Electron microscopy study of platinum nanoparticle catalysts supported on different carbon nanostructures for fuel cell applications

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Low electrocatalytic activity and high cost of platinum (Pt)-based catalysts have hindered broad applications of direct ethanol and methanol fuel cells. One strategy to overcome the hindrance is to investigate novel carbon materials as catalyst supports to effectively disperse Pt-based catalyst particles. In this study, Pt nanoparticles were synthesized on different carbon nanostructures, including single-walled carbon nanotubes, multi-walled carbon nanotubes, graphene, and Vulcan XC-72R carbon black, using the same reaction parameters; and a series of scanning electron microscopy/scanning transmission electron microscopy techniques, using secondary electrons, backscattered electrons, transmitted electrons, and forward-scattered electrons, were employed to characterize the morphology of Pt nanoparticles and various carbon nanostructures as well as the distribution of the Pt nanoparticles on the carbon supports. Experimental results demonstrate that different imaging modes provide a variety of information about a specimen, and various imaging modes need to be selectively used in order to effectively analyze Pt nanoparticles supported on various carbon nanostructures.

Keywords fuel cell; carbon nanotube; graphene; platinum; nanoparticles; catalyst

1. Introduction

As one of the most promising alternative energies, fuel cells have been receiving increased attention recently due to the depletion of fossil fuels and the increase in environmental pollution. Among different types of fuel cells, direct ethanol fuel cells (DEFCs) and direct methanol fuel cells (DMFCs) are excellent power sources due to their high energy density, low pollutant emission, low operating temperature, and ease of handling liquid ethanol/methanol fuel [1-3]. However, critical obstacles remain that inhibit broad applications of DEFCs and DMFCs, including low electrocatalytic activity of anode/cathode electrodes and the high cost of noble metal, platinum (Pt)-based catalysts. In order to enhance catalytic activity and to reduce the usage of Pt-based catalysts, one strategy is to explore novel carbon materials as catalyst supports and to effectively disperse Pt-based particles on these supports. Vulcan XC-72R carbon black has been the most widely-used catalyst support for the preparation of fuel cell catalysts because of its exceptional electronic conductivity and surface area. During the past several years, a number of research groups have investigated carbon nanotubes and graphene, two types of novel carbon nanostructures, as catalyst supports and have demonstrated that both carbon nanotubes and graphene can improve the electrocatalytic activity of Pt nanoparticles more effectively for methanol and ethanol oxidation than Vulcan XC-72R carbon black [4-10].

With the aim of investigating the dispersion of Pt nanoparticles on various carbon nanostructures, we used the same reaction parameters to synthesize Pt nanoparticles on different carbon nanostructures, including single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene, and Vulcan XC-72R carbon black. In comparison to optical microscopy and transmission electron microscopy (TEM), scanning electron microscopy (SEM) can provide a better depth-of-field for revealing the morphology of Pt nanoparticles and their distributions on the surface of various carbon supports. In this study, a series of SEM/scanning transmission electron microscopy (STEM) techniques, using secondary electrons, backscattered electrons, transmitted electrons, and forward-scattered electrons, were employed to characterize the morphology of Pt nanoparticles and different carbon nanostructures as well as the distribution of the Pt nanoparticles on various carbon supports. These systematic characterizations provide detailed information on the morphology and structures of Pt nanoparticles supported on different carbon nanostructures, and the information will help us design and synthesize desirable catalyst supports and Pt nanoparticles for fuel cell applications.

2. Synthesis of Pt nanoparticles supported on different carbon nanostructures

Pt nanoparticles supported on different carbon nanostructures were synthesized using the same procedures and reaction parameters by an ethylene-glycol (EG) reduction method, the details of which are described elsewhere [9, 10]. Briefly, certain amounts of carbon nanostructures (carbon nanotubes, carbon black, and graphene) were suspended in EG solution followed by sonication for 30 minutes. Hexachloroplatinic acid was added into the solution and mechanically stirred for 2 hrs. Sodium hydroxide (NaOH) was added to adjust the pH of the solution to 13.0; subsequently, the solution was fluxed at 130 °C for 3 hrs under argon gas flow. The precipitation was filtered, washed four times with deionized water, and dried in an oven at 80 °C for 12 hrs.
3. Imaging Pt nanoparticles using different electron detectors

