

A comparison of mixed phase titania photocatalysts prepared by physical and chemical methods: The importance of the solid–solid interface

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Received 26 January 2007; received in revised form 11 May 2007; accepted 14 May 2007

Available online 18 May 2007

Abstract

Mixed phase titania photocatalysts, such as Degussa P25, typically show higher photocatalytic activity than pure phase titania, as reported by many researchers. Our previous experimental results indicate that the solid–solid interface is a key factor in enhancing the photocatalytic reactivity of mixed phase titania and may be the location of catalytic “hot spots”. In this study, titania photocatalysts consisting of varying amount of anatase and rutile phases are prepared by reactive dc magnetron sputtering and by a modified sol–gel method. These titania materials are characterized with a variety of techniques and are tested in the photocatalytic degradation of acetaldehyde. Mixed phase titania thin films prepared by magnetron sputtering have a high density of anatase–rutile interfaces and display the highest photocatalytic activity among the catalysts tested. Studies by electron paramagnetic resonance spectroscopy show a unique distribution of charge trapping sites which are characteristic of the sputtered films. The role of anatase–rutile interface to separate charge and improve the photoactivity of mixed phase materials is discussed.

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Keywords: Titania; Photocatalysis; Magnetron sputtering; Sol–gel

1. Introduction

Despite wide interest dating back to the work of Fujishima and Honda [1], there is a surprising lack of knowledge about what controls the chemical reactivity of photocatalysts. Titania is considered an ideal photocatalyst since it is stable, inexpensive, safe, and highly reactive [2]. The initial process for titania photocatalysis is the generation of electron–hole pairs in titania particles. The excited conduction band electrons and valence band holes may recombine, may be trapped in metastable surface states, or may react with electron donors and electron acceptors adsorbed on the titania surface [3]. The excitation of anatase requires near UV radiation. Rutile, with a smaller bandgap, has a photoresponse which extends slightly into the visible light region, but it tends to display high rates of charge recombination. Usually, the fast recombination of charge carriers

(electrons and holes) competes with charge trapping and transfer and consequently limits the quantum efficiencies of photocatalytic processes [4].

A significant portion of research efforts over the past 30 years has focused on the environmental applications of semiconductor photocatalysis [5,6]. More recently, titania has been incorporated into many novel processes and applications beyond the remediation of contaminated air or water, including solar energy conversion, disinfection, sensors, photochromic and electrochromic devices, self-cleaning and superhydrophilic surfaces, and corrosion protection [7,8]. Yet, the development of these and other innovative applications of modern titania photocatalysis is hampered by our limited understanding of the relationship between catalyst structure and reactivity [7]. Research efforts are directed towards three objectives: (i) to achieve tailored photoactivity and selectivity, (ii) to improve the photoefficiency, and (iii) to extend the photoresponse of titania to visible light region [9,10].

A commercial mixed phase titania, Degussa P25, displays superior photocatalytic activity and has been widely used as

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the gold standard for comparing photocatalytic activity [11,12]. Degussa P25 in powder form contains both anatase phase and rutile phase (anatase/rutile ratio $\sim 70/30$) and has a surface area of $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ [13]. In an attempt to explain the superior photocatalytic activity of Degussa P25, Bickley et al. proposed an enhancement of the spatial charge separation in mixed phase titania that consisted of anatase and rutile phases in close contact [14]. Since, thermodynamically, the energy position of the conduction band edge of anatase is higher than that of rutile, photogenerated electrons were assumed to flow from anatase to rutile, while the holes transfer from rutile to anatase [15,16]. Electron paramagnetic resonance (EPR) studies by Hurum et al., however, indicated that photogenerated electrons actually migrate from rutile to lower energy anatase trapping sites [17–19]. This process is energetically allowed since the anatase trapping site is 0.8 eV lower in energy than the anatase conduction band and is also below ($\sim 0.6 \text{ eV}$) the rutile conduction band [20]. Electrons trapped on anatase surface were observed when Degussa P25 was illuminated with visible light, confirming the electron transfer from rutile to anatase since anatase can only be activated by UV radiation. Furthermore, an interfacial electron trapping site was identified in mixed phase titania [21]. The morphology of the nanocluster interface was found to influence the synergistic effect between anatase and rutile [17,22].

