Carbon Surface Layers on a High-Rate $LiFePO_4$

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Abstract

Transmission electron microscopy (TEM) was used to image particles of a high-rate $LiFePO_4$ sample containing a small amount of *in situ* carbon. The particle morphology is highly irregular, with a wide size distribution. Nevertheless, coatings, varying from about 5-10 nm in thickness, could readily be detected on surfaces of particles as well as on edges of agglomerates. Elemental mapping using Energy Filtered TEM (EFTEM) indicates that these very thin surface layers are composed of carbon. These observations have important implications for the design of high-rate $LiFePO_4$ materials in which, ideally, a minimal amount of carbon coating is used.

Introduction

In 1997, Goodenough introduced $LiFePO_4$ (triphylite) as a possible cathode for rechargeable Li-ion batteries. The abundant availability of Fe at a relatively low price and the good environmental compatibility make this an attractive alternative to currently used $LiCoO_2$ or $LiMn_2O_4$ cathodes. $LiFePO_4$ has a flat voltage plateau at about 3.4 V against Li and a theoretical capacity of 170 mAh/g.[1] The practical discharge capacity of $LiFePO_4$ electrodes, however, is often much lower than the theoretical value, especially when high current densities are used. This has been attributed to low mobility of Li ions across the $FePO_4$ /$LiFePO_4$ interface and a low electronic conductivity of ~10^{-9} S/cm.[2]

Several approaches have been used to address the rate limitations of $LiFePO_4$ electrodes. The most promising of these involves producing very small particles and coating them with conductive carbon. For example, Ravet et al. reported a capacity of 160 mAh/g at C rate during cycling at 80°C for a sample with 1 wt.% carbon coating.[3] Yamada et al. investigated the influence of particle size, and found a strong correlation

between particle size and performance; the best performing materials were synthesized below 600ºC, where particle growth is inhibited.[4] Capacities of 120 mAh/g at 5C rate were recently reported for carbon-coated $LiFePO_4$ with particle sizes ranging from 100-200 nm.[5]

While carbon has beneficial effects upon the rate capability of the $LiFePO_4$ electrode, addition of even relatively small amounts adversely affect the tap density and energy density.[6] It is therefore critical that the amount of coating be minimized. It has recently been shown that the structure of the carbon (disordered vs. graphitic) covering the $LiFePO_4$ particles is crucial in determining electrode rate capability; in some cases, electrodes having more a more graphitic coating outperform those having more carbon with a more disordered structure.[7] It is not yet clear, however, what the ideal distribution of the carbon over the particle surfaces should be and if further reductions can be achieved. The details of carbon coating (surface fraction covered, nature of bonding, film thickness) may give important insights into the design of a high-rate electrode material in which energy density is not compromised. Herein we describe a detailed study of the carbon coating on a $LiFePO_4$ sample with excellent high rate characteristics, which may lead to answers to these important questions.

Experimental

$LiFePO_4$ powder was produced using a sol-gel method starting from $Fe(NO_3)_3 \bullet 9H_2O$ (Sigma Aldrich, 98+%), $C_2H_3O_2Li \bullet 2H_2O$ (Sigma Aldrich), and H_3PO_4 (EMP). Precursors were dissolved in water in a stoichiometric ratio of 1:1:1 and then combined with two stoichiometric equivalents of $HOCH_2CO_2H$ (glycolic acid, Sigma Aldrich, 70% solution in water). The pH was adjusted to between 8.5 and 9.5 using

NH_4OH (EMD) and the water evaporated on a hot plate. The sample was then calcined at 500° C for 10 hours under a flow of nitrogen before being planetary ball milled with 6 wt.% $C_6H_2(CO_2H)$ (pyromellitic acid, Sigma Aldrich) and 1 wt.% ferrocene (Alfa Aesar, recrystallized) for 1 hour in acetone. The solvent was then evaporated and the resulting powder fired to 600° C under flowing nitrogen for an additional 10 hours. The phase purity of the sample was verified using X-ray diffraction (XRD) performed on a Philips X'Pert diffractometer using an X'Celerator detector with Cu Kα radiation (λ = 1.54 Å). Elemental carbon analysis was performed by Luvak Inc. (Boylston, MA).

