



# Synthesis and catalysis of copper sulfide/carbon nanodots for oxygen reduction in direct methanol fuel cells

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## ARTICLE INFO

### Article history:

Received 16 September 2012

Received in revised form

13 November 2012

Accepted 3 December 2012

Available online 13 December 2012

### Keywords:

Carbon nanodots

Cathode catalyst

Cu<sub>2-x</sub>S

Fuel cells

Oxygen reduction reaction

## ABSTRACT

We have fabricated Cu<sub>2-x</sub>S/carbon nanodot (C dot) electrodes for direct methanol fuel cells (DMFCs). To the best of our knowledge, this is the first time that Cu<sub>2-x</sub>S/C dot nanomaterials (NMs) were proposed to be used as a cathode catalyst for oxygen reduction reaction (ORR) in acidic media. The structural characterizations revealed that Cu<sub>2-x</sub>S alloy possessed two types of crystalline phases, such as Cu<sub>9</sub>S<sub>5</sub> and Cu<sub>2</sub>S in the structure of Cu<sub>2-x</sub>S/C dot NMs. The onset potential of the ORR for Cu<sub>2-x</sub>S/C dot NMs is 0.92 V (vs. Ag/AgCl), revealing a good ORR activity of these NMs. The Cu<sub>2-x</sub>S/C dot electrodes (mass loading: 2.26 mg cm<sup>-2</sup>) provide a mean limiting density of -1.77 mA cm<sup>-2</sup> at a scan rate of 5 mV s<sup>-1</sup> and rotation rate of 3600 rpm. Electrochemical impedance spectrometry (EIS) results revealed that the charge-transfer resistance (*R*<sub>ct</sub>) of the Cu<sub>2-x</sub>S/C dots was smaller than that of Cu<sub>2-x</sub>S/CNT. In addition, compared with Pt/C electrodes, Cu<sub>2-x</sub>S/C dot electrodes were more tolerant against MeOH poisoning. The low-cost, electrochemically stable, and highly active Cu<sub>2-x</sub>S/C dot electrode has great potential for use in DMFCs.

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## 1. Introduction

Efficient catalysts for the oxygen reduction reaction (ORR; O<sub>2</sub> + 4H<sup>+</sup> + 4e<sup>-</sup> → 2H<sub>2</sub>O) are essential for the fabrication of high-performance direct methanol fuel cells (DMFCs) [1]. When using a Pt cathode, the ORR rate is much slower than that of its anodic counterpart, leading to significant overpotential that reduces the performance of DMFCs [2]. Many nanomaterials (NMs) such as nitrogen-doped carbon [3–6], CuS [7], and CoSe<sub>2</sub>/C [8,9] have been prepared and employed as effective catalysts for high-rate ORR kinetics by taking advantage of their large surface area and high catalytic activities [10,11]. Low-cost MS (M = Co and Cu) exhibits metal-like electrical conductivity, a property that has attracted significant interest in electrochemistry; however, current MS electrodes have much lower ORR activities than Pt electrodes [12,13].

Carbon supports are commonly used in fuel cells to improve the electrochemical activity and stability of catalysts mainly because of their large surface area, low cost, and unique electrical properties [14–16]. Carbon-supported Co<sub>3</sub>S<sub>4</sub> and CoSe<sub>2</sub> NMs with onset potential values of 0.67 V and 0.72 V, respectively, are more active in the ORR than a reversible hydrogen electrode in acidic media [12,16]. To strengthen the interaction between MS NMs and carbon supports, the direct growth of Co<sub>1-x</sub>S NMs on reduced graphene oxide has been demonstrated [12,13]. The reduced graphene oxide

not only assists in the growth of small-sized Co<sub>1-x</sub>S NMs, which yields larger surface area, and thus higher electroactivity, but also enhances the ORR catalytic activity of the Co<sub>1-x</sub>S NMs through strong electrochemical coupling.

In this study, our goal is to fabricate high-performance cathodic catalysts in DMFCs using Cu<sub>2-x</sub>S NPs and carbon nanodots (C dots). Cuprous sulfide (Cu<sub>2</sub>S) has been used extensively as a photonic material as it exerts two distinct localized surface plasmon resonance modes [17], as a cathode reaction catalyst in a vanadium redox flow battery [18], and as a catalyst for the nucleation of In<sub>2</sub>S<sub>3</sub> nano-crystals [19]. Adsorbed onto the surface of a polymer such as polypropylene, Cu<sub>2</sub>S is capable of catalyzing the molecular recognition of ammonia gas [20]. C dots have large surface area, good electrical conductivity, and excellent mechanical strength [14–16], while inexpensive Cu<sub>2-x</sub>S NPs exhibit high ORR activity. Cu<sub>2-x</sub>S/C dot NMs were synthesized from Cu(NO<sub>3</sub>)<sub>2</sub>, C dots, and Na<sub>2</sub>S (S<sup>2-</sup> source) using polyvinylpyrrolidone (PVP) as a stabilizer. PVP is commonly used to enhance the dispersion and adhesion of NMs on substrates such as CNTs [21]. We investigated the roles that various carbon supports played in controlling the direct growth of Cu<sub>2-x</sub>S on their surfaces, and thus their catalytic efficiency for ORR.

## 2. Materials and methods

### 2.1. Materials

Commercially available copper nitrate (≥99.8 wt%), carbon nanotubes (30–40 nm O.D. × 5–9 μm length, CNTs), Vulcan XC-72R

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carbon black (particle size  $\sim 50$  nm), graphite powder (particle size  $\sim 2$   $\mu\text{m}$ ), methanol ( $\geq 99.8$  wt%), ethanol ( $\geq 99.8$  wt%), and PVP ( $M_w$  10,000) were purchased from Sigma (St. Louis, MO, USA). Sodium sulfide ( $\geq 99.5$  wt%) and diamine hydrate ( $\geq 95$  wt%) were purchased from Seedchem (Melbourne, VIC, Australia). Platinum on activated carbon (Pt/C, 40 wt%) was purchased from Alfa Aesar (Ward Hill, MA, USA). Coffee grounds were collected from used Blue Mountains coffee (Taipei, Taiwan). Nafion 117 (5 wt%) and sulfuric acid ( $\geq 99.8$  wt%) were purchased from Fluka (Buchs, Switzerland). Highly purified water (18.2 M $\Omega$  cm) from a Milli-Q ultrapure system (London, UK) was used throughout this study.

## 2.2. Synthesis of C dots by a hydrothermal method

C dots were prepared from used coffee grounds of blue mountain coffee beans through a hydrothermal route according to our previous study [16]. We note that C dots prepared from different brands of coffee grounds were slightly different with respects to fluorescence quantum efficiency, yield, and surface properties. Used coffee ground was dried in an oven at 110 °C. After calcination at 300 °C for 2 h, black carbonized powder ( $\sim 5$  mg) was cooled to 20 °C and dispersed in ethanol (5 mL). The solution was then centrifuged at 3000 rpm for 10 min to remove large particles. The supernatant containing C dots was filtered through a 0.22- $\mu\text{m}$  membrane to further remove large particles. The concentration of as-synthesized C dots was about 63.8  $\mu\text{g}/\text{mL}$ .

## 2.3. Synthesis of C dots ( $C_{dh}$ ) by laser irradiation

C dots ( $C_{dh}$ ) were prepared from graphite powder through the laser irradiation method [22]. Nd:YAG pulsed laser with a wavelength of 1064 nm and power density of  $6.0 \times 10^6$  W  $\text{cm}^{-2}$  was used to irradiate 0.1 mg of graphite powder dispersed in 0.5 mL of diamine hydrate. Stirring was employed during the laser irradiation to expedite the movement of carbon particles. After being irradiated for 2 h, a homogeneous black suspension was obtained, which was centrifuged (3000 rpm, 10 min) to separate the black carbon precipitate and the colorful supernatant. The supernatant was then filtered through a 0.22- $\mu\text{m}$  membrane to remove the larger particles. The concentration of as-synthesized  $C_{dh}$  was about 72.3  $\mu\text{g}/\text{mL}$ .

## 2.4. Preparation of $\text{Cu}_{2-x}\text{S}/\text{C}$ dot, $\text{Cu}_{2-x}\text{S}/\text{CNT}$ , $\text{Cu}_{2-x}\text{S}/\text{C}_{dh}$ , and $\text{Cu}_{2-x}\text{S}/\text{carbon black NMs}$

$\text{Cu}(\text{NO}_3)_2$  (0.2 mL 0.5 M),  $\text{Na}_2\text{S}$  (0.2 mL 0.5 M), C dots (0–0.02 mg), and PVP (0.04 g) were mixed together with ethanol (final volume 2.6 mL). Each of the mixtures reacted separately in a Teflon autoclave at 120 °C for 4 h. The color of the mixture turned dark-green, indicating the formation of  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot NMs. We then applied a similar procedure to prepare  $\text{Cu}_{2-x}\text{S}/\text{CNT}$ ,  $\text{Cu}_{2-x}\text{S}/\text{C}_{dh}$ , and  $\text{Cu}_{2-x}\text{S}/\text{carbon black NMs}$  using CNTs,  $C_{dh}$ , and carbon black (0–0.2 mg), respectively, instead of C dots. Each  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot,  $\text{Cu}_{2-x}\text{S}/\text{CNT}$ ,  $\text{Cu}_{2-x}\text{S}/\text{C}_{dh}$ , and  $\text{Cu}_{2-x}\text{S}/\text{carbon black NMs}$  solution was subjected to sonication for at least 30 min and then to two centrifugation (6000 rpm, 10 min)/wash (EtOH, 1.5 mL) cycles. Each of the  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot,  $\text{Cu}_{2-x}\text{S}/\text{CNT}$ ,  $\text{Cu}_{2-x}\text{S}/\text{C}_{dh}$ , and  $\text{Cu}_{2-x}\text{S}/\text{carbon black NMs}$  was then re-dispersed in EtOH (1.0 mL) prior to use.

