

Contents lists available at ScienceDirect

## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

# Confirmation of the assignment of vibrations of goethite: An ATR and IES study of goethite structure



SPECTROCHIMICA ACTA

Haibo Liu<sup>a,b</sup>, Tianhu Chen<sup>a,\*</sup>, Chengsong Qing<sup>a</sup>, Qiaoqin Xie<sup>a</sup>, Ray L. Frost<sup>b,\*</sup>

<sup>a</sup> School of Resources & Environmental Engineering, Hefei University of Technology, China <sup>b</sup> School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, Australia

#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- We have studied the molecular structure of goethite using vibrational spectroscopy.
- Surface hydroxyl units are observed.
- Chemisorbed and adsorbed water are
- distinguished.Changes in the spectra with adsorbed
- phosphate are demonstrated.



### ARTICLE INFO

Article history: Received 6 May 2013 Received in revised form 24 June 2013 Accepted 27 June 2013 Available online 5 July 2013

Keywords: Goethite structure Surface hydroxyls Infrared spectroscopy Hydroxyl Hydrogen bonding

## ABSTRACT

Transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM/EDS) and X-ray diffraction (XRD) were used to characterize the morphology of synthetic goethite. The behavior of the hydroxyl/water molecular units of goethite and its thermally treated products were characterized using Fourier transform-infrared emission spectroscopy (FT-IES) and attenuated total reflectance–Fourier transform infrared (ATR–FTIR) spectroscopy. The results showed that all the expected vibrational bands between 4000 and 650 cm<sup>-1</sup> including the resolved bands (3800–2200 cm<sup>-1</sup>) were confirmed. A band attributed to a new type of hydroxyl unit was found at 3708 cm<sup>-1</sup> and assigned to the FeO–H stretching vibration without hydrogen bonding. This hydroxyl units, involving three surface hydroxyls, a bulk hydroxyl, a FeO–H without hydrogen bonding, a nonstoichiometric hydroxyl and a reversed hydroxyl were observed, and three kinds of adsorbed water were found in/on goethite.

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## Introduction

Goethite ( $\alpha$ -FeOOH) occurs in soils, rocks and throughout the various compartment of the global ecosystem and is frequently used as an important raw material to produce magnetic iron oxide and pigments [1,2]. Besides, goethite plays an important role in

regulating the transport, mobility and bioavailability of some anions, especially the phosphate anion, which determines the soil fertility which is dependent upon the surface functional groups of goethite [3–6].

The structure of goethite is orthorhombic and each iron atom has six octahedrally distributed oxygen and hydroxyl neighbors in an almost perfect hexagonal close-packing with the 6-folded coordinated Fe atoms occupying the octahedral position [7–9]. The Fe atoms are arranged in double rows to form what can be described as double chains of octahedra running the length of the *c*-axis, while the bond between the double chains consists of

<sup>\*</sup> Corresponding authors. Tel.: +86 13956099615 (T. Chen), tel.: +61 7 3138 2407; fax: +61 7 3138 1804 (R.L. Frost).

*E-mail addresses:* chentianhu168@vip.sina.com (T. Chen), r.frost@qut.edu.au (R.L. Frost).

<sup>1386-1425/\$ -</sup> see front matter  $\odot$  2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.saa.2013.06.102

relatively weak hydrogen bonding directed through the apical oxygen ions along the *a*-axis [10]. In this case, non-stoichiometric hydroxyl units incorporated into the goethite structure during crystal growth were found and researched widely [11–13]. Excess OH or non-stoichiometric OH occurs in goethite and mostly strongly affects the unit cell dimension and has the effect of reducing the goethite dehydroxylation temperature [11,12,14–17]. Besides, goethite formed from Fe<sup>2+</sup> systems usually contains more excess OH and has a lower dehydroxylation temperature than goethite synthesized from Fe<sup>3+</sup> systems.