Composite cathodes consisting of 80 wt.% $LiFePO_4$, 8 wt. % Kynar poly-vinylidene fluoride (PVdF) binder (grade 2801-00, lot 97C8118, Elf Atochem North America, Inc., Technical Polymers Department), 6 wt. % SFG-6 synthetic flake graphite (Timcal Ltd., Graphites and Technologies), and 6 wt. % compressed acetylene black were fabricated as previously described.[7] Carbon-coated aluminum current collectors were used as backings for the positive electrodes. The thickness of the carbon coating was approximately 5 μm. 2032 size coin cells were assembled in a helium-filled glove box, using lithium metal as a counter electrode and 1 M LiPF6 in 1:2 ethylenecarbonate/dimethyl carbonate (EC/DMC) electrolyte solution. Cells were discharged and charged using a MacPile II galvanostat/potentiostat (BioLogic SA, Claix, France).

TEM specimens were prepared by crushing $LiFePO_4$ powder using a mortar and pestle and dispersing the particles onto a holey carbon grid. The specimens were studied at 200kV in a JEOL 2010 TEM. Energy filtered imaging (EFTEM) was carried out in a Philips CM200 equipped with a field emission gun, operated at 200kV and a GATAN Image Filter (GIF). In EFTEM images are formed using only those electrons that have undergone an element specific energy loss through inelastic interaction with core shell electrons of atoms in the specimen. Image processing was performed following the three

windows method to form jump ratio images for carbon, iron, phosphorous and oxygen using the intensities of the K and L absorption edges: The intensities of two pre-edge images are extrapolated to the energy values of the post edge image and subtracted from the post edge image. The formed jump ratio images contain information about elemental distributions in the specimen.

Results and Discussion

Figure 1 shows discharges at various rates for lithium cells containing the $LiFePO_4$ used in this study. This sample was processed with pyromellitic acid as a carbon source and ferrocene, a graphitization catalyst, and contained 1.45 wt. % carbon. This procedure gives *in situ* carbon with low D/G (disordered/graphene) and H/C ratios,[8] resulting in improved electronic conductivity for the sample.[9] As a result, the performance in lithium cells is greatly improved over those with $LiFePO_4$ powders prepared similarly, but without additives. The high-rate behavior of the material used to produce the data in Figure 1 compares favorably to $LiFePO_4$ from several other sources[10] when cell design parameters are normalized.[11]

Figure 2 shows the morphology and size of the synthesized particles of the $LiFePO_4$ sample. The size distribution observed by TEM varies about an order of magnitude from values <100nm to about approximately 1 μm. The morphology varies distinctly with some particles consisting of a continuous mass of material while others are agglomerates of smaller particles (compare A and B in Fig. 2). In Fig. 3 a section of a similar particle is shown (3a) together with the enlarged region of the contact zone between two particles (3b). The lattice planes in both grains are oriented at different angles with respect to each other as indicated by the lines drawn into the image.

Dislocations in the contact zone between two particles in Fig.4 indicate that the particles indeed are joined together, separated by a grain boundary. Analysis by EDS showed the characteristic peaks for carbon, oxygen, iron and phosphorus.

Imaging at higher magnification illustrates the presence of a thin surface layer on the $LiFePO_4$ particles. The layer seems continuous and is approximately 5-10 nm thick (Fig. 5a,b). A comparison between the particles imaged in Fig.5a and 5b shows that the surface layer is not of uniform thickness. From details in Fig. 5b it can be seen that lattice fringes within the particle stop at the interface between particle and surface layer indicating that the surface layer is of a different material than the substrate.

More information about the nature of the surface layer can be obtained by EFTEM. In Fig. 6a a bright field image of a $LiFePO_4$ particle covered by a film about 5-10 nm thick is shown. Imaging the same particle with electrons that have undergone energy losses characteristic for the absorption edges for core shell ionization of the elements forming $LiFePO_4$ and of carbon enables us to form elemental distribution maps. Brightness in an elemental map obtained by EFTEM corresponds to the presence of the atomic species whose absorption edge has been used for imaging. A comparison between Fig.6b, c, and 6d shows a high image intensity at the location of the surface layer when the carbon absorption edge has been used for imaging (Fig. 6b). Less than average image intensity is observed at the particle edge for imaging with electrons of the oxygen or iron absorption edges. This corresponds to absence of oxygen and iron in the carbon layer.

Figure 7a shows the image of an agglomerate, with a highly irregular shape, having many little steps. As with the individual particle shown in Figure 6a-d, EFTEM shows that O, Fe, and P (Figures 7c, d, and e) are evenly distributed, and C (Figure 7b) is

located at the periphery. Careful examination of Figure 7b shows faint white lines located at the edges of the steps (see arrow), indicating that there is a carbon coating on the irregular surfaces.

A number of unanswered questions remain concerning the role of the carbon coating upon the electrochemical behavior of $LiFePO_4$. Irregularly shaped particles and agglomerates are more difficult to cover completely, and would require more carbon than more regular spherical ones. Thus, one method for reducing the amount of carbon that is required would be to use synthesis techniques that result in nearly mono-disperse samples. However, it is not yet known whether a continuous coating or one with porosity, which could allow Li ions to diffuse more rapidly, is preferable. Further investigations using microscopic techniques may lend insight to these and other questions.