![Diagram showing the position of electron detectors](image)

Fig. 1  Photo (a) and schematic detector position diagram (b) of an FEI Quanta 200 FESEM specimen chamber equipped with a SE detector and a BSE detector; photo (c) and schematic detector position diagram (d) of the FESEM chamber equipped with a SE detector, a BSE detector, and a retractable STEM detector. The STEM detector includes three segments: BF, DF, and HAADF (at the bottom right corner in Fig. 1d). SE, secondary electron; BSE, backscattered electron; STEM, scanning transmission electron microscopy; BF, bright field; DF, dark field; HAADF, high angle annular dark field.

The versatility of SEM detectors results from the rich variety of interactions between an incident electron beam and a specimen. These interactions can be divided into two types: elastic scattering and inelastic scattering. Elastic scattering does not alter the kinetic energy of the beam electrons yet influences their trajectories inside bulk samples, such as backscattered electrons (BSEs) and forward scattered electrons; inelastic scattering transfers energy from the beam electrons to the atoms of the specimen, resulting in the generation of secondary electrons (SEs), Auger electrons, characteristic and Bremsstrahlung (continuum) X-rays, lattice vibrations (phonons), and electron oscillations in metals (plasmons) [11]. In principle, all of these interactions can be used to reveal information about the nature of a specimen if captured by a detector dedicated to the specific interaction. The most commonly used electron detector is the Everhart-Thornley secondary electron (SE) detector followed by the solid state backscattered electron (BSE) detector. An FEI Quanta 200 SEM equipped with a SE detector and a BSE detector is illustrated in Fig. 1a and 1b. The SE detector is positioned above and to one side of the specimen, and the BSE detector is positioned above the specimen, concentric with the opening of the final lens and the electron beam in a “doughnut” type arrangement. Low energy SEs (less than 50 eV, with a most probable energy of 3 - 5 eV) are emitted from the surface and immediate sub-surface of a specimen and provide information regarding the surface topography of the specimen; high energy BSEs reveal areas having different chemical compositions because heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number). With the development of technology and improved manufacturing techniques, SEMs are more commonly equipped with a scanning transmission electron microscopy (STEM) detector to reveal internal structures of the specimen. An FEI Quanta 200 SEM system, equipped with an SE detector, a BSE detector, and a STEM detector is illustrated in Fig. 1c and 1d. The retractable STEM detector provides three different modes of detection: bright field (BF), dark field (DF), and high angle annular dark field (HAADF). The STEM-BF detector collects electrons transmitted through the specimen. Both mass-thickness and diffraction contrast contribute to the BF image formation; the STEM-DF detector gathers electrons diffracted in crystalline areas and incoherent Rutherford scattering electrons; and the STEM-HAADF detector collects electrons scattered to high angles (50 to 200...
mrad) where the scattering is predominately incoherent Rutherford scattering and roughly proportional to the square of the atomic number (Z). SE and BSE in combination with BF/DF/HAADF provide information about the surface and throughout the specimen at the same time. One prerequisite for STEM imaging is that the specimen needs to be thin enough to enable the transmission of incident electrons. Usually, the thickness of the specimen is less than 100 nm.

In this study, electron microscopy imaging of Pt nanoparticles was conducted with an FEI Quanta 200 field emission scanning electron microscope (FESEM) equipped with an Everhart-Thornley SE detector, a BSE detector, and a retractable STEM BF/DF/HAADF detector. As shown in Fig. 1a-1d above, characterizations can be conducted with two different configurations of detectors. One configuration serves to examine the surface features and relative elemental composition of a specimen using SE/BSE detectors (Fig. 1a-1b), and the other configuration serves to examine internal structures of the specimen besides its surface topography using SE/BSE/BF/DF/HAADF detectors (Fig. 1c-1d). All electron microscopy characterizations were conducted with an acceleration voltage of 20 kV for comparison. For a sample characterization using SE/BSE detectors, a sample consisting of a specific amount of Pt nanoparticles supported on various carbon supports was directly affixed onto the surface of double-stick conductive copper tape, which in turn was attached to an aluminum sample stub. For a sample characterization using SE/BSE/BF/DHAAF, sample powder was dispersed in an ethanol solution and sonicated for 5 min. Several drops of suspension were transferred subsequently onto a holey carbon film supported by a TEM copper grid.

