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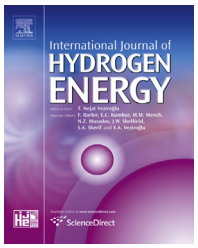

Fabrication of new gas diffusion electrode based on carbon quantum dot and its application for oxygen reduction reaction

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ABSTRACT

Carbon quantum dots (CQDs) are prepared by one-pot electrochemical techniques cyclic voltammetry (CV) and AC impedance spectroscopy (EIS) at different potentials using graphite rods in ethanol alkaline electrolyte. The electrochemically synthesized CQD is carefully characterized by scanning electron microscopy, Transmission electron microscopy, X-ray diffraction, Ultra violet absorption, Fourier transform infrared spectrometry, Raman spectrum, Chemiluminescence emission and electrochemical techniques. The morphology and microstructure methods confirm the formation of high quality CQD. The EIS of graphite electrode in NaOH/EtOH confirms the corrosion loop at low frequencies and as potential increases the charge transfer resistance decreases. Finally, we design a new gas diffusion electrode based on CQD pasted on carbon paper for the oxygen reduction reaction in fuel cells and compared it with commercially Pt–C catalysts using cyclic voltammetry, linear sweep voltammetry and chronoamperometry.

Introduction

The key components of polymer electrolyte fuel cells (PEFCs) are oxygen reduction reaction (ORR). In PEFCs, however numerous functional components work in order to produce electricity from the fuel and oxygen, the majority of the cost and durability arise from the cathode, where the electrochemical ORR occurs [1,2]. Platinum or other expensive constituents remain the most efficient ORR electro-catalysts, though the high cost and scarcity of platinum hinder further development of PEFC technologies based on these sources. In recent year, scientists have concentrated on developing relatively cheap and efficient ORR electro-catalyst with Pt-grade activity such as N- or halogen-carbon based material [2–5].

Carbon nanomaterials, such as fullerenes, carbon nanotubes and graphene, have generated much excitement for a wide variety of promising applications in nanotechnology, biosensing, and mobile energy [6–8]. Recently, carbon quantum dots (CQDs), a new class of carbon nanomaterials, have great attention because of their interesting properties, such as

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non-blinking, water solubility, optical characteristics and nontoxicity according to currently available cytotoxic and in vivo toxic evaluation results [9,10].

It is known that the surface area and surface functional groups of carbon materials, especially the oxygen-containing groups, play a key role in improving the activities of methanol oxidation reaction (MOR) and ORR [11,12]. Therefore CQD and graphene quantum dot (GQD), as oxygen group enriched materials, are used in fuel cell with and without metal electrocatalysts [13,14].

Carbon nanostructures are usually prepared by laser ablation of graphite [15],, thermal oxidation of suitable molecular precursors [16], microwave/ultrasonic passivation [17,18] and plasma treatment [19]. All these are efficient approaches to fabrication of CQDs. But, in most cases, the CQDs were produced with expensive carbon sources such as citric acid [20], glycerol [21], coffee grounds [22], soy milk [23], grass [24], bovine serum albumin [25] and egg [19].

However, electrochemical method is an effective tool to modify electronic states through adjusting the external power source to vary the Fermi energy level of electrode material surface from low-cost source such as graphite. In recent years, some researchers have attempted to produce CQDs by using electrochemical oxidation [26–28].

Here, we report for the first time, to the best of our knowledge, the fabrication of CQDs by using graphite and NaOH/EtOH as reactants by cyclic voltammetry (CV). Moreover, we can obtain information about the graphite exfoliation during the corrosion phenomena by EIS rout. The electrochemically synthesized CQD has been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), ultra violet absorption (UV–Vis), FT-IR, raman and chemiluminescence (CL) emission. Finally, we report the high performance metal-free electro-catalyst for oxygen reduction reaction (ORR) in alkaline media by CQDs as a gas diffusion electrode (GDE) with CV, linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).

Experimental section

CQDs preparation

The electrochemical preparation of CQDs was carried out in a tree-electrode configuration. The electrolyte of the electrochemical process was organized by mixing ethanol/H_2O (100 mL; volume ratio = 99.5:0.5) with a suitable amount (0.2–0.5 g) of NaOH, by using graphite rods as working electrode. We synthesized CQDs by CV [29] and EIS techniques in several potentials. A high-purity graphite rod was used as working electrode.

Ink preparation

A mixture containing a homogeneous suspension of CQDs, Nafion solution and water were homogenized by sonication for 20 min, and then painted on to glassy carbon electrode. The obtained composite was dried at 100 °C for 1 h and denoted as (CQD/GC) electrode.

GDE making and electrochemical measurements

The preparation of the GDEs described previously [30]. But we shall briefly repeat the main features here. The ORR was studied at the GDE (geometric exposed area of 1 cm^2) in 0.5 M potassium hydroxide (Merck) and constant temperature. The GDEs were fixed onto a Teflon holder containing a high pyrolytic graphite disk and oxygen purged from the back of the electrode. The electrochemical cell was connected to a potentiostat–galvanostat (VSP-300) for I–V polarization measurements, CA and also to a frequency response. The LSV measurement was recorded at 5 mV^{-1}.

Results and discussion

Physical characterizations of CQDs

XRD analysis was carried out to analysis the structure of the CQDs and pristine graphite (obtained by grinding a graphite rod) as the comparison. The XRD patterns of the CQDs and pristine graphite are shown in Fig. 1a, b. The spectrum of the graphite reflects one prominent peak at 26.49°, corresponding to the (002) planes of graphite, while for the pattern of CQDs there is one superimposed reflection at around 22–29°, suggesting the interlayer spacing of (002) diffraction peak is 0.39 nm. The larger interlayer spacing than that of graphite (0.34 nm) is ascribed to the existence of more functional groups [31]. This peak (d 002 = 3.9°A) is attributed to highly disordered carbon in CQDs. The decrease in the peak intensity and the increase of the full width half maximum (FWHM) are due to the small size of the resultant CQDs [32]. The crystallite size was estimated using the Scherer equation for the (002) peak, yielding value of 3.5 nm for CQDs.

Further characterization studies provided convincing evidence for the graphite fragment structure of the as synthesized CQDs. Typical ultra violet absorption (UV/Vis) spectrum of CQDs is shown in Fig. 2. The absorption spectrum exhibits two peaks around 250 and 350 nm. The peak at 250 nm represents the aromatic π system absorption, which is similar to that of polycyclic aromatic hydrocarbons (π–π* transition) [33]. While a peak at 350 nm is attributed to a n–π* transition [34].

Fig. 3 displays the Raman spectroscopes for CQDs. The well-known characteristics of CQDs in Raman spectra are the G band (~1524 cm^{-1}), which is generally assigned to the E2g phonon of sp^2 bonds of carbon atoms, and the D band (~1130 cm^{-1}) as a breathing mode of k-point phonons of A1g symmetry [35], which is attributed to local defects and disorders. Hence, the smaller ID/IG peak intensity ratio of a Raman spectrum can indicate lower defects and disorders of the structures [35]. The ID/IG ratio is about 0.73.

Fig. 4 reveals the Fourier transform infrared (FT-IR) spectrum of the as-prepared CQDs. The characteristic absorption bands of OH^- at 3447 cm^{-1}, the stretching vibration band of C=O in –COOH at 1651 cm^{-1}, and the stretching vibration bands of C–O at 1088 and 880 cm^{-1} indicate the presence of carboxylic acid and other oxygen-containing functional groups at their surfaces. Moreover, three obvious absorption