A carbon dot-based total green and self-recoverable solid-state electrochemical cell fully utilizing O$_2$/H$_2$O redox couple

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Electrochemical cell can overcome the inherent intermittence of the renewable energy sources, thus showing great potentials in applications ranging from electrical energy storage to future smart grid. However, the current electrochemical cells could not achieve the “total green” feature by fully utilizing the clean and abundant O$_2$/H$_2$O redox couples due to the enormous overpotentials for both oxygen reduction reaction (ORR) and oxygen release reaction (OER). Herein, we report a “total green” electrochemical composite film cell based on carbon dots (CDots), which can realize both ORR and OER in the acid environment. The in-air voltage generation (0.95 V, with a maximum power of 5.3 $\mu$W) relies on the multiple-electron-transfer redox chemical reaction between the two active components inside the composite film, that is, ORR/OER of CDots and the redox reaction of polyaniline (PANI) on the electrode and the resulting proton concentration gradient. Interestingly, the cell can be self-recovered at low load, recharged by adding H$_2$O$_2$, or electrocharged at high load. We anticipate that current study may open up new opportunities for designing and developing total-green energy storage and conversion systems for diverse applications.

Keywords
carbon dots, electron/proton transfer, O$_2$/H$_2$O redox couples, total green electrochemical cell
1 | INTRODUCTION

The consumption of nonrenewable fossil fuels and emissions of greenhouse gases such as carbon dioxide have led to serious global problems, such as environmental pollution, climate change, etc.\textsuperscript{1–4} The environmental concerns have stimulated the great attentions in generating the electricity from clean energy sources, for example, solar, wind, etc, which provide efficient and environmentally preferable alternatives to minimize the environmental impacts.\textsuperscript{5–8} However, these renewable energy sources are all inherently intermittent, which represent the main obstacle toward their practical utilization in everyday life.\textsuperscript{9–12}

To resolve the intermittency of these clean energy sources while still keeping the sustainability, renewability and low greenhouse gas emission feature, the use of “total green” electrochemical energy storage from renewable sources that balances the sustainability and the energy becomes necessary.\textsuperscript{13–19} In order to achieve the “total green” feature, oxygen and water (O\textsubscript{2}/H\textsubscript{2}O) redox couples are considered as the ideal candidates because of their cleanness and abundance.\textsuperscript{20–22} However, the fully utilization of O\textsubscript{2}/H\textsubscript{2}O redox couples is very challenging due to the enormous overpotentials for both ORR and OER.\textsuperscript{23} Carbon Dots (CDots, monodisperse graphite nanoparticles with diameters smaller than 10 nm) exhibit high chemical catalytic activity due to its unique electron transfer, storage and electrochemical properties.\textsuperscript{24–32} Previous studies have shown that CDots catalyzed oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) could be achieved separately under alkaline or neutral conditions based on their excellent electrocatalytic activity.\textsuperscript{33–35} In addition, due to the more positive redox potential (1.23 V vs RHE), the electrochemical cell based on a single layer solid-state composite film consisting of CDots and polyaniline (PANI), thus rendering the total greenness of this unique electrochemical cell. More interestingly, multiple-electron-transfer redox chemistry (ie, ORR/OER of CDots and the redox reaction of PANI) in an acidic environment to shuttle charges between the binary constituents with H\textsubscript{2}O\textsubscript{2} as an intermediate enables both the regenerative property, the self-recovery feature, and even the operation in a process similar to a fuel cell. We anticipate that the current study may open up new opportunities toward the design and development of total-green energy storage and conversion systems.