3.1 Imaging Pt nanoparticles supported on carbon nanotubes using SE/BSE detectors

![Fig. 2](image)

**Fig. 2** SE (a, c) and BSE (b, d) images recorded simultaneously from Pt nanoparticles supported on MWCNTs and SWCNTs, respectively. The Z-contrast effect in the BSE images permits unambiguous identification of Pt nanoparticles, yet these nanoparticles are observed with difficulty in the SE images. However, SE images demonstrate the surface morphology of carbon nanotubes not evident in the BSE images. All images were acquired at the same magnification for comparison.

Fig. 2a and Fig. 2c are SE images of Pt nanoparticles supported on MWCNTs and SWCNTs, respectively. SWCNTs largely aggregated into bundles. In comparison to SWCNTs, MWCNTs separated from one other with a diameter ranging from 5 nm to 20 nm. Some particles exist on the surface of both MWCNTs and SWCNTs, but it is difficult to identify the location of the particles due to the weak contrast between particles and nanotubes. However, simultaneously obtained BSE images (Fig. 2b and Fig. 2d) clearly reveal the dimension and distribution of those nanoparticles on the
surface of carbon nanotubes, an observation which confirms that BSE imaging is a Z-contrast technique that yields compositional contrast information. Atomic numbers (Z) for Pt and C are 78 and 6, respectively. The signal from the BSE detector is proportional to the backscatter coefficient, which nearly monotonically increases with increasing Z. In Fig. 2b and Fig. 2d, the higher Z particles appear brighter than the lower Z background structures. The bright particles are Pt nanoparticles with a size of less than 10 nm. These nanoparticles are difficult to identify in SE images (Fig. 2a and Fig. 2c). SE images reveal the morphology and dimension of carbon nanotubes, while BSE images (Fig. 2b and Fig. 2d) demonstrate the morphology and distribution of Pt nanoparticles associated with the surface of carbon nanotubes. SE and BSE imaging are complementary concurrent techniques for the characterization of Pt nanoparticles supported on carbon nanotubes.

3.2 Imaging Pt nanoparticles supported on carbon blacks using SE/BSE/STEM detectors

![Fig. 3](image)

**Fig. 3** Pt nanoparticles supported on Vulcan XC-72R carbon black were imaged simultaneously with SE (a), BSE (b), STEM-BF (c), and STEM-HAADF (d) detectors. Different detectors concurrently reveal different information about the morphology of carbon black particles and Pt nanoparticles as well as the distribution of Pt nanoparticles on carbon black particles.

As demonstrated in Fig. 3a, carbon black particles aggregate together and have a dimension that varies from 30 nm to 100 nm. No obvious information on Pt nanoparticles can be obtained from the SE image (Fig. 3a). In contrast, BSE imaging (Fig. 3b) provides much more information on Pt nanoparticles than carbon black particles. The bright particles are Pt nanoparticles, with a size less than 10 nm, that are difficult to detect in the SE image (Fig. 3a). The same region of the specimen can be simultaneously characterized using STEM detector modes, such as the BF detector and the HAADF detector. Under STEM-BF imaging mode, electrons might not pass through the regions containing aggregated carbon particles and, thereby, the aggregated carbon particles demonstrated in Fig. 3a reveal themselves as black clusters without concurrently providing any information on the relative location of carbon particles or Pt nanoparticles. Instead, primary incident electrons can pass through individual particles, which appear to be positioned at the edges of aggregated carbon particles. In Fig. 3c, individual carbon particles and Pt nanoparticles are in bright and dark contrast, respectively. As a complementary detector to the STEM-BF detector, the STEM-HAADF detector collects the electrons incoherently scattered at high angles to form compositional sensitive images. As opposed to Bragg-scattered electrons, the high-angle scattering is proportional to $Z^2$, where $Z$ is the atomic number of the element under the electron beam. As
shown in Fig. 3d, the heavier Pt atoms appear brighter than the lower Z carbon background structures in comparison to its corresponding BF image in Fig. 3c. Besides Pt nanoparticles, some thick regions of aggregated carbon particles with Pt nanoparticles appear bright due to multi-scattering of electrons in these thick regions. HAADF imaging largely reveals information on Pt nanoparticles and their distribution among carbon particles; BSE imaging mainly shows Pt nanoparticles that are located on the surfaces of carbon particles.

