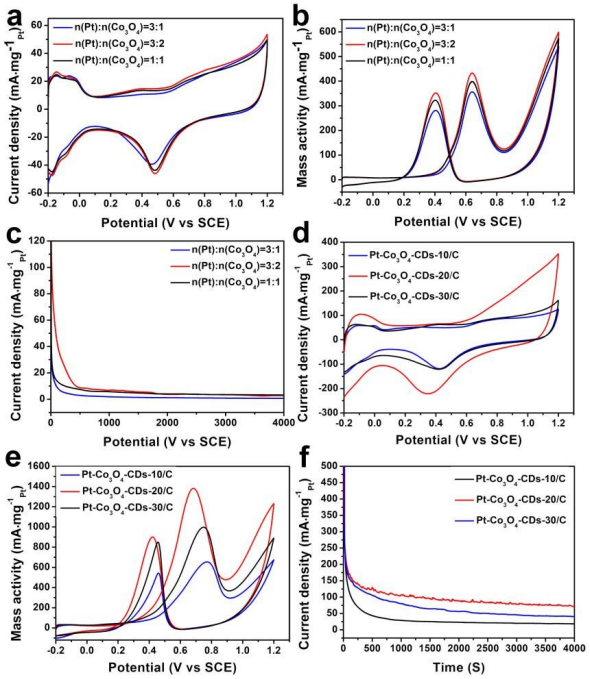


**Fig. S1** (a) CV curves of Pt-$Co_3O_4$-CDs/C with different ratio of Pt and $Co_3O_4$ ( n(Pt) : n($Co_3O_4$)=3:1, n(Pt) : n($Co_3O_4$)=3:2 and n(Pt) : n($Co_3O_4$)=1:1)) in 0.5 M $H_2SO_4$ with a scan rate of 50 mV $s^{-1}$. (b) CV curves of Pt-$Co_3O_4$-CDs/C with different ratio of Pt and $Co_3O_4$ ( n(Pt) : n($Co_3O_4$)=3:1, n(Pt) : n($Co_3O_4$)=3:2 and n(Pt) : n($Co_3O_4$)=1:1)) in 0.5 M $H_2SO_4$+ 1 M $CH_3OH$ with a scan rate of 50 mV $s^{-1}$. (c) The chronoamperometric curves of Pt-$Co_3O_4$-CDs/C with different ratio of Pt and $Co_3O_4$ ( n(Pt) : n($Co_3O_4$)=3:1, n(Pt) : n($Co_3O_4$)=3:2 and n(Pt) : n($Co_3O_4$)=1:1)) in 0.5 M $H_2SO_4$ + 1 M $CH_3OH$ at 0.65V (vs SCE)**.** (d) CV curves of Pt-$Co_3O_4$-CDs-10/C, Pt-$Co_3O_4$-CDs-20/C and Pt-$Co_3O_4$-CDs-30/C in 0.5 M $H_2SO_4$ with a scan rate of 50 mV $s^{-1}$. (e) CV curves of Pt-$Co_3O_4$-CDs-10/C, Pt-$Co_3O_4$-CDs-20/C and Pt-$Co_3O_4$-CDs-30/C in 0.5 M $H_2SO_4$ + 1 M $CH_3OH$ with a scan rate of 50 mV $s^{-1}$. (f) The chronoamperometric curves of Pt-$Co_3O_4$-CDs-10/C, Pt-$Co_3O_4$-CDs-20/C and Pt-$Co_3O_4$-CDs-30/C in 0.5 M $H_2SO_4$ + 1 M $CH_3OH$ at 0.65V (vs SCE). (The composite catalyst possesses 10, 20 and 30mg CDs were recorded as Pt-$Co_3O_4$-CDs-10/C, Pt-$Co_3O_4$-CDs-20/C and Pt-$Co_3O_4$-CDs-30/C, respectively.)