Conclusions

A high rate $LiFePO_4$ sample containing 1.45 wt. % *in situ* carbon was studied using TEM. The particles that were examined show evidence of a coating that varies in thickness from about 5-10 nm. EFTEM studies show conclusively that this coating is composed of carbon. The coating was evident even upon steps and surfaces of highly irregular agglomerates.

Acknowledgments

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Figure Captions

Figure 1. Discharge curves at differing current densities for a lithium cell containing the $LiFePO_4$ sample used in this study. Current densities used were 0.055 mA/cm^2 corresponding to C/25 rate, 0.31 mA/cm^2 (C/5), 0.7625 mA/cm^2 (C/2), 1.525 mA/cm^2 (C), 3.05 mA/cm^2 (2C), 4.575 mA/cm^2 (3C), and 7.62 mA/cm^2 (5C).

Figure 2. Transmission electron micrograph showing particle morphology and size distribution of $LiFePO_4$ powder.

Figure 3. Transmission electron micrograph showing agglomerate of $LiFePO_4$ particles. The enlarged contact zone in Fig.3b shows that lattice planes in the adjacent grains.

Figure 4. Transmission electron micrograph showing dislocation arrays in region between $LiFePO_4$ particles.

Figure 5. Higher magnification transmission electron micrographs of two particles showing surface layers.

Figure 6. (a) Bright field image of a particle. (b) EFTEM carbon jump ratio (c) oxygen jump ratio, and (d) iron jump ratio.

Figure 7. (a) Bright field image of agglomerate. (b) EFTEM carbon jump ratio (c) oxygen jump ratio (d) phosphorus jump ratio, and (e) iron jump ratio.

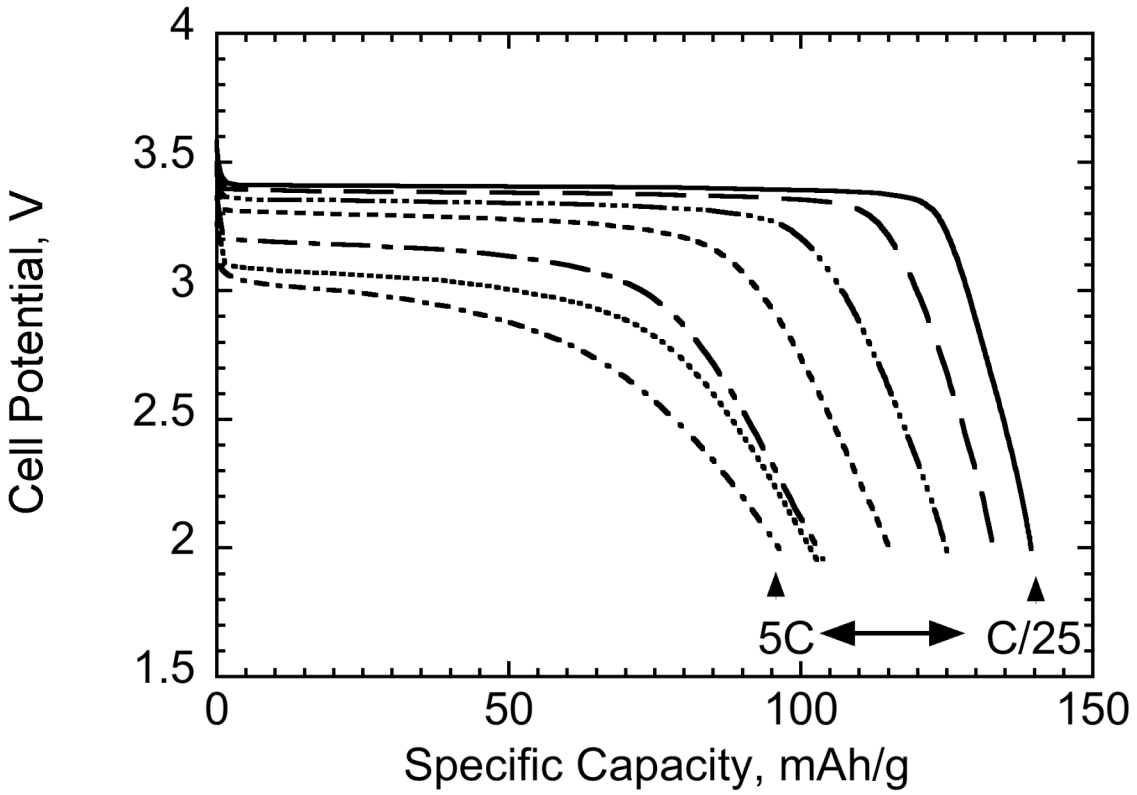

4
3.5
3
2.5
2
1.5
Cell Potential, V
0
50
100
150
Specific Capacity, mAh/g
5C
C/25