The studies of mixed phase titania reveal that effective interparticle charge transfer can promote charge separation and enhance the photoactivity and photoefficiency of titania-based photocatalysts. Although in a pure phase photocatalyst the rutile is relatively inactive due to high rates of recombination, in mixed phase materials it serves as an antenna to shift the photoreponse of anatase into the visible light region and promotes photoefficiency by hindering charge recombination. Agrios et al. showed that only Degussa P25 supported unique chemical reactivity in the formation of a charge transfer complex that was correlated to the interfacial surface area [23,24]. Based on this and other work, phase interfaces are likely locations of unique active sites for charge trapping, transfer, and chemical reactions.

In this study, we test the hypothesis that mixed phase titania photocatalysts having a high density of interfacial sites will display enhanced photoactivity. We have synthesized both pure and mixed phase nanocrystalline titania by two different methods (sol–gel process versus reactive magnetron sputtering), characterized the materials by a variety of techniques, and compared their reactivity in the photooxidation of acetaldehyde.

2. Experimental materials and methods

The preparation of titania thin films with varying phase composition by reactive dc magnetron sputtering is described in detail elsewhere [25]. Titania was deposited by magnetron sputtering onto clean borosilicate glass slides. Pure titanium (99.95%) was used as the sputtering target. High-purity argon and oxygen were used as sputtering and reactive gas, respectively. The base pressure in the coating chamber was maintained below $5.3 \times 10^{-4} \text{ Pa}$. The sputtering system used for this work

utilized a dual cathode, closed-field unbalanced magnetron configuration. By varying factors such as total power, total gas pressure, and deposition angle, a series of pure phase and mixed phase films was prepared [25].

Mixed phase titania materials were also synthesized by a modified sol–gel method [26]. First, amorphous titania was prepared by the traditional sol–gel process using titanium tetraisopropoxide (Sigma–Aldrich, 97%) as the titanium precursor. Then the amorphous titania was refluxed at 373 K for 22 h in the presence of a certain amount of concentrated hydrochloric acid. Titania thin films were prepared by dip-coating the resulting colloidal titania on glass slides. The dip-coated titania films were then dried at 373 K for 5 min. Three consecutive coating cycles were applied for each sample. Finally, the titania samples on glass slides were sintered and crystallized at 773 K for 2 h. Degussa P25 was also dip-coated on glass slides and was dried at room temperature.

X-ray diffraction (XRD) was used to determine the phase composition and to estimate the particle sizes of the synthesized titania photocatalysts. Diffraction patterns were recorded with a Rigaku XDS 2000 diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) over the range of $20^\circ < 2\theta < 60^\circ$ in 0.1° steps with a 1-s counting time per step. The synthesized titania thin films were also examined on a Hitachi S-4500 scanning electron microscope (SEM) equipped with a cold field emission electron gun. The quantitative analysis of surface areas of the titania films were determined by a JSPM-5200 atomic force microscopy (AFM) according to a method described previously [25].

For EPR studies, titania thin films were coated on quartz rods by reactive dc magnetron sputtering. The quartz rod with sputtered film was immersed in distilled water and purged with nitrogen. Titania powder samples prepared by the sol–gel method and Degussa P25 in powder form were dispersed in distilled water and were also purged with nitrogen prior to EPR studies. EPR spectra were collected on a Varian E-9 spectrometer equipped with a helium cryostat. Samples were cooled to 10 K and illuminated with a Xe lamp at that temperature while spectra were acquired [17].

Photocatalytic degradation of acetaldehyde was carried out in a batch reactor [25]. A specific amount of water vapor and 1500 ppm acetaldehyde were loaded into the reaction cell. The gaseous mixture was then circulated through the reactor until the acetaldehyde concentration reached a constant value. A Black Ray[®] UV lamp was used as the light source, providing illumination with wavelengths greater than 365 nm. The concentration of acetaldehyde was monitored as a function of time using an HP 5890 gas chromatograph equipped with a flame ionized detector.