2 | RESULTS AND DISCUSSION

2.1 | Characterization of CDots/PANI composite

The CDots/PANI composite is obtained based on the oxidation polymerization of aniline in the presence of CDots, as illustrated in Figure S1. The resulting CDots/PANI film has a dark appearance (Figure 1A) with rough and porous surface morphology (as can be seen from the scanning electron microscopy [SEM] image shown in Figures 1B and S2), which may be beneficial for the ORR/OER due to the more exposed active sites. The composite film consists of PANI which is amorphous (transmission electron microscopy [TEM] image shown in Figure 1C) with embedded CDots which is crystalline as evidenced by the lattice structure (101 lattice of graphitic carbon with a lattice spacing of 0.21 nm) shown in the high-resolution transmission electron microscopy (HRTEM) image (Figure 1D). The X-ray photoelectron spectroscopy (XPS) spectrum of the CDots/PANI shows the presence of C, N, and O elements in the composite (Figure S3). The detailed XPS analysis is shown in Table S1, and CDots and PANI are well combined. Among them, the three deconvolution peaks of N 1s prove the existence of proton doping in PANI, and the O 1s indicates the hydroxyl groups adsorbed on the surface of the sample. The composite film exhibits the characteristic fourier transform infrared (FTIR) peaks originating from CDots (3443 cm\textsuperscript{-1} [hydroxyl, O-H], 1639 cm\textsuperscript{-1} [C=O], 1392 cm\textsuperscript{-1} [-COO]) and PANI doped with protic acid (3423 cm\textsuperscript{-1} [N-H], 1350 cm\textsuperscript{-1} [C-N\textsuperscript{+}]), as shown in Figure 1E, thus confirming the presence of both components. Moreover, as can be seen from Figure 1F blue curve, the UV-vis spectrum of the CDots/PANI composite shows the absorption peaks derived from PANI (Figure 1F, red curve) at 250 nm (\(\pi-\pi^*\) transition of the benzene), and 700 nm (n-\(\pi^*\) transition of the quinone) and from CDots (Figure 1F, black curve) at 220 nm (polycyclic aromatic hydrocarbons), further confirming these two constituent parts.

The CV curve in Figure 1G (at a scan rate of 50 mV/s) shows the two characteristic couples of redox waves of CDots/PANI composites (Figure 1G, blue curve), which are attributed to the transitions between different doping states of PANI (Figure 1G, red curve), namely, leucoemeraldine (LEB) to emeraldine (EM) (around 0.2 V) and emeraldine (EM) to pernigraniline (PNB) (around 0.6 V), respectively (detailed reversible reaction of PANI are shown in Figure S4).\textsuperscript{39–41} In addition, the CV curve also shows a high electric double layer charging current because of the electrochemical activity and large specific surface area of CDots.\textsuperscript{42} The CDots/PANI composites have excellent rate capability and can maintain well-defined redox peaks even if the scan rate reaches 100 mV/s. All the CV curves are
FIGURE 1 (A) CCD image, (B) SEM image, (C) TEM image, and (D) HRTEM image of the CDots/PANI composite film. (E) FTIR and (F) UV-vis spectra of the CDots/PANI composite (blue curve), pristine CDots (black curve) and pristine PANI (red curve). (G) Cyclic voltammograms of CDots/PANI composite. (H) The HOMO and LUMO energy levels of CDots and PANI with respect to the electrochemical potentials of \( \text{H}_2/\text{H}_2\text{O} \), \( \text{O}_2/\text{H}_2\text{O} \) and the current collector. The vacuum level is shown for comparison.

quite stable, indicating that the CDots/PANI composites show good electrochemical stability and fast response to oxidation and reduction.\(^{43-45}\)

The band structure diagram of CDot and PANI can be determined through the onset oxidation potential (\( E^{\text{ox}} \)) and the onset reduction potential (\( E^{\text{red}} \)) of CV to be around \(-6.37\) eV (HOMO)/\(-4.01\) eV (LUMO) and \(-6.10\) eV (HOMO)/\(-3.88\) eV (LUMO), respectively (detailed calculations are shown in Section S1 and Figure S5).\(^{46}\) The electrons can be spontaneously transferred from the higher LUMO level of PANI into current collector (Au electrodes) and then to the CDots, as can be seen from the band structure diagram of CDots shown in Figure 1H, indicating the presence of the Schottky contact and potential difference between metal and the PANI semiconductor (Section S2 and Figure S6).\(^{47-50}\) Note that LUMO of CDots is more negative than the potential of oxygen reduction and HOMO of CDots is more positive than the potential of water oxidation, which suggest CDots have the ability to oxidize water and reduce oxygen simultaneously.