In theory, there are 12 possible hydroxyl vibrations in goethite, of which 5 hydroxyl vibrations are infrared active [1]. However, the existence of physically adsorbed water and chemisorbed water, the isomorphous substitution and crystal defects makes the analysis of hydroxyl groups of goethite difficult. Furthermore, the types and numbers of hydroxyl groups of goethite, especially the surface functional groups, significantly affect the stability of this mineral and its adsorption activity to environmental contaminants [3,18-21]. In the past several decades, much research about the hydroxyl groups involving the structural hydroxyl, surface functional groups, and the interface between goethite and aqueous solutions have been reported based on the application of infrared techniques [22–28]. Some reports about the behavior of hydroxyl groups/ molecular water vibrations of goethite are listed in Table 1. The research of Russell et al. [22] shows that three kinds of hydroxyls are found at high wavenumbers including the bulk hydroxyl vibration at 3145 cm<sup>-1</sup> and the other new types of hydroxyls arising from protonation of the oxide ions in the (001) plane. Rochester and Topham [23] also found the existence of three kinds of surface hydroxyl groups in goethite using infrared spectroscopic techniques. Busca et al. [29] further studied the OH vibrations in goethite involving relatively broad wavenumbers, demonstrated the existence of surface hydroxyls, and ascribed the vibration at 1640 and 1780 cm<sup>-1</sup> to molecular water bending vibrations. This result responds well with the previous report that significant quantities of residual water remain on the goethite surface after extended evacuation on the basis of DTA data and the remnant water was assigned to chemisorbed water [30,31]. Ruan et al. [32] reported the infrared spectrum of goethite and stated that two hydroxyl stretching modes, and three bending and two deformation modes were observed for goethite. Similar research confirms these reports [33-35]. In a word, the same bands containing the surface hydroxyl and bulk hydroxyl were detected whether the sample is examined by transmission; diffuse reflectance or internal reflectance spectroscopy, although different intensity and band widths were involved.

However, no comprehensive report about the hydroxyl/water vibration with a band between 4000 and  $650 \text{ cm}^{-1}$  of goethite has been published. In addition, to the best of our knowledge, the bands below  $650 \text{ cm}^{-1}$  are attributed to Fe–O/Fe–OH [29,35]. Therefore, in present study, the ATR–FTIR and FT-IES techniques are used to characterize the hydroxyl/water vibrations in/on goe-

thite to display an overall understanding when the vibrations occur between 4000 and 650 cm<sup>-1</sup>. The utilization of FT-IES technique can avoid false assignments resulting from re-adsorbing water onto goethite. The objective is to make the assignment of hydroxyl/water units of goethite clear, to understand better the structure of goethite and provide a combined technique for the characterization of minerals.

#### Experimental

## Preparation of goethite

Hundred gram of  $Fe(NO_3)_3 \cdot 9H_2O$  and 400 mL deionized water were placed in a 1000 mL beaker.  $Fe(NO_3)_3 \cdot 9H_2O$  was dissolved by stirring continuously. After dissolution, KOH with a concentration of 5 mol/L and a concentration of 0.1 mol/L were used to regulate the pH at  $13.9 \pm 0.1$  pH units. After finishing the above, the beaker was sealed with film to prevent evaporation and placed in a thermotank controlled at 70 °C. After 6 days, the beaker was taken out to removal of excess KOH by centrifugation several times. After centrifugation, the deposits were dried at 105 °C, cooled to room temperature and ground to obtain goethite powder for further characterization.

#### Characterizations

#### XRD

XRD patterns were recorded using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) on a Philips PANalytical XPert Pro multipurpose diffractometer. The tube voltage was 40 kV and the current, 40 mA. All XRD diffraction patterns were taken in the range of 10–70° at a scan speed of 2° min<sup>-1</sup> with 0.5° divergence slit size. Phase identification was carried out by comparison with those included in the Inorganic Crystal Structure Database (ICSD).

#### ATR-FTIR

A single-beam Fourier transform infrared spectrophotometer (5700 Nicolet) was used to for the ATR–FTIR spectroscopy. The ATR cell was equipped with a diamond (50° angle of incidence). 64 scans with a resolution of 4 cm<sup>-1</sup> were averaged to obtain each spectrum over the 4000–650 cm<sup>-1</sup> spectral range. To make peaks clear in the high wavenumber region, the broadening band between 3800 and 2200 cm<sup>-1</sup> was resolved using the Jandel 'Peakfit' software package. The band fitting was carried out after smoothing, baseline adjustment and normalization was performed using Grams software package. The fitting was undertaken until reproducible results were obtained with squared correlations of  $r^2$  greater than 0.995.