Figure 1

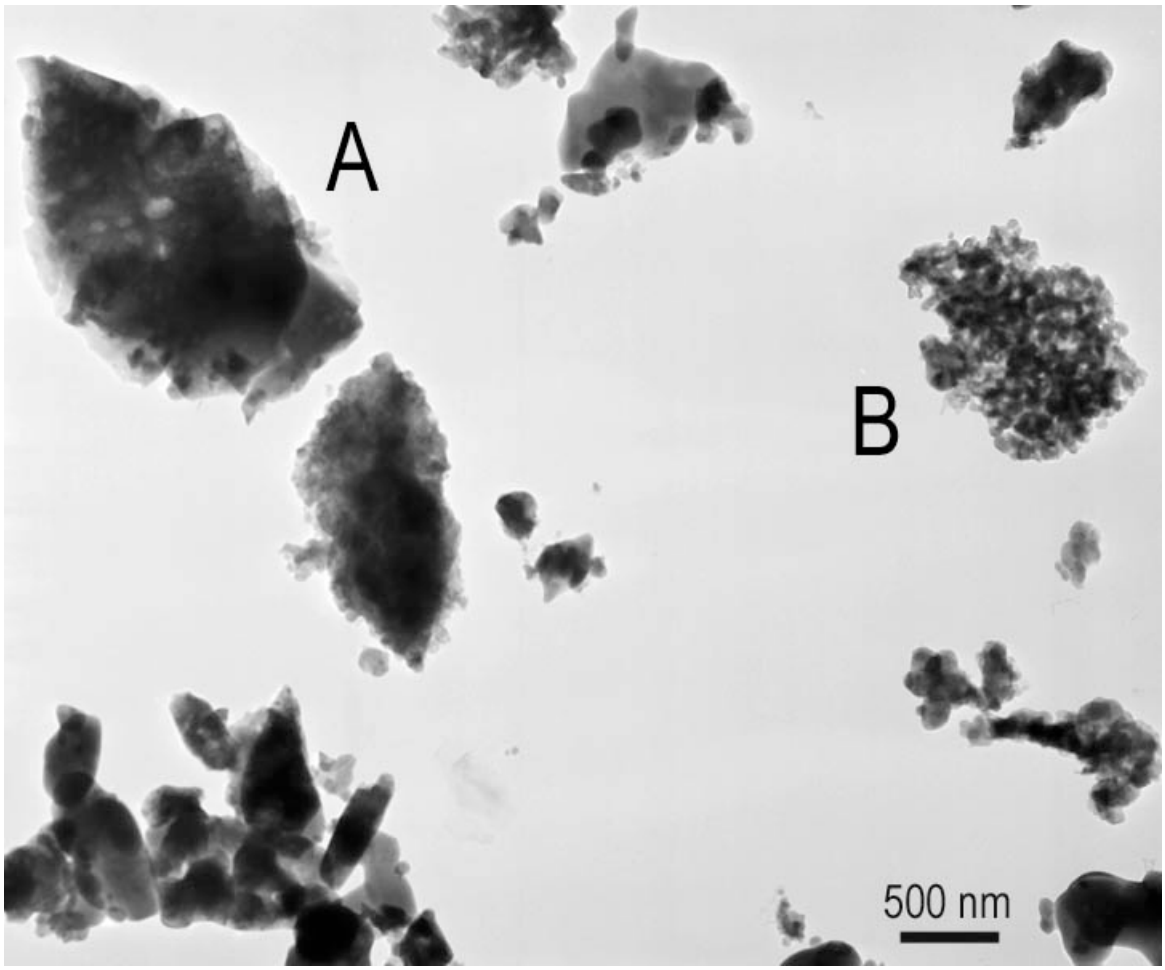
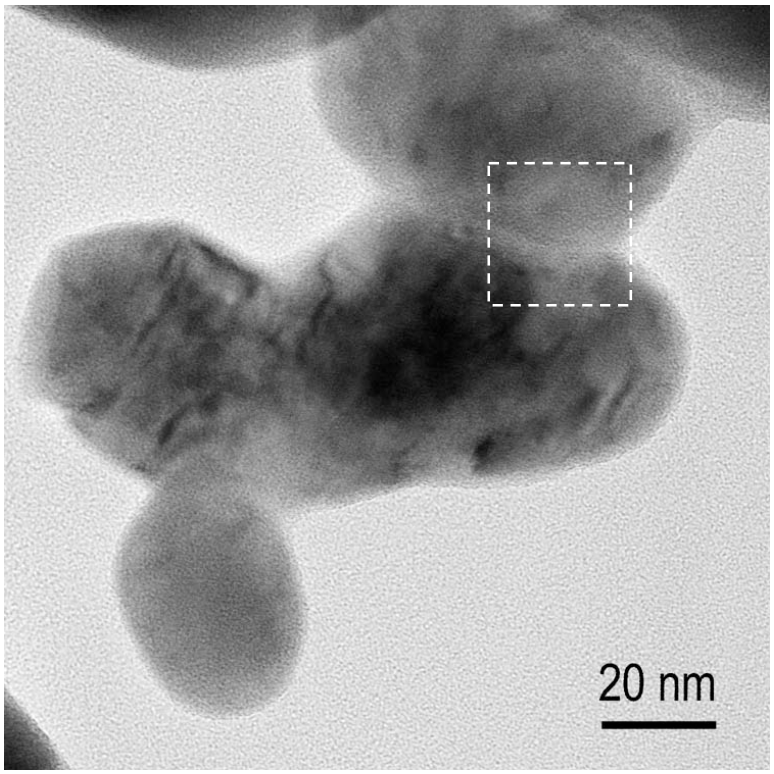
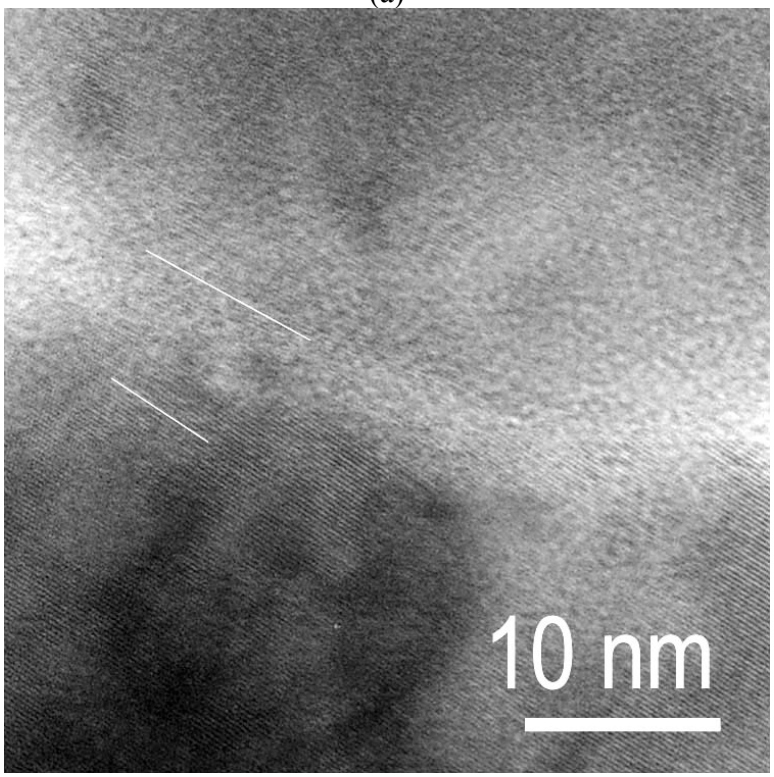


Figure 2



(a)



(b)

Figure 3

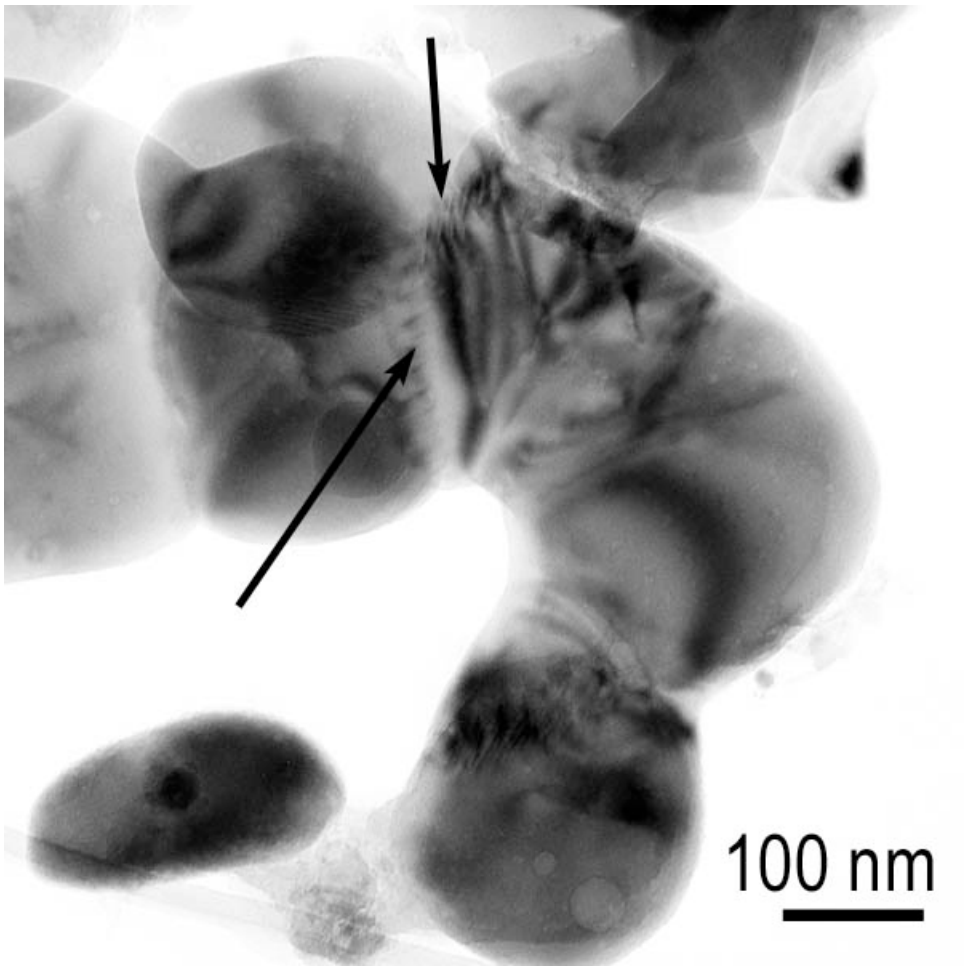
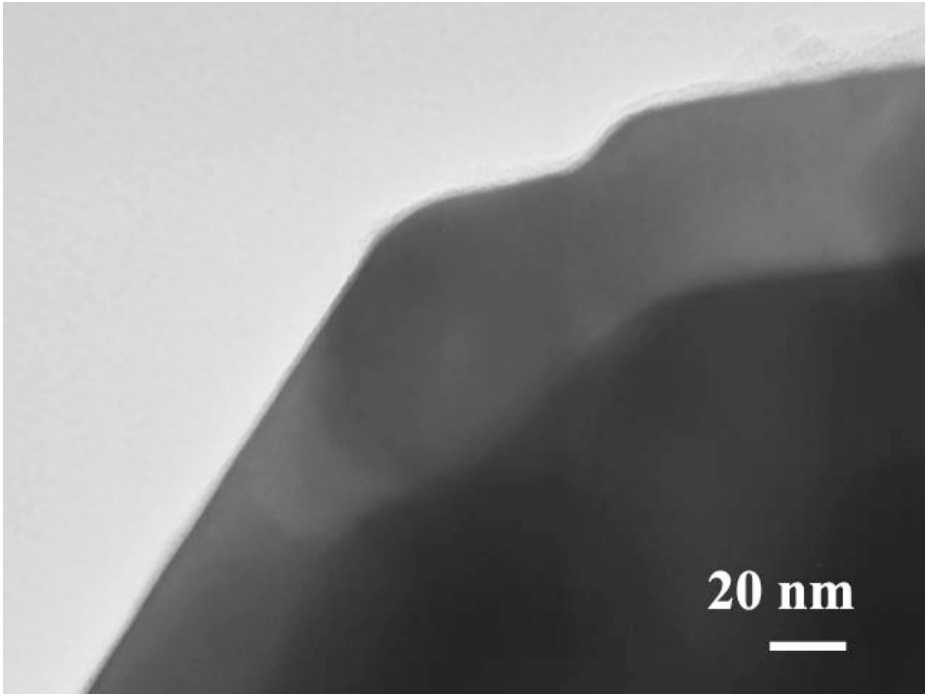
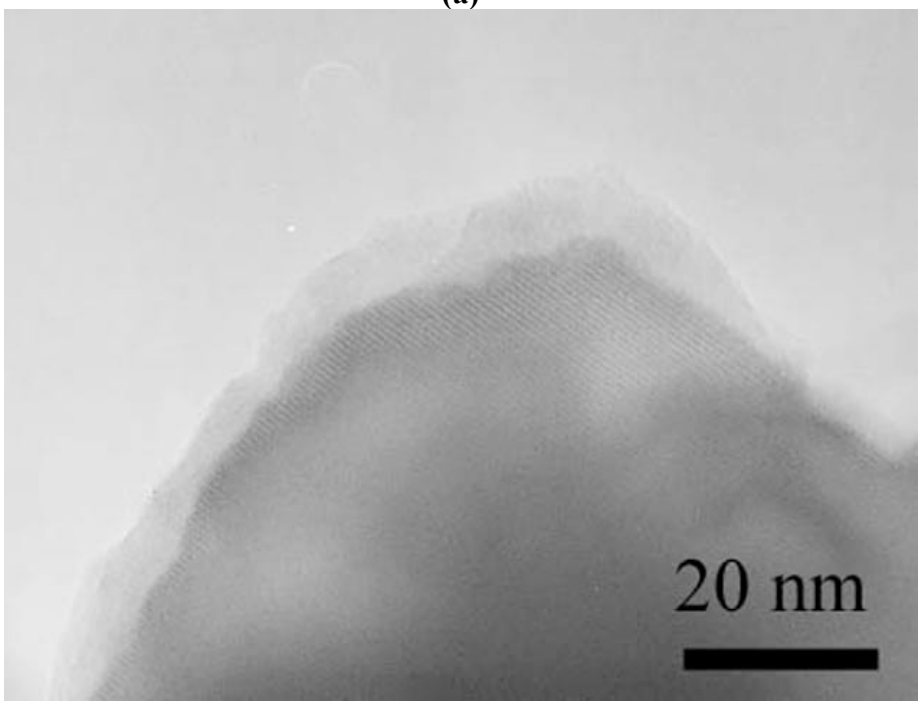