3.3 Imaging Pt nanoparticles supported on graphene using SE/BSE/STEM detectors

![Image of Pt nanoparticles supported on graphene sheets](image)

**Fig. 4** Pt nanoparticles supported on graphene sheets were simultaneously imaged with SE (a), BSE (b), STEM-BF (c), and STEM-HAADF (d) detectors. Different detectors concurrently reveal different information regarding the morphology of graphene sheets and Pt nanoparticles as well as the distribution of Pt nanoparticles on the graphene sheets. Sheet folds, black arrows; multiple graphene layers, white arrows.

SE, BSE, STEM-BF, and STEM-HAADF images of Pt nanoparticles supported on graphene sheets further demonstrate different characteristics of the various imaging techniques. A graphene sheet is a single atomic layer of carbon that is thin enough to allow incident electrons to pass completely through it; therefore, all four images in Fig. 4 illustrate the distribution of Pt nanoparticles on both surfaces of the graphene sheets and inside them as well; different imaging techniques have their unique advantages for morphology and structural characterization. For example, the SE image (Fig. 4a) demonstrates noticeably the morphology of the Pt nanoparticles and their distribution on the surfaces of graphene sheets. The STEM-BF image (Fig. 4c) clearly shows various features of graphene substrates, such as folds (indicated by black arrows in Fig. 4c) and regions of multiple layers of graphene (indicated by white arrows in Fig. 4c). The number of electrons that pass through a specimen is inversely related to the thickness of the specimen. In comparison to BSE and STEM-HAADF images of Pt nanoparticles supported on carbon black (Fig. 3b and Fig. 3d), the BSE and STEM-HAADF images present a nearly identical appearance. This appearance is generated mainly because graphene layers (one or several atomic layers) are much thinner than carbon black (30 nm to 100 nm). Both BSE and STEM-HAADF images simultaneously show the distribution of Pt nanoparticles and their dimensions, yet lack information regarding graphene support morphology. Fig. 3 and Fig. 4 comparatively demonstrate that either BSE or STEM-HAADF imaging is sufficient for the characterization of Pt nanoparticles supported a relatively uniform and thin
catalyst support, such as graphene sheets; otherwise, both BSE and STEM-HAADF need to be used for the characterization of Pt nanoparticles on a thick and non-uniform support, such as carbon black particles.

Electron microscopy characterizations above demonstrate that Pt nanoparticles are localized on carbon nanotubes and graphene sheets much more uniformly than on carbon blacks, observations that are consistent with electrochemical measurements of these materials. Pt nanoparticles supported on carbon nanotubes and graphene sheets exhibit superior catalytic characteristics for both ethanol oxidation and methanol oxidation than Pt nanoparticles supported on carbon black particles. A next step will be to explore interactions between Pt nanoparticles and different carbon supports through atomic imaging of their interfaces using TEM/STEM with a high acceleration voltage (e.g., 200 kV) [12] or aberration-corrected TEM/STEM [13-15].

4. Conclusions

In conclusion, all signals produced via interactions between incidence electrons and a specimen can be used to investigate morphology and structures of the specimen. In this study, several scanning electron imaging techniques, including SE, BSE, STEM-BF, and STEM-HAADF, were used to study Pt nanoparticles supported on different carbon nanostructures (SWCNTs, MWCNTs, black carbon, and graphene). Different imaging techniques reveal different characteristics of the specimen. For example, SE imaging, the most commonly-used technique, can provide information on the morphology of Pt nanoparticles and carbon nanostructures as well as the distribution of Pt nanoparticles on the surface of the carbon nanostructures. BSE, a compositional characterization technique, reveals the morphology of Pt nanoparticles and their locations on the surface of different carbon supports, while some nanoparticles may not be identified via SE characterizations. STEM-BF/HAADF imaging collects transmitted electrons and forward scattered electrons that exhibit the distribution of Pt nanoparticles both on the surface of carbon supports and in their interiors. One useful strategy is to simultaneously image a specimen with all of the detectors in order to reveal different information about the specimen. Electron microscopy characterizations will help us to design and synthesize desirable catalyst supports and Pt nanoparticles for fuel cell applications.

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