3. Results and discussion

Among the three naturally occurring crystal phases of titania, anatase and rutile are the most studied phases in photocatalytic applications. Anatase is generally considered as the active component based on the comparison between anatase and rutile in charge carrier dynamics [27,28], chemical properties [29,30], and activity in photocatalytic degradation of organic compounds

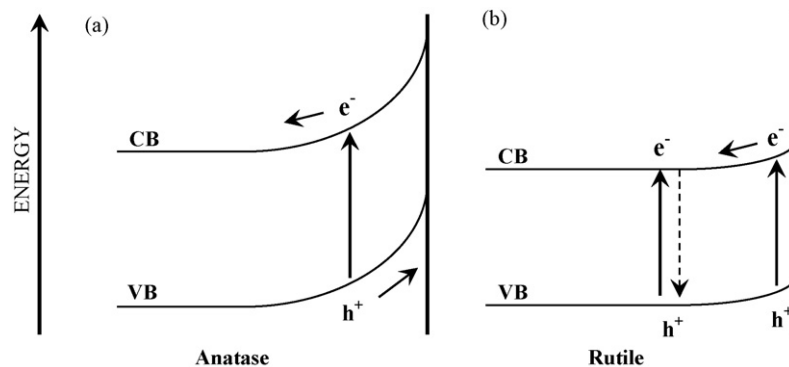


Fig. 1. Surface band bending of (a) anatase and (b) rutile.

[31,32]. For example, charge carriers generated in anatase have longer lifetimes than those in rutile [27]. It is suggested that anatase has inherent surface band bending that is spontaneously formed in a deeper region with a steeper potential in comparison with rutile (Fig. 1) [33,34]. In anatase, surface hole trapping dominates since spatial charge separation can be realized by the transfer of photogenerated holes towards the particle surface along the strong upward band bending (Fig. 1a). In rutile, however, bulk recombination of electrons and holes prevails such that only the holes very close to surface are trapped and transfer to the surface (Fig. 1b) [27].

Reactive magnetron sputtering has been used to deposit titania thin films on substrates by evaporating titania or titanium using accelerated Ar ions in the presence of oxygen [35–38]. The oxygen partial pressure and the energy of particles impinging on the substrate have been found to be important parameters which determine the phase composition of the resulting film [25]. Fig. 2 shows the XRD patterns of titania thin films prepared by reactive dc magnetron sputtering. The weight fraction

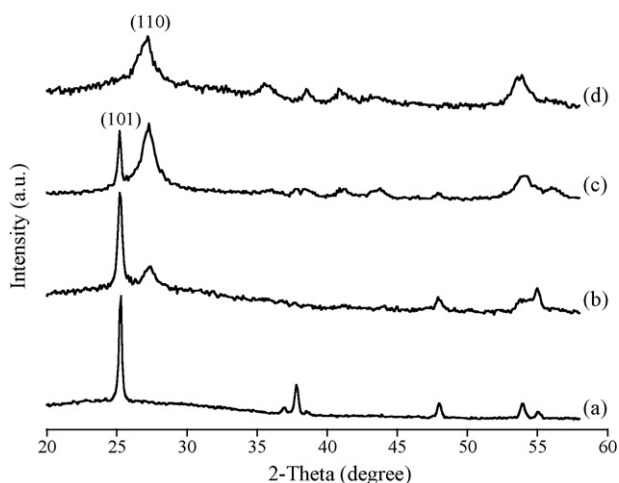


Fig. 2. XRD patterns of titania thin films prepared by reactive dc magnetron sputtering. The weight percentages of rutile phase are: (a) 0%, (b) 29%, (c) 78%, and (d) 100%, respectively. The deposition conditions for the thin films are: (a) low angle deposition, power 3 kW, bias 300 V, total gas pressure 6.0 mTorr, annealing at 673 K for 1 h; (b) low angle deposition, power 5.8 kW, bias 120 V, total gas pressure 3.5 mTorr; (c) perpendicular deposition, power 5.8 kW, bias 120 V, total gas pressure 3.5 mTorr; (d) perpendicular deposition, power 5.9 kW, bias 150 V, total gas pressure 3.5 mTorr.

of rutile phase (W_R) can be calculated from the equation [39]:

$$W_R = \frac{A_R}{0.884 \times A_A + A_R}$$

where A_A and A_R represent the integrated intensities of the anatase (1 0 1) peak and the rutile (1 1 0) peak, respectively. Fig. 2 shows that mixed phase titania with varying phase composition can be systematically prepared by magnetron sputtering. By varying the deposition parameters as described in Fig. 2 we were able to synthesize pure phase anatase and rutile films, as well as mixed phase films, in this case 30% rutile and 70% anatase, and 78% rutile and 22% anatase.

The sol–gel method is another approach to prepare mixed phase titania with controlled phase composition, as indicated by the XRD patterns shown in Fig. 3. By tuning the relative amounts of HCl and water, we were able to fabricate at low temperatures a comparable set of pure phase and mixed phase titania materials [26]. The average particle sizes can be calculated from the full-width at half-maximum (FWHM) of anatase (1 0 1) and rutile (1 1 0) peaks using Scherrer's equation. For titania samples synthesized by the sol–gel method, the average particle sizes of anatase and rutile were estimated to be 10 and 20 nm, respectively. For titania samples prepared by magnetron sputtering,

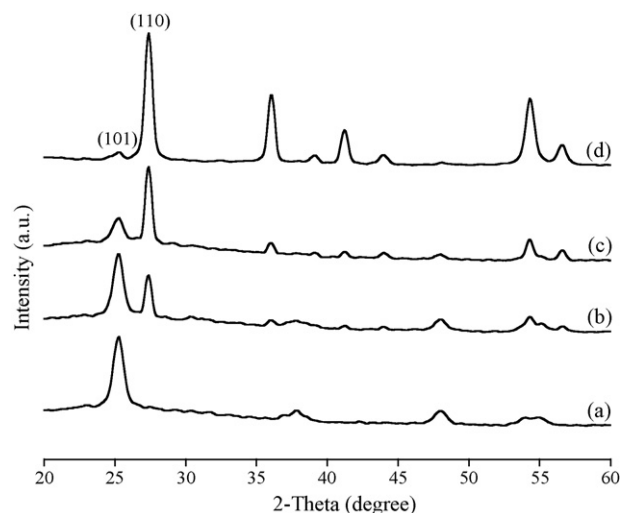


Fig. 3. XRD patterns of titania prepared by the sol–gel method. The weight percentages of rutile phase are (a) 0%, (b) 32%, (c) 75%, and (d) 94%.

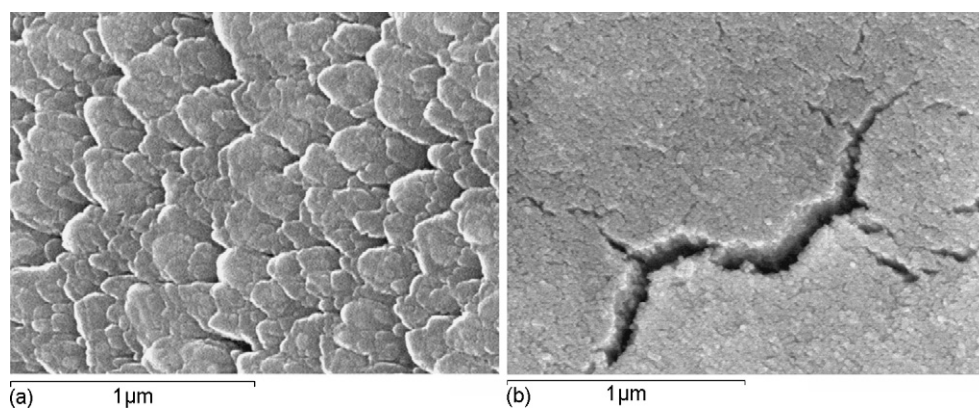


Fig. 4. SEM images of typical mixed phase titania films prepared by (a) reactive dc magnetron sputtering and (b) the sol-gel method. Scale bar is 1 μm .

however, the average particle size of anatase (~ 30 nm) is atypically much larger than that of rutile (~ 10 nm).

The SEM images of typical mixed phase titania thin films prepared by magnetron sputtering and the sol-gel method are shown in Fig. 4. The titania thin film prepared by magnetron sputtering has a scale-like, columnar morphology (Fig. 4a). A closer look at the sputtered titania films by TEM indicates that the sputtered thin films are composed of highly textured polycrystals with random orientations in the plane normal to the sputtering direction [25]. The nanodiffraction patterns of the sputtered films show that all anatase and rutile crystals are completely mixed together, producing a high density of anatase-rutile interfaces [25]. The films prepared by the sol-gel method are much smoother than those by magnetron sputtering; however, cracking is a common feature for films prepared by dip-coating the sol-gel nanocrystals on glass substrates (Fig. 4b).