#### FT-IES

FTIR emission spectroscopy (FT-IES) was carried out on a Nicolet spectrometer equipped with a TGS detector, which was modified by replacing the IR source with an emission cell. A thin

Table 1	1
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Observed peak position and infrared vibrational modes of goethite in previous reports.

Vibration	References	Assignment					
	[22]	[23]	[29]	[32]	[34]	[35]	
Stretching	3660 3486 3145	3660 3500 3160	3440 3140 1640	3479 3206 1707	3407 3177 1634	3150	Surface OH (Type B/C) Surface OH (Type A) Bulk OH
Bending			1780	1685 1638			Molecular water
Deformation			907/795	890/799	887/795	892/795	δ(OH)/γ(OH)

layer (approximately 0.2  $\mu$ m) on a platinum surface with 6 mm diameter and held in an inert atmosphere within a nitrogenpurged cell during heating. The spectra were acquired by coaddition of 1024 scans at the temperature of 100, 150, 200, 512 scans at 250, 256 scans at 300, 350, and 128 scans at temperature from 400 to 800 °C. The band between 3800 and 2200 cm<sup>-1</sup> was also resolved as mentioned above.

## **Results and discussions**

#### XRD, TEM and FE-SEM

Fig. 1 shows the XRD patterns of goethite and thermally treated goethite at different temperatures. Comparison with those included in the ICSD (96-900-2159), only goethite is observed in the synthetic product. These reflections of thermally treated goethite over 200 °C are indentified as hematite when compared with the standard reference pattern (ICSD (96-900-0140)). It indicates that the transformation of goethite to hematite occurs in this study between 200 and 250 °C which is consistent with related reports. As reported in previous papers [32,36,37], transformation of goethite to hematite occurred at different temperatures between 180 and 300 °C. The TEM and FESEM images provide clear shape about the synthetic products which display a kind of acicular substance with different length and almost the same width. Furthermore, the EDS indicates that the sample is composed of Fe 61%, O 38%, Si 0.54% and K 0.42%. The existence of K (deriving from residual KNO<sub>3</sub>) and Si (impurity in precursors) can be omitted due to the extremely low content and without effect on the analysis of FT-IES and ATR-FTIR. Furthermore, the existence of low content of KNO<sub>3</sub> and Si does not affect the analysis of infrared spectrum. Therefore, largely pure goethite is obtained based on the preparation method described above.

## Low wavenumber spectral range $(1000-650 \text{ cm}^{-1})$

The spectra of FT-IES and ATR–FTIR about thermally treated synthetic goethite are recorded in the mid infrared range between 4000 and 650 cm<sup>-1</sup> as shown in Figs. 2 and 3. In the two figures, each spectrum is divided into low wavenumbers (hydroxyl deformation, 1000–650 cm<sup>-1</sup>), middle wavenumbers (water bending, 1800–1000 cm<sup>-1</sup>), and high wavenumbers (3800–2200 cm<sup>-1</sup>) region. Due to the limitation in the mid infrared analysis, the lowest wavenumber is recorded at 650 cm<sup>-1</sup>, however, the limitation does not influence the analysis of hydroxyl/water vibrations in the structure of goethite.

As shown in Fig. 2, two strong absorbance peaks at 885 and  $782 \text{ cm}^{-1}$  are observed in the hydroxyl deformation region. The



Fig. 1. XRD patterns of goethite and thermally treated goethite.



Fig. 2. IES between 4000 and 650 cm<sup>-1</sup> of synthetic goethite.



**Fig. 3.** ATR–FTIR between 4000 and 650 cm<sup>-1</sup> of synthetic goethite.

two vibrations are assigned to  $\delta(OH)$  and  $\gamma(OH)$  according to previous studies. As is well known, many previous researchers have reported and confirmed the existence of the two kinds of hydroxyl groups in goethite. Schwarzmann and Sparr [38] firstly found the two vibration modes at 892 and 795  $cm^{-1}$  and attributed them to the vibration in and out, respectively, of the (001) plane labeled as  $\delta(OH)$  and  $\gamma(OH)$ . Moreover, hydroxyl groups in this low wavenumber region are really important diagnostic bands and also provide significant information about crystallinity of goethite and the extent of (Al, Co)-substitution in goethite [11,12,35,39,40]. Furthermore, the two peaks show a considerable decrease in peak position with the increasing temperature, especially as the temperature approaches to 200 °C. This is ascribed to the transformation of goethite to hematite and its dehydration. The ATR-FTIR spectrum of goethite displays practically the same wavenumber for hydroxyl deformation. The unique difference is the change temperature of vibration intensity, one is 200 °C but the other is 250 °C. Undoubtedly, the difference results from the thermal treatment method. The IES gets an in situ heating and with very slight thin sample ( $\sim 2 \mu m$ ), however, ATR has an out situ heating sample and the thermal treatment efficiency looks not good as the in situ equipment. Actually, the dehydration temperature differs with different samples and research methods between 180 and 300 °C [33,34].