2.2 The performance of the CDots/PANI film cell

The CDots/PANI film exhibits an open circuit voltage (OCV) of 0.95 V (Figure 2A-C) with a current of \( 1.2 \times 10^{-5} \) A in air once contacted with the current collector, which are higher than the reported cell using \( \text{O}_2/\text{H}_2\text{O} \) redox couples. The OCV is irrelevant to the oxidant in the film (Figure S7) and is the highest for the composite film containing prepared from CDot solution (Figure S8), verifying that the reaction rate is dependent on the CDot content. The OCV and the current slightly increase with the increasing time (Figure 2C), which may be ascribed to the water formation near the current collector that accelerates the reaction rate of ORR. It can be seen from Figure 2D-F that the CDots/PANI film cell can be stably and continuously discharged in air for 25 hours (\( \sim 0.9 \) V, constant current mode). After that, the voltage decreases to 0.4 V despite of the CDot content inside the CDots/PANI film cell (Figure S8), indicating that 0.4 V is caused by the Schottky contact,
FIGURE 2 (A) CCD image and the illustration showing the OCV of the CDots/PANI film cell. (B) The OCV measured by a multimeter. (C) The current (green curve) and the OCV (red curve) of the CDots/PANI film cell measured by the electrochemical workstation. (D) Schematic indicating the discharge of the CDots/PANI film cell. The discharge of CDots/PANI film cell in constant current mode ($10^{-6}$ A) for (E) 25 and (F) 50 hours. (G) Schematic diagram of the CDots/PANI film cell powers an electric resistance. (H) Short circuit current (green curve) and OCV (red curve) of the CDots/PANI film cell as a function of the external load resistance. (I) The output power versus the external load resistance. (J) The schematic of the CDots/PANI film cell connected in series. (K) The CCD image showing the CDots/PANI film cell connected in series can light up a small LED bulb (2.2 V). (L) The OCV gradually increases with the increase of the number of CDots/PANI film cells connected in series.

that is, work function difference between current collector (Au) and PANI. The discharge time increases with the increasing contact area between the CDots/PANI film and the current collector (Figure S9), which indicates that the PANI film has the ability to store charges, and the location of the reaction may be at the contact interface. In addition, it can be seen from Figure 2G-I that the CDots/PANI film cell can power an electric resistance with an OCV of 0.97 V and a maximum power of 5.3 μW. The energy density and power density of the CDots/PANI film cell are, respectively, 50.19 mWh/kg and 8.44 μW/cm², as shown in Section S3 and Figures S10 and S11, and the performance is relatively good compared with other works (Tables S2 and S3). Interestingly, single CDots/PANI film cell can be connected in series (Figure 2J) so that a light-emitting diode (LED, 2.2 V) can be lightened (Video S1) for over 25 hours without obvious brightness variation (Figure 2K). An individual cell of four such cells connected in series exhibits an
OCV of 3.76 V (Figure 2L). In addition, when connecting the cells in parallel, and the current in the parallel circuit is equal to the sum of the current of each branch (Figures S12 and S13). The above results indicate that the CDots/PANI film cells may have great potential in the practical applications.

2.3 Mechanism of the CDots/PANI film cell

In order to elucidate the discharging mechanism (Figure 3A), we have studied the electrochemical property of CDots and PANI. The shift of the oxidation and reduction CV peaks of the PANI before and after discharging (Figure S14) indicates the green protonated emeraldine PANI (EM) loses electrons and protons, leading to the formation of the violet pemigraniline base (PB) (Figure S4). A single cathodic reduction peak of CDots in the O2-saturated KOH solution observed in the CV curve disappears in the N2-saturated solution (Figure 3B). Since the PANI does not exhibit an obvious single peak even in the O2-saturated KOH solution (Figure S15), while the CDots/PANI composite shows a single peak under the same condition (Figure S16), the electrochemical study confirms that the CDots can catalyze the ORR reaction. As can be seen from the current measured by the RDE and RRDE shown in Figure 3C and the detailed calculation shown in Section S4, the concentration gradient is obtained by taking the partial derivative, as follows:

$$Dyz \frac{\partial^2 C(x, t)}{\partial x^2} \bigg|_{x=0} = \frac{yzC_0}{2} \sqrt{\frac{D}{t}},$$

(2)

where \(y\) and \(z\) are the width and the thickness of the CDots/PANI film, and \(C_0\) is the initial concentration of proton.

The voltage can be generated through the proton gradient, which can be expressed by the following equation:

$$U = 4.82 \times 10^4 yzC_0 \sqrt{\frac{D}{t} R}.$$  

(3)

In order to further elucidate the mechanism, we study the relationship between the proton migration and voltage and current. The OCV increases with the increasing distance between the cathode and the anode, as shown in Figure 3H, I. This verifies that the proton migration, which is distance dependent, produces the voltage. In addition, when the contact area between the current collector and the CDots/PANI film is decreased (Figure 3F, G), the current decreases accordingly. This further indicates that the electrochemical reaction occurs at the contact interface, as confirmed by the control experiments shown in Figures S21-S23. These experiments thus verify the theory, that is, the proton gradient can indeed generate voltage. Note that the increase of O2 concentration in the atmosphere leads to a ~10 times increase in the current (Figure S24), which indicates that the ORR reaction based on CDots is the rate-determining step (RDS) for the entire reaction process (Figure 3A).

2.4 The recovery of the CDots/PANI film cell

The CDots/PANI film cell can be self-recovered under low load conditions (Figure 4A). When the constant current discharges of the cell is over and the voltage drops to 0.4 V, the voltage of the film cell could self-recover when placing it in air, as shown in Figure 4B. The OCV of the self-recovery cell increases with the increasing time of the CDots/PANI film self-recovery in air within 4 hours and then plateaus (Figure S25). During the self-recovery process, the characteristic UV-vis absorption peak red-shifts (Figure 4C), indicating that PANI is reduced from PB to EM through protic acid (from H2O2 decomposition) doping. Therefore, the discharging and self-recovery cycles are likely as follows: (1) During discharging, PANI can be converted from the oxidized state to the reduced state by losing
FIGURE 3  (A) The schematic of the working mechanism of the CDots/PANI-based electrochemical cell that couples the ORR/OER of CDots and the autoxidation reaction of PANI. Location 1 is the contact interface between the CDots/PANI film and current collector, while location 2 is the position away from the contact interface. (B) ORR performance of CDots in an N₂- and O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV/s. (C) RRDE linear sweep voltammograms (LSV) curves of CDots with GC disk ring electrodes rotating at a speed of 1600 rpm in 0.1 M KOH (scan rate, 10 mV/s). (D) Calculated number of ORR transferred electrons of CDots by RRDE, \( n \approx 2 \). (E) The OCV changes when changing the pH at the contact interface between the CDots/PANI film cell and the current collector. (F) The current and (G) the OCV of the CDots/PANI film cell change with the different contact area between the current collector and the cell. (H, I) Schematic showing the change of the contact area between the current collector and the CDots/PANI film cell
(A) The schematic showing the mechanism of the self-recovery of the CDots/PANI film cell. (B) The voltage increases to 0.8 V (in constant current mode [10⁻⁶ A]) after self-recovery in air for 4 hours. (C) The UV-vis spectra of CDots/PANI before discharge (black curve), discharged for 25 hours (green curve) and self-recovery in air for 4 hours (orange curve). (D) The schematic indicating the recovery mechanism of the CDots/PANI film cell through the addition of H₂O₂. (E) The voltage is increased to 0.9 V in constant current mode (10⁻⁶ A) when H₂O₂ is added after discharging. (F) The UV-vis spectra of the discharged CDots/PANI before (black curve) and after (orange curve) the addition of H₂O₂. (G) The schematic showing the mechanism of the electrochemical charging of the CDots/PANI film cell. (H) OER performance of CDots in 0.1 M KOH solution at a scan rate of 10 mV/s. (I) The CV of the recharged CDots/PANI film cell, the scan rate is 50 mV/s.