Figure 4

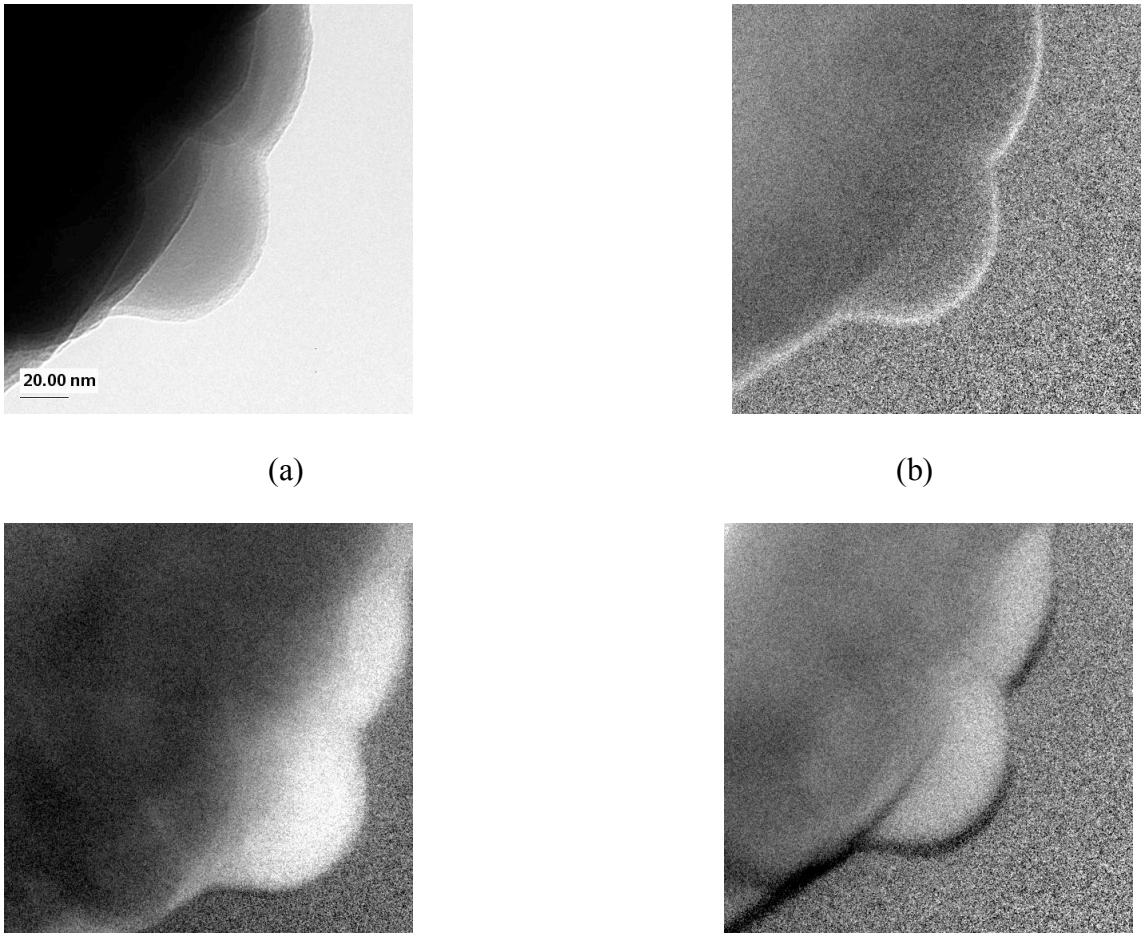


(a)