Fig. 5 compares the EPR spectra of three titania samples having similar phase composition (approximately 70% anatase and 30% rutile). As mentioned in Section 2, mixed phase titania thin films were coated on quartz rods by magnetron sputtering for EPR studies under UV/visible light illumination. Slurries of Degussa P25 and sol-gel powder samples were dispersed in water and were purged with nitrogen prior to EPR studies. In the absence of oxygen, electrons trapped in anatase ($g = 1.995$) and rutile ($g = 1.977$) can be clearly identified for Degussa P25 and the sol-gel sample; trapped holes are characterized by resonances around $g = 2.016$ (Fig. 5). The EPR spectrum of the sputtered titania film, however, shows a small and broad signal of trapped electrons, suggesting that the domain of crystallinity is likely small. In addition to the hole signals around $g = 2.016$, a strong resonance with a g tensor at 2.0065, possibly an axially symmetric signal within the anatase interior, is prominent for the sputtered titania sample. The reduced crystallinity may be the consequence of a high proportion of interfacial area relative to the anatase and rutile nanocrystalline areas. These data are a preliminary indication that the sputtered materials contain a different population of trapping sites in comparison to Degussa P25 and the sol-gel sample.

Titania thin films deposited by magnetron sputtering demonstrated high photocatalytic activity, as measured by the photooxidation of acetaldehyde and in comparison to Degussa

P25 and the sol-gel films. Fig. 6 plots the conversion of acetaldehyde as a function of rutile content using titania materials prepared by different methods. The conversion of acetaldehyde has been normalized to the surface areas of the titania films, as reported in a previous paper [25]. After irradiation for 5 min, the conversion of acetaldehyde in the presence of mixed phase titania prepared by magnetron sputtering is significantly greater than those of pure phase titania prepared by the same method and is also significantly greater than that of Degussa P25, as shown in Fig. 6. Based on this measure of photoactivity, the sputtered materials also performed better than the corresponding sol-gel materials.

The deposited films having high proportions of rutile also showed relatively high activity, reinforcing the notion that anatase is, in fact, activating the rutile. Furthermore, pure phase rutile prepared by magnetron sputtering displayed greater

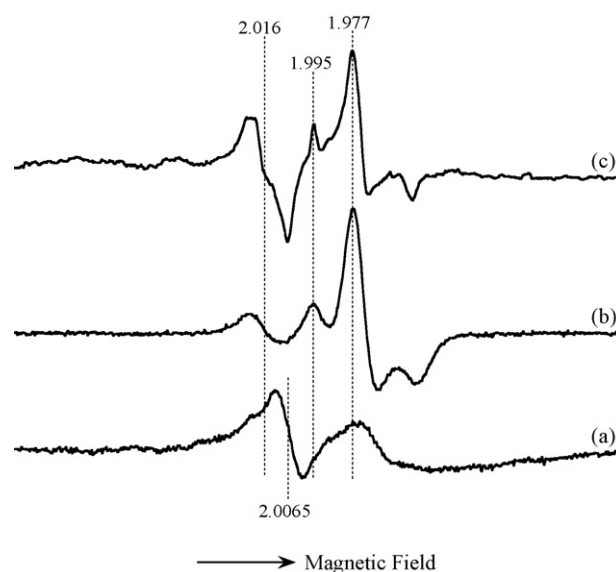


Fig. 5. EPR spectra of different titania samples under UV/visible light illumination: (a) a mixed phase titania thin film prepared by magnetron sputtering, (b) a mixed phase titania in powder form prepared by a modified sol-gel method, and (c) Degussa P25. Background signal in dark was subtracted from the corresponding spectrum. The mixed phase titania samples have phase compositions similar to that of Degussa P25 ($\sim 70\%$ anatase and $\sim 30\%$ rutile).