## *Middle frequencies* $(1800-1000 \text{ cm}^{-1})$

It is well known that the vibrational bands between 1800 and  $1000 \text{ cm}^{-1}$  generally belongs to water bending modes. Busca et al. [29] has reported the band at 1640 cm<sup>-1</sup> with an overtone

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at 1780 cm<sup>-1</sup> corresponds to the bending vibration of molecular water adsorbed on goethite. In addition, related studies still demonstrated the existence of chemisorbed water coordinated to Lewis sites on the surface of goethite [29,31]. The report of Ruan et al. [32] and Prasad et al. [34] showed that three bending vibration and one bending vibration are observed for goethite, respectively. Therefore, it seems complicated for identification the water bending vibration and the assignment for goethite. To make clear the assignment of the bending vibration, ATR and IES are used to characterize the variation of bending vibration. Two bands are observed in the water bending region in IES (Fig. 2) while four bands are observed in the ATR (Fig. 4). Confirmation can be made from the comparison of ATR and IES results. The same band at  $\sim$ 1780 cm<sup>-1</sup> disappears when the transformation of goethite to hematite occurs irrespective of the temperature. Thereby, the band at  $\sim 1780 \text{ cm}^{-1}$  should be the structure hydroxyl bending. The IES is carried out at different temperatures with hot samples resulting in no re-absorbing of water, however, a cooled sample is used for ATR analysis. Therefore, the band at  $\sim 1650 \text{ cm}^{-1}$  disappears after heating to 200 °C in IES, on the contrary, it reappears despite the thermal treatment temperature at 250 °C in ATR. So, this band contributed to the intensity of the bending mode of physically adsorbed water. These results agree well with previously reported results [30,35]. Another two bands at 1522 and 1345 cm<sup>-1</sup> disappear in IES ascribed to the effect of heating temperature because IES starts from 100 °C. For this reason, it is speculated that these two bands also correspond to different physically adsorbed water molecules. A shoulder near to 1649 cm<sup>-1</sup> is observed in IES, which indicates not all the absorbed water is desorbed at the temperature of 100 °C probably due to weak hydrogen bond with the bulk, and in this circumstance does not happens for the band at  $1345 \text{ cm}^{-1}$ . Furthermore, the results of TG/DTG show that a kind of adsorbed water experiences desorption at 38 °C with a gas purging demonstrating the existence of weakly adsorbed water on goethite [37]. Therefore, one conclusion that can be made is that the band at 1649 and 1345  $\text{cm}^{-1}$  is assigned to the water bending with a weak hydrogen bond and weakly adsorbed water, respectively.



Figs. 2 and 3 present the original high wavenumber regions of goethite using different IR techniques. The two figures display different spectra with no consistent broad band (one centered near 3151 cm<sup>-1</sup> and the other near 3116 cm<sup>-1</sup>), which generally is regarded as a combination of several fundamental stretching vibrational modes of liquid water, mainly due to the different spectroscopic methods. As for IES, the broad band has a dramatic decrease as the temperature reaches 200 °C and seemingly disappears as the temperature reaches 250 °C. However, the broad band in the ATR spectrum at  $3116 \text{ cm}^{-1}$  shifts to  $3387 \text{ cm}^{-1}$  after heating to 250 °C and the intensity decreases with increasing temperature. No matter how these changes occur, the changes are apparently ascribed to dehydration. To identify the broad bands and confirm the assignment of relative adsorption peaks, peakfit software is used to resolve the broad bands. Figs. 4 and 5 display the resolved high wavenumber region between 3800 and 2200 cm<sup>-1</sup> with selected expanded spectra. It has been reported that bulk hydroxyl stretching vibration with different bands was observed, as may be observed in Table 2. Meanwhile, another O-H stretching vibration is also observed and assigned to surface hydroