Stable Pt atomic clusters on carbon nanotubes grafted with carbon quantum dots as electrocatalyst for H₂ evolution in acidic electrolyte

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Abstract
Preparing stable highly dispersed Pt based electrocatalyst is promising to reduce material expense of H₂ product via electrocatalytic water splitting. However, it is still a great challenge to obtain stable single atomic Pt catalysts which can be applied in acidic electrolyte. In the present work, we synthesized Pt atomic clusters on carbon quantum dots (CQDs) grafting multiwall carbon nanotube (CNT) (Pt content: 1 wt.%) catalysts and then loading the catalysts on carbon cloth (Pt content: 0.01 mg cm⁻²) for activity test. The overpotential of 29 mV versus RHE was obtained over 1%Pt/CQDs/CNT catalysts at the current density of 10 mA cm⁻², and the Tafel slope of 22 mV decade⁻¹ was obtained, too. Especially, the catalysts showed significant stability in hydrogen evolution reactions (HER) in acidic solution, of which the overpotential was still smaller than that of 20%Pt/C after 10,000 CV cycles. CQDs provided coordinating sites for dispersing Pt atomic clusters and improved the H⁺ concentration in adjacent area around the Pt clusters. This method provides a general strategy to design the highly efficient electrocatalysts with ultra-low precious metals for H₂ evolution in acidic electrolyte.

KEYWORDS
acidic electrolyte, carbon nanotubes, carbon quantum dots, H₂ evolution, Pt atomic clusters

1 | INTRODUCTION

H₂ generation via electrolyzing water splitting in acid electrolytes has been considered as the most efficient method compared with those in pH-neutral and basic electrolytes. However, the harsh conditions lead to several ticklish problems which preventing the industrialization of electrolyzing water splitting in acid electrolytes, such as the dissolution of metal catalysts, large usage amount of precious metal (mainly Pt) and low stability of support or current collector.¹⁻⁶ Although catalysts working in mild pH conditions became increasingly attractive, the current activity of catalysts in pH neutral electrolytes is far from applicable, because the low H⁺/OH⁻ concentration in electrolytes may lead to low reaction rate governed by water dissociation on electrode. Especially, on the metal atomic
clusters (ACCs) or single atomic catalysts (SACs), the dissociation of H₂O can only be achieved by the cooperation between single atoms or atomic clusters and the surrounding coordinates on supports.[1–12]

Synthesizing ACCs may enlarge atom efficiency and then reduce the use amount of precious metal, which become very hot in catalysis researches including electrolysis.[1–13] To stabilize the metal atomic clusters, supports with high surface areas and specific coordination species are required to maintain a strong interaction between metal atoms and supports. Various supports have been explored for the stabilization of metal atomic clusters, such as heteroatom doped carbon (graphene,[6–10] carbon nanotube,[11,12] carbon nitride,[13] porous carbon,[14–16]) metal oxides,[17–19] metal hydroxides,[20] metal carbides,[21,22] metal sulfides,[23] metal selenide,[24] and porous metal.[25,26] The key issue to prepare ACCs for water splitting is finding a good support which has enough anchoring sites and good stability in wide-pH conditions as well as good conductivity. Pt atomic clusters on carbon catalysts were proved to exhibit better stability than traditional nanoparticulated counterparts in acidic electrolyte.[8,24] Besides the stability concerns of ACCs, for an energy-efficient HER, a catalyst must be able to trigger proton reduction with minimal overpotential and have fast kinetics. Unfortunately, heteroatom free carbon materials are not good supports for the dissociation of H₂O molecules although they are good current collector because of high conductivity, such as well crystalized graphene and carbon nanotube. Therefore, the HER activity of metal catalysts on heteroatom free carbon materials are much lower than those on supports which have water dissociation characterizations, such as metal/metal oxides.[27–31] CQDs is a new kind of functional nanocarbon which is less than 10 nm in diameter and has over 30% heteroatoms. Importantly, CQDs have abundant surface/edge sites and excellent electron acceptor/donor capability, which can disperse the atomic metal well and modify their electronic structures.[32–35] Theoretical calculations showed that CQDs improved the adsorption and dissociation of water molecules on Ru and enhancing electron-transfer ability of catalyst.[32] But the extremely strong hydrophilicity of CQDs restrains its usage in the electrode.[36] Our strategy is loading CQDs on CNT to make full use of the good conductivity of CNT and the heteroatom-rich surface of CQDs for dispersing Pt atomic clusters. The CQDs and nanotube was integrated via chemical bonds featuring a large surface area, high conductivity, and excellent electro/chemical/mechanical stability electrode. More importantly, CQDs could facilitate the water dissociation adjacent the Pt atomic clusters.

Generally, several steps are needed to obtain ACCs. For example, in the “bottom-up” synthetic route, mononuclear metal complexes are usually selected to load the atomic dispersion of metal on supports against aggregation. Further post-treatment is always needed for the removal of ligands of metal complexes. To avoid the formation of nanoparticles, the metal content (<1 wt.%), loading conditions (solvent type, temperature, and solution pH, etc.) and the post treatment must be controlled carefully. Such a long synthetic route and strict preparation conditions will increase the risk of failure in synthesizing ACCs and the expense of materials preparation. Recently, G. J. Hutchings reported low-boiling-point solvent assisted impregnation method to prepare atomic clusters dispersion of cationic metal species on activated carbon.[35] Similarly but differently, we prepared Pt atomic clusters on carbon quantum dots grafted multiwall nanotube (MWNT) via a modified method using chloroplatinic acid dissolved in methanol, self-made carbon quantum dots and commercial MWNT as the starting materials. All the starting materials were mixed by ultrasonic method and then kept at 80 °C for 6 hours to obtain the atomic clusters Pt/CQDs/CNT catalyst without further treatment (Scheme 1). CQDs addition is essential to obtain Pt atomic clusters on CNT, not the methanol. The present method was facile to prepare ACCs.

### RESULTS AND DISCUSSION

#### 2.1 Structural characterizations

**Figure 1A** shows the STEM images of 1%Pt/CNT, in which uniformly dispersed Pt nanoparticles in average sizes of 2.3 nm can be seen. Differently, many Pt atomic clusters on CQDs (5 nm) are found in 1%Pt/CQDs/CNT from Figure 1B–D. It is reasonable that CQDs grafting onto the trunks of MWCNTs can disperse the Pt species well due to many coordinative terminal oxygen groups on the surfaces of CQDs. However, the MWCNTs with few defects can only physically adsorb Pt nanoparticles as shown in Figure 1A. The actual Pt loading of catalysts is listed in Table 1 determined by ICP-OES.

**Figure 1E** shows the XRD profiles of catalysts. All the profiles are similar with CNTs. No structural changes of

| Catalysts     | Theoretical loading [wt.%] | Actual loading [wt.%] |
|---------------|-----------------------------|------------------------|
| 1%Pt/CQDs/CNT | 1                           | 0.947                  |
| 1%Pt/CNT      | 1                           | 0.963                  |

**TABLE 1** Pt loading of catalysts
CNTs can be detected after grafting CQDs and loading Pt species. The characteristic peaks of Pt are not observed in 1%Pt/CQDs/CNT, suggesting that Pt species are very uniformly dispersed on the CNT grafted with CQDs and there are no nanoparticles on it. Figure 1F is the Raman spectra of catalysts, in which only the typical bands of MWCNTs present. CQDs doesn’t lead to the re-construction of the surfaces of MWCNTs. Interestingly, CNTs can also act as the support for dispersing CQDs as indicated that no Raman signals of amorphous carbon can be found on 1%Pt/CQDs/CNT and no aggregation of CQDs in STEM images (Figure 1B–D) can be seen.

Figure 2 and Table 2 show the XPS results of catalysts. The peak fitting method is adopted as the primary approach to qualify and quantify the oxygen, carbon and platinum groups measured by XPS. The high-resolution O 1s seconds spectra (Figure 2C) of all samples indicate the co-existence of both O-C (533 eV) and O = C (532 eV). An increased proportion of O-C is clearly observed with the introduction of CQDs, which is due to the abundant...
hydroxyl groups on the surface of CQDs (Figure 2C and Table 2). Interestingly, compared with pure CNT, the binding energy (BE) of O-C is reduced by 0.3 eV and the BE of O = C is increased by 0.3 eV after CQDs grafting on CNT, which indicates that electrons have shifted from O = C to O-C. Considering that there are only carbonyls on CNT and most of the functional groups on CQDs are hydroxyls, this further indicates that the C-OH on CQDs has an electronic interaction with the O = C of carbonyls on CNT by hydrogen bonds which could facilitate the transfer of electrons from CNT to CQDs. However, the O 1s seconds spectra of 1%Pt/CQDs/CNT is almost the same as that of CQDs/CNT, which indicates that there is no charge transfer between Pt and CQDs/CNT, implying Pt species in 1%Pt/CQDs/CNT may be atomic clusters. Figure 2D shows the high-resolution Pt 4f spectra of 1%Pt/CQDs/CNT and 1%Pt/CNT. Both of them exhibit obvious elemental state (70.9 eV), indicating Pt species mainly exist in the form of atomic clusters. However, the Pt in 1%Pt/CQDs/CNT also show an oxidation state (71.9 eV), which may be ascribed to the oxidation of some Pt clusters on the surface of catalyst in the air. Figure 3 shows the X-ray absorption near-edge structure spectra (XANES) and the extended X-ray absorption fine structure (EXAFS) of 1%Pt/CQDs/CNT. The results of XANES spectra (Figure 3A) show that the white-line peak of 1%Pt/CQDs/CNT is completely same as that of Pt foil, indicating the Pt in 1%Pt/CQDs/CNT exists in a metallic state. However, in the Fourier transforms of EXAFS (Figure 3B), the only prominent peak of 1%Pt/CQDs/CNT is located between those of Pt foil and PtO₂, rather than being consistent with the peak position of Pt foil. Furthermore, XRD didn’t detect any signal of metal Pt. The above results indicate that the main form of Pt in 1%Pt/CQDs/CNT is atomic clusters rather than nanoparticles or single atoms, which is consistent with the result of XRD and XPS.

2.2 | Catalytic performance

The HER performance of catalysts was first investigated in a 0.5 M H₂SO₄ electrolyte, and the results are shown in Figure 4A–C. For comparison, commercial 20%Pt/C

| Catalysts | 1%Pt/CQDs/CNT | 1%Pt/CNT | CQDs/CNT | CNT |
|-----------|---------------|-----------|-----------|-----|
| C-C (%)   | 56.69         | 72.79     | 57.84     | 71.93 |
| C 1s      | 34.93         | 17.16     | 34.75     | 18.87 |
| C = O (%) | 8.38          | 10.04     | 7.41      | 9.20 |
| O 1s      | 22.26         | 51.19     | 19.98     | 47.03 |
| O-C (%)   | 77.74         | 48.81     | 80.02     | 52.97 |
was also measured under the same test conditions. 1%Pt/CQDs/CNT, 1%Pt/CNT and 20%Pt/C show onset overpotentials of 8, 10, and 50 mV versus the reversible hydrogen electrode (RHE), suggesting that Pt atomic clusters loading on CQDs grafting CNTs is far more active in acidic H\textsubscript{2} evolution than Pt nanoparticle catalysts. Moreover, 1%Pt/CQDs/CNT exhibits the smallest overpotential (29 mV) at the current density of 10 mA cm\textsuperscript{-2} compared with those of 1%Pt/CNT (86 mV) and 20%Pt/C (41 mV). Furthermore, the resulting Tafel slope of 1%Pt/CQDs/CNT is only 22 mV decade\textsuperscript{-1}, obviously smaller than that of 20%Pt/C (40 mV decade\textsuperscript{-1} in Figure 4C), suggesting that the reaction was catalyzed through a Volmer-Tafel process\textsuperscript{[33,37]} However, the Tafel slope value of 1%Pt/CNT is 155 mV decade\textsuperscript{-1} which means the Volmer–Heyrovsky mechanism is the HER pathway\textsuperscript{[33]} The reasonable explanation is that the grafting of CQDs onto MWCNT not only increase the surface coordinative oxygen groups for dispersing Pt into atomic clusters but also improve the surface H\textsuperscript{+} concentration because of the oxygen-containing groups and therefore lead to lower overpotential and smaller Tafel slope for the reaction. Furthermore, to make
a comparison to other catalysts for HER, we summarized the literatures about Pt or other metal catalysts in Table 3.

The HER performance of 1%Pt/CQDs/CNT was further studied in a 1.0 M PBS solution (Figure 4D) and aqueous KOH solution (Figure 4E). A remarkable deactivation exists on the catalytic performances of Pt atomic clusters catalysts under neutral pH and basic conditions, although Pt species also function as effect catalysts under these conditions. 1%Pt/CQDs/CNT shows increasing overpotentials along with increased pH value of electrolyte, achieving 41.0 mV in PBS solution and 49 mV in KOH solution at current density of 10 mA cm$^{-2}$. The Tafel slope of 1%Pt/CQDs/CNT rise to 80 and 193 mV decade$^{-1}$ sharply with the increase pH of electrolyte due to the low concentration of H$^+$ in solution.

The electrochemical stability of 1%Pt/CQDs/CNT was also evaluated using a long-term cycling (10,000 cycles) test in a 0.5 M aqueous H$_2$SO$_4$ solution (Figure 4F). After 10,000 cyclic voltammetry (CV) cycles, the polarization curve of 1%Pt/CQDs/CNT shifted negatively by 37 mV at a current density of 10 mA cm$^{-2}$, which is still lower than that of pristine 20%Pt/C, indicating an acceptable decrease in the acidic electrolysis.

### 2.3 Advantages of Pt atomic clusters on CQDs/CNT in HER in acidic electrolyte

In electrolysis reactions of water splitting, HER proceeds through the first formation of adsorbed hydrogen intermediates (H$^+$+_e$^{-}$→H$_{ad}$, Volmer step, 120 mV decade$^{-1}$) on catalysts surface, followed by the Tafel step (H$_{ad}$ + H$_{ad}$→H$_2$, 30 mV decade$^{-1}$) or the Heyrovsky step (H$^+$ + H$_{ad}$ +e$^{-}$→H$_2$ in acidic electrolyte or H$_2$O + H$_{ad}$ + e$^{-}$→H$_2$ + OH$^-$ in alkaline electrolyte, 40 mV decade$^{-1}$). All above-mentioned process relies on the optimal electron transfer behavior of the electrocatalysts. The catalysts surface, where the charge transfers, reactant adsorption and product desorption occur, is the core of the electrochemistry. One-dimensional MWCNTs have been widely applied as conductive substrates in electrolysis due to their superior electrical conductivity and large surface area. However, fewer defective surface of MWCNTs lead to weak interactions between MWCNTs and active components such as Pt metals. CQDs possess a high concentration of oxygen-contained functional groups and the high surface area to volume ratio, not only facilitating the dispersion of Pt species but also profiting the adsorption and migration of protons. Furthermore, CQDs and MWCNTs are both allotropes of carbon. Hence, their interaction may be very strong to prevent the dissolution of CQDs into electrolyte and enhance the hydrophilicity of MWCNTs in solution.

The effective mass transfer of protons to the active Pt site is another key factor that determines hydrogen evolution activity. Carbonyls, hydroxyls and epoxy groups are common species on surface of CQDs. Oxygen-containing polar groups on surface of CQDs are proved to be energetically favorable for the H-adsorption. The O species will form a weak inter-molecular H-bond to further stabilize the H$^+$ from a nearby group. Therefore, high reactant H$^+$ concentration around the active sites, Pt atomic clusters, can be obtained. The charge-transfer between different neighboring groups can be imagined: (1) electrons from carbon clothe can transfer to MWCNTs without any restrains and then to active sites; (2) high concentration of protons on the surface of CQDs surrounding the active sites will be reduced more quickly and then release the hydrogen molecules; (3) protons from solution recover the surface of CQDs.

In pH neutral and alkaline HER, the catalytic cycle is initiated by adsorption of H$_2$O onto the active sites. Therefore, the performance of catalysts depends on the adsorption of H$_2$O molecule by Pt atomic clusters and carbon-oxygen species. Unfortunately, although CQDs are negatively charged at different pH (Figure 5), the concentration of H$^+$ in neutral and basic electrolyte is much lower than that in acidic electrolyte, which will lead to the remarkable reduced proton adsorption on CQDs. Due to this, the rate of hydrogen production in neutral and basic

### Table 3 Performance of Pt or other metal catalysts for HER

| Catalysts | Overpotential at 10 mA cm$^{-2}$ [mV] | Tafel slope [mV decade$^{-1}$] | Ref. |
|-----------|-------------------------------------|-------------------------------|------|
| 1%Pt/CQDs/CNT | 29                                | 22                            | This work |
| Ru@CQDs480 | 10                                | 47                            | [32] |
| RuNi/CQDs-600 | 13                               | 40                            | [33] |
| Pt atomic clusters loaded on N-doped graphene/graphitic-C3N4 | 35                       | 27                            | [37] |
| NiCoPt/Graphene-dot | 45.5                   | 33.9                          | [38] |
| Pt-FeNi@C,P | 53                                | 35.9                          | [39] |
| N-doped Ru/P,N,P doped carbon | 20.5                        | 31                            | [40] |

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electrolyte will be controlled by the concentration of H\(^+\) around Pt atomic clusters. Therefore, how to increase the concentration of H\(^+\) around active sites and make more Pt atomic clusters may be the following research focus.

3 | CONCLUSIONS

Pt atomic clusters on CQDs grafting MWCNTs were designed and synthesized via a facile route. The catalyst exhibited excellent HER activity in acidic electrolyte. CQDs help to dispersing Pt atomic clusters and provide proton-rich area surrounding the Pt atomic clusters, enhancing the charge transfer process and H\(_2\) evolution rate. CNTs acted as the good current collector and support to disperse CQDs and Pt species. The 1\%Pt/CQDs/CNT had overpotential of 29 mV at the current density of 10 mA cm\(^{-2}\) and Tafel slope of 22 mV decade\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\) solution. The presented strategy to design good and stable Pt atomic clusters catalysts provides a new prospect in promoting the practical application of HER in acidic electrolyte.

4 | EXPERIMENTS

4.1 | Chemicals

Glucose (GC, \(\geq 99.5\%\)) was purchased from Aladdin (Shanghai), methanol (AR, \(\geq 99.5\%\)), ethanol (AR, \(\geq 99.7\%\)) and Chloroplatinic acid (H\(_2\)PtCl\(_4\)) were purchased from Macklin. 5 wt.% Nafion solution was obtained from Alfa Aesar (China) Chemicals Co. Ltd.. All the chemicals were used as received without further purification.

4.2 | Synthesis of CQDs

The CQDs were prepared by a typical thermal method. Briefly, 20 g glucose heated at 180 °C under stirring for 30 minutes in air and then cooled to room temperature. After dissolving, dialyzing and freeze-drying, the CQDs with light yellow color were obtained.

4.3 | Synthesis of 1\%Pt/CQDs/CNT

Typically, weigh 100 mg of CNT, 10 mg of CQDs, then add 1 mL of methanol, and then add 100 \(\mu\)L H\(_2\)PtCl\(_6\) (10 mg/mL). After sonicating for 30 minutes, dry at 80 °C for 6 hours.

4.4 | Synthesis of 1\%Pt/CNT

1\%Pt/CNT was synthesized without the addition of CQDs.

4.5 | Synthesis of CQDs/CNT

CQDs/CNT was synthesized without the addition of H\(_2\)PtCl\(_6\).

4.6 | Characterization

The crystalline structure of catalysts was investigated by a Bruker D8 Advance X-ray diffractometer (XRD) using Cu K\(_\alpha\) (\(\lambda = 1.5406 \text{ Å}\)) radiation. The 2\(\theta\) angles were scanned from 5° to 90° at 5° min\(^{-1}\). Chemical states and composition of catalysts were characterized by X-ray photoelectron spectra (XPS, PHI-5000 Versaprobe, II) with monochromatic Al K\(_\alpha\) radiation. The microstructure and morphology were observed using field emission transmission electron microscopy (TEM, FEI Tecnai G\(^2\) F30) equipped with a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) accessory. Extended X-ray absorption fine structure spectra (EXAFS) at Pt K-edge were collected at the Singapore Synchrotron Linght Source (SSLS) center, in which the X-ray beam was monochromatized with channel-cut Si (III) crystals, and Pt foil and PtO\(_2\) were used as references. The Raman spectra were measured by a HORIBA LabRAM HR800 Raman microscope with HeNe laser of 532 nm. The metal concentration of Pt is determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo IRIS Intrepid II).
4.7 Electrochemical measurements

The electrochemical measurements were carried out with an electrochemical work station (CHI630E, Shanghai, China) in a conventional three-electrode cell system at room temperature with a graphite rod as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a carbon fiber cloth (1x2 cm²) as the working electrode. The electrolyte was 0.5 M H₂SO₄, 1 M PBS or 1 M KOH aqueous solution. The working electrode was prepared as follows: 5 mg of catalysts, 970 µL ethanol and 30 µL 5 wt.% Nafion solution were mixed together with ultrasonic for about 30 minutes. Then 200 µL of the catalyst ink suspension thus obtained was dropped dropwise onto the carbon cloth (1x1 m²) and left to dry in air (giving a catalyst loading of 1 mg cm⁻² on the carbon cloth). The potential, measured against a SCE electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{\text{vs RHE}} = E_{\text{vs SCE}} + E^\theta_{\text{SCE}} + 0.059 \, \text{pH}$. All catalysts were measured under the same conditions.

Linear sweep voltammetry (LSV) measurements were carried out with a sweep rate of 2 mV s⁻¹. Cyclic voltammetry (CV) was conducted from -0.3 V to -0.2 V in 0.5 M H₂SO₄ at a sweep rate of 50 mV s⁻¹ for 10,000 cycles to investigate the cycling stability. All measurements were corrected without IR compensation.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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