(b)

Figure 5



(a) (b)

(c) (d)

Figure 6

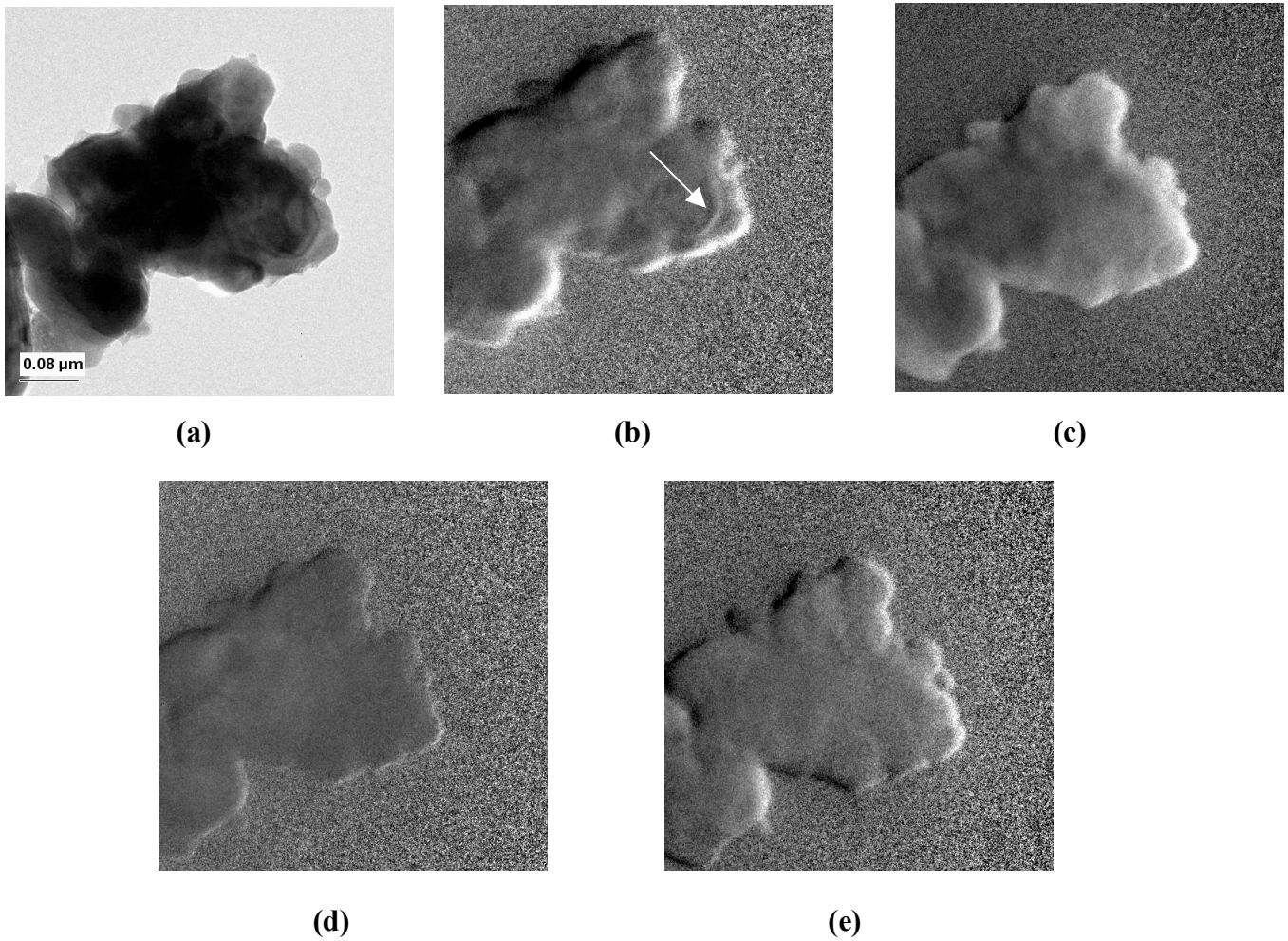


Figure 7