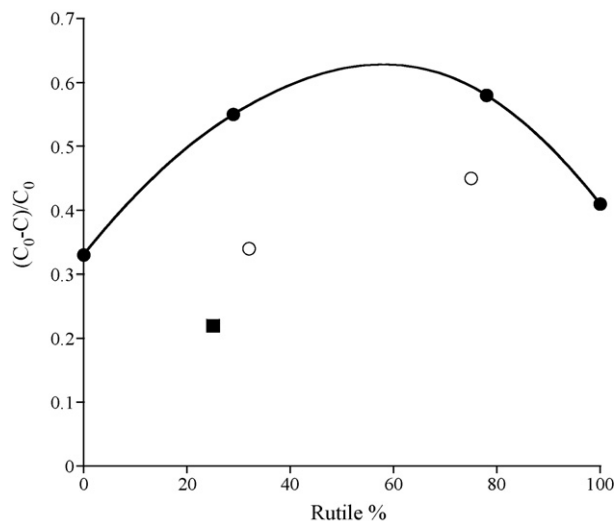


Fig. 6. Conversion of acetaldehyde as a function of rutile content after UV irradiation for 5 min using titania photocatalysts prepared by magnetron sputtering (solid circle), the sol-gel method (open cycle), and Degussa P25 (solid square).

photocatalytic activity than both pure phase anatase prepared by the same method and Degussa P25, in contrast to other pure phase rutile materials which exhibit very low activities in many photocatalytic reactions [6]. This observation suggests that the sputtering methodology may have special advantage for catalyst synthesis.

Besides phase composition, there are many other factors that influence the photocatalytic activity of titania-based materials. Generally, titania photocatalysts with smaller particle sizes and greater specific surface areas are more effective in the oxidative degradation of organic molecules. Crystallinity is also important for high photoactivity since charge recombination usually prevails in titania photocatalysts with low crystallinity. It remains a challenge to optimize the photocatalytic activity of titania by post-synthesis treatments, such as sintering, because heating titania materials at relatively high temperatures usually results not only in improved crystallinity (hindered recombination) but also decreased surface areas [40,41].

In this study, mixed phase titania materials prepared by reactive dc magnetron sputtering have a lower degree of crystallinity than Degussa P25 and those prepared by the sol-gel method, as shown by the XRD results (Figs. 2 and 3). However, the sputtered mixed phase titania thin films displayed the highest photocatalytic activity among the materials tested in this present study (Fig. 6). The microscopic comparison suggests that the sputtered titania thin films have better interparticle contact than those prepared by the sol-gel method (Fig. 4). As mentioned earlier, all anatase and rutile crystals in the sputtered titania films are completely intermixed, creating a high density of anatase-rutile interfaces [25]. Greater synergy between the anatase and rutile phases, then, tends to occur in the sputtered titania samples. In addition, the sputtered materials have electron trapping sites that are populated differently from what is typically observed in anatase and rutile phases. The existence of the unique electron trapping sites and the effective interfacial charge transfer between anatase and rutile, then, promote charge separation and

hinder charge recombination, as observed for Degussa P25 [17]. These phenomena likely explain the enhanced photocatalytic activity of the sputtered films. Further EPR studies including spin trapping experiments are underway in order to probe the electron transfer between anatase and rutile nanocrystals in the sputtered samples.

4. Conclusions

Titania photocatalysts with varying phase composition can be systematically prepared by reactive dc magnetron sputtering and by a modified sol-gel method. Titania thin films containing both anatase and rutile phases demonstrated higher photocatalytic activity than pure phase samples. The results reported in this paper suggest that charge trapping and transfer at phase interfaces in nanocomposite materials is important for high photocatalytic activity. Magnetron sputtering appears to have special advantages in creating a high density of the solid-solid interface and a unique population of electron trapping sites that result in higher chemical reactivity, presumably by hindering charge recombination.

Acknowledgements

The authors thank Dr. Zoran Saponjic, Dr. Nada Dimitrijevic, and Dr. Tijana Rajh of Argonne National Laboratory for their kind assistance on EPR spectroscopy. Funding from the US Department of Energy (DE-FG02-03ER15457/A003 and 5F-00546/W-31-109-ENG38) and the National Science Foundation (CHE-9810378) and the generous donation of Degussa P25 by Degussa are greatly appreciated. Dr. Gonghu Li was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under contract DE-AC02-06CH11357. The characterization (XRD and SEM) was performed in the MRSEC and NUANCE center at Northwestern University.

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