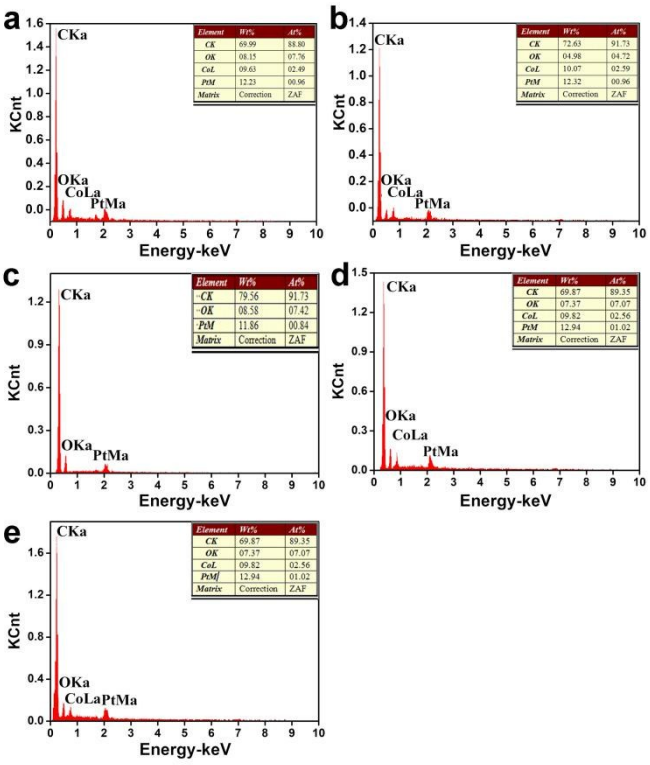


**Fig. S2** EDX patterns of (a) Pt-$Co_3O_4$-CDs/C, (b) Pt-$Co_3O_4$/C, (c) Pt-CDs/C, (d) Pt-$Co_3O_4$-CDs-1/C and (e) Pt-$Co_3O_4$-CDs-2/C.

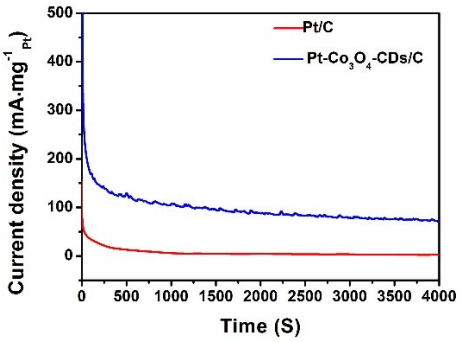


**Fig. S3** The chronoamperometric curves of Pt/C, Pt-$Co_3O_4$-CDs/C in 0.5 M $H_2SO_4$ + 1 M $CH_3OH$ at 0.65 V (vs SCE).