In addition to the above-mentioned self-recovery capability, the CDots/PANI film cell can also be self-charged by adding H₂O₂, a process similar to H₂O₂ fuel cell (Figure 4D). By adding H₂O₂ (0.3%) at the contact interface of the discharged cell, the voltage of the cell rises to 0.95 V, as shown in Figure 4E, indicating that it can be reused. After adding H₂O₂ to the discharged cell, it is also found that the UV-vis absorption peak has a red-shift (Figure 4F), which is similar to the self-recovery case (Figure 4C, green curve). This further proves the involvement of H₂O₂, which generates protons and reduces the oxidized PANI, thus regenerating the CDots/PANI film cell. The continuous power supply could thus be achieved when the H₂O₂ fuel is continuously supplied to the cell.

Under high load or high-power situation, the CDots/PANI film cell can also be electrically recharged (Figure 4G). As can be seen from Figure S27, the fully discharged cell could be recharged, as evidenced by the recovery of OCV to 0.95 V. We have studied the recharging mechanism. As shown in the LSV curves of CDots (Figure 4H), the lower initial potential (1.5 V vs RHE) indicates that CDots can catalyze the OER. The pH of PANI during charging decreases with the increasing time (Figure S28), indicating that an OER reaction occurred on CDots leads to the formation of protons. The protons and electrons (transferred from CDots first to the current collector and then PANI) reduce the oxidized PANI, as evidenced by the shift from the oxidation peak to the
reduction peak (Figures 4I and S19). The fully recovery PANI can work again on the basis of these processes. In addition, the CDots/PANI film cell can be recovered for at least five cycles through electrocharging (Figure S29).

3 | CONCLUSION

In summary, we have demonstrated a CDot-based electrochemical film cell which is “total-green” by fully utilizing the O₂/H₂O redox couples. This cell produces electricity with an OCV of 0.95 V and a maximum power of 5.3 μW in air. The work mechanism of the CDots/PANI film cell relies on the redox of PANI, the ORR of CDots and the proton concentration gradient generated on the film. Interestingly, this CDots/PANI film cell can be self-recovered at low load, recharged by adding H₂O₂, or electrocharged at high load. The “total-greenness” makes the CDots/PANI film promising as an energy storage and conversion system.

4 | EXPERIMENTAL SECTION/METHODS

4.1 | Materials

Aniline, ferric chloride hexahydrate (FeCl₃·6H₂O), polyvinyl alcohol (PVA, Mw = 9000-10,000), ammonium persulphate ((NH₄)₂S₂O₈), potassium persulfate (K₂S₂O₈), hydrogen peroxide (H₂O₂), Nafion, acetonitrile (ACN), potassium sulphate (K₂SO₄), tetrabutylammonium hexafluorophosphate (TBAP), potassium hydroxide (KOH), and ferrocene were purchased from Aladdin Company. Graphite rod (99.99%, length 13 cm, diameter 0.6 cm) was obtained from Alfa Aesar Company. These materials were used directly without further purification.