## 2.5. Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of as-prepared NMs were recorded using JEOL JSM-1230 (Hitachi, Tokyo, Japan) and FEI Tecnai-G2-F20 (GCE-Market, NJ, USA) systems operating at 200 kV, respectively. High angle annular dark-field scanning TEM (HAADF-STEM) images

were recorded using Philips Tecnai F20 G2 FEI-TEM (Roanoke, VA, USA) equipped with an energy-dispersive X-ray spectrometer (EDS). The as-prepared NMs were carefully deposited onto 400-mesh C-coated Ni grids and the excess solvents were evaporated at ambient temperature (25 °C) and pressure. For X-ray diffraction (XRD) studies, a PANalytical X'Pert PRO diffractometer (Almelo, Netherlands) with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) was used. X-ray photoelectron spectroscopy (XPS) measurement was conducted using a VG ESCA210 electron spectroscope from VG Scientific (West Sussex, UK). The binding energy (BE) for Au was used as an internal reference to eliminate the charging effect. The samples for XPS measurements were prepared by depositing drops of the as-prepared NMs onto Si substrates and then evaporating the solvents at ambient temperature and pressure. An Elan 6000 inductively coupled plasma mass spectrometer (ICP-MS) from Perkin-Elmer (Wellesley, MA, USA) was employed to determine Cu contents in the as-prepared  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot,  $\text{Cu}_{2-x}\text{S}/\text{CNT}$ ,  $\text{Cu}_{2-x}\text{S}/\text{C}_{dh}$ , and  $\text{Cu}_{2-x}\text{S}/\text{carbon black NMs}$ . Prior to ICP-MS measurements, the as-prepared  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot and  $\text{Cu}_{2-x}\text{S}/\text{CNT}$  NMs were dissolved in 2%  $\text{HNO}_3$ . Photoluminescence images were recorded using an Olympus IX71 (Tokyo, Japan) fluorescence microscope with a DP70 digital camera. The excitation wavelength was in a range of 340–365 nm.

## 2.6. Fabrication of electrodes and electrocatalytic analysis

Aliquots ( $\text{Cu}_{2-x}\text{S}$  catalyst mass loading: 2.26 mg  $\text{cm}^{-2}$ ) of the as-synthesized NMs solutions were placed separately onto the clean glassy carbon surface of each RDE (diameter: 5 mm). After being air-dried for 1 h at ambient temperature, Nafion solution (0.5%, 1  $\mu\text{L}$ ) was placed onto each of the electrodes. A commercial Pt/C solution was used to prepare control electrodes in a similar way. Three-electrode electrochemical cells were constructed using one of the modified RDE as the working electrode, a Pt wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference. The electrocatalytic activities of the as-synthesized NMs in the three-electrode cells were measured using a CHI 760D electrochemical workstation (Austin, TX, USA). Cyclic voltammetry (CV) measurements of the  $\text{Cu}_{2-x}\text{S}/\text{C}$  dot RDEs in  $\text{O}_2$ -saturated and  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  were conducted over a potential range from 0 to 1.0 V at a scan rate of 5 mV  $\text{s}^{-1}$ . Linear sweep voltammetry (LSV) measurements of the as-prepared RDEs in  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  were conducted over a potential range from 0 to 1.0 V at a scan rate of 5 mV  $\text{s}^{-1}$  with different rotation speeds. The kinetics of ORR occurring at the RDEs was explored using Koutecky–Levich equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} \quad (1)$$

$$J_L = 0.62nFC_0D_0^{2/3}\nu^{-1/6}\omega^{1/2} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

where  $J$  is the measured current density,  $J_K$  and  $J_L$  are the kinetic and diffusion limiting current densities, respectively,  $n$  is the overall number of electrons transferred,  $F$  is the Faraday constant,  $C_0$  is the  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  ( $\sim 1.1 \times 10^{-6}$  mol  $\text{cm}^{-3}$ ),  $D_0$  is the diffusion coefficient of  $\text{O}_2$  ( $\sim 1.4 \times 10^{-5}$   $\text{cm}^2 \text{s}^{-1}$ ),  $\nu$  is the kinetic viscosity of the solution (0.01  $\text{cm}^2 \text{s}^{-1}$ ),  $k$  is the kinetic rate constant, and  $\omega$  is the rotation rate (rpm) [23]. The slopes of their best linear fit lines in Fig. 4B were used to calculate the number of electrons transferred ( $n$ ) according to the Koutecky–Levich equation.

$\text{Cu}_{2-x}\text{S}/\text{C}$  dot NMs and commercial Pt/C catalyst were conducted in 0.5 M  $\text{H}_2\text{SO}_4/1.0$  M MeOH over the same potential range. The data were used to obtain Tafel plots to investigate MeOH tolerance of the electrodes. All electrochemical data were recorded over 10 reproducible cycles. The electrochemical impedance spectrometer

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