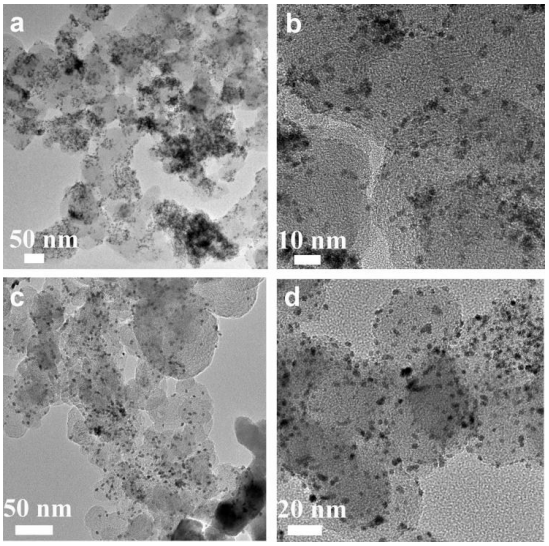


**Fig. S4** (a) and (b) TEM images of Pt-$Co_3O_4$/C; (c) and (d) TEM images of Pt-CDs/C.

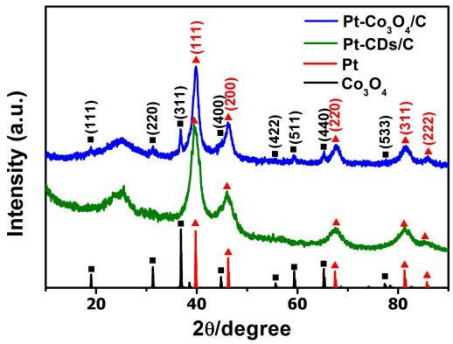


**Fig. S5** XRD patterns of Pt-$Co_3O_4$/C and Pt-CDs/C.

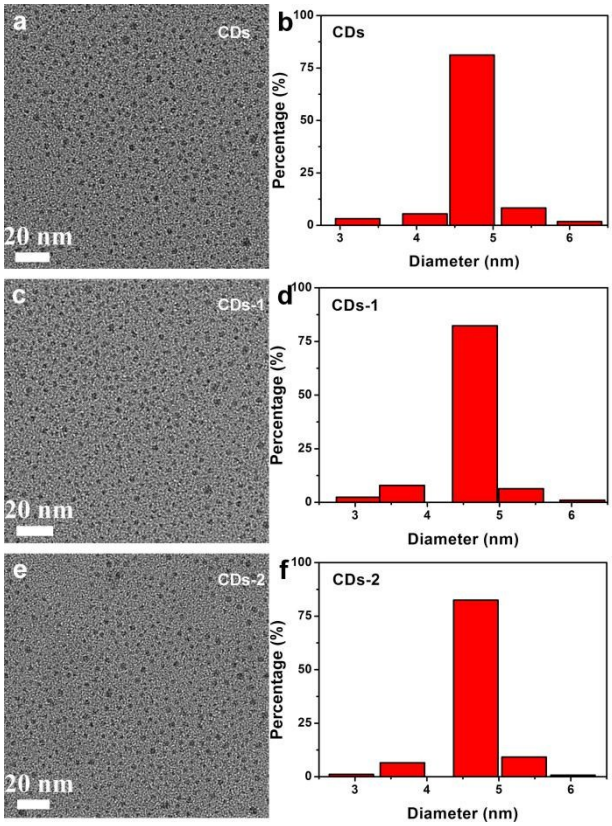


**Fig. S6** TEM images and the size distribution of CDs, CDs -1 and CDs-2.

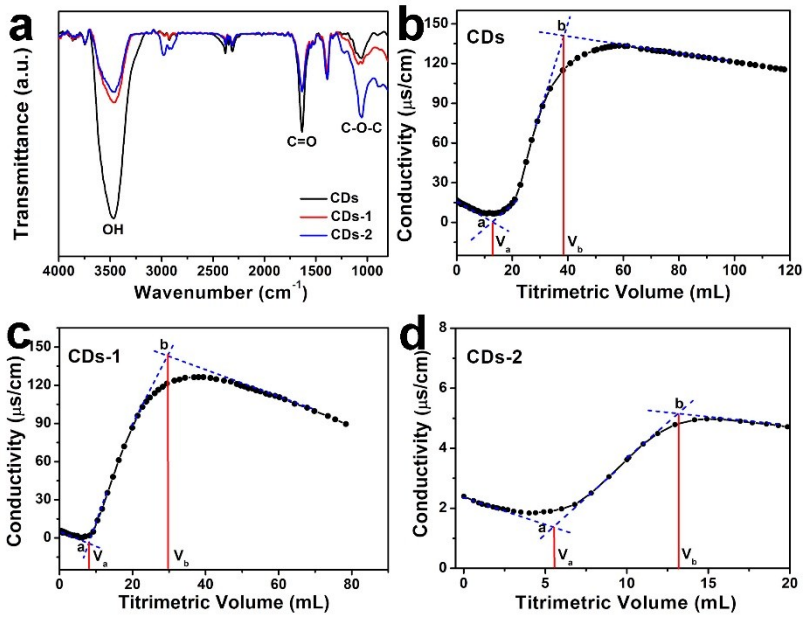


**Fig. S7** (a) FTIR spectrum of CDs, CDs-1, CDs-2. The conductivity-titrant amount curves of CDs (b), CDs-1 (c) and CDs-2 (d). The relative ratio of hydroxyls and carboxylic acid for CDs, CDs-1 and CDs-2 were about 1.99:1, 2.73:1 and 1.38:1, respectively.

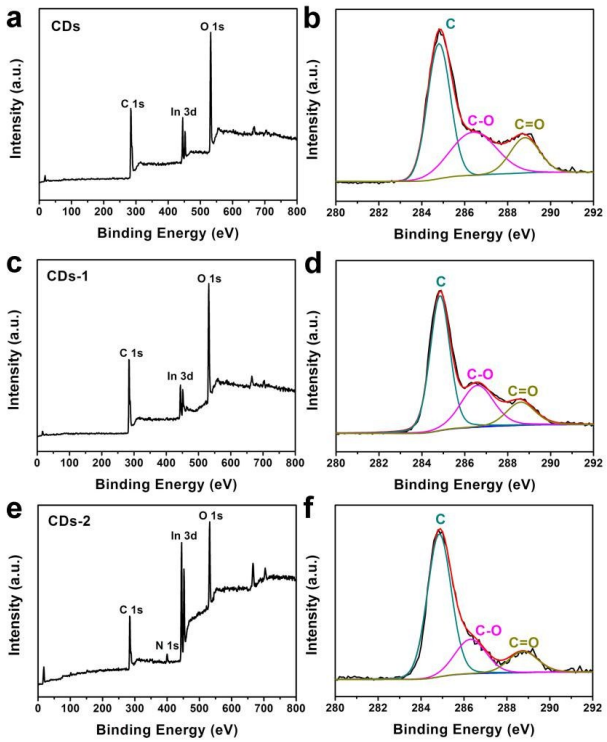


**Fig. S8** (a, c and e) XPS full survey spectra of CDs, CDs-1 and CDs-2. (b, d and f) High resolution C 1s XPS spectra of CDs, CDs-1 and CDs-2.