4.2 | Synthesis of CDots

Two graphite rods were inserted into ultrapure water at a distance of 7.5 cm vertically, and a DC power supply was utilized to connect the two graphite rods. A bias of 30 V was applied to the rod. The solution was continuously stirred for 20 days.32 After about a week, it was found that the anode graphite rod was etched and the solution color in the beaker gradually turned into dark brown. Then, the solution was continuously stirred for 20 days.32 After about a week, it was found that the anode graphite rod was etched and the solution color in the beaker gradually turned into dark brown. The graphite particle precipitation was stirred and redispersed in pure water with a concentration of 0.1 mg/mL.

4.3 | Preparation of the CDots/PANI film

PVA (0.5 g) was dissolved in 10 mL of deionized water, and 100 μL of hydrochloric acid (1 M) was mixed with the PVA solution at 60 °C and stirred for 30 minutes. Sixty-nine microliters of aniline and 2 mL of CDots solution (1 mg/mL) were added to the above mixture under ice-water bath. Then, 0.63 g of FeCl₃·6H₂O was added and ultrasonically dispersed for 24 hours. The resulting solution was purified by ultrafiltration (13,000 rpm, 3 times) and redispersed in 10 mL of deionized water. The prepared dispersed solution was drop cast on a glass slide and dried under room temperature.

4.4 | Electrochemical measurements

The electrochemical measurements of the device were conducted using a CHI660E electrochemical workstation in a standard two-electrode system. The studied CDots/PANI (prepared from CDot solution with concentration of 0, 1, 2, 3, 4 mg/mL) was employed as the counter electrode and the reference electrode, while current collector served as the working electrode in air.

The ORR and OER activities of CDots were carried out in a standard three-electrode system. Ag/AgCl (or Hg/HgO) electrode, graphite rod electrode, and GC electrode were used as reference electrode, auxiliary electrode and working electrode for supporting catalyst ink, respectively. Before use, the working electrode was polished with 0.03 μm polishing powder and ultrasonically rinsed with water, ethanol and dried. To prepare the working electrode, 5 mg of samples were dispersed in an aqueous solution containing 0.95 mL of deionized water and 0.05 mL of 5 wt% Nafion under sonication. The prepared catalyst slurry was applied evenly on the working electrode. The obtained homogeneous catalyst ink (4 μL) was added dropwise onto a mirror-polished glassy carbon electrode. RRDE-3A rotating ring-disk electrode (ALS Co., Ltd, Japan) measurements were performed by LSV at a scan rate of 10 mV/s with various rotating speeds ranging from 400 to 2500 rpm. The working electrodes were a rotating disk electrode (glassy carbon disk, 3 mm in diameter, RRDE) and a rotating ring-disk electrode (glassy carbon disk, 4 mm in diameter; platinum ring, 5 mm i.d. and 7 mm o.d., RRDE).

The CV curve of PANI and CDots was obtained in N₂-saturated 0.1 M TBAP ACN solution with 5 mg/mL ferrocene as the external standard. GC electrode coated with CDots and PANI (140 μg/cm²) worked as the working electrode. A carbon electrode and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The scan rate was 100 mV/s. Before all the
electrochemical measurements, a number of CVs at a scan rate of 100 mV/s in 0.5 M K2SO4 (or 1.0 M KOH) were carried out to obtain a steady state. LSVs were tested in 0.5 M K2SO4 (or 1.0 M KOH) at a scan rate of 5 mV/s. All tests were performed at room temperature.

4.5 Characterization

The surface morphologies were examined by a Zeiss Supra55 SEM with an accelerating voltage of 10 kV. TEM and HRTEM were carried out on a FEI-Titan G280-200 Chemi scanning transmission electron microscope with an accelerating voltage of 200 kV. The FTIR spectrum (Shimadzu UV3600, Bruker HYPERION) of the samples was acquired over the scan range of 400-4000 cm⁻¹. A UV-vis spectrophotometer (Lambda750, PerkinElmer) was employed to obtain the UV-vis absorption spectra. Video and pictures were taken by the SONY DSC-RX10III digital camera.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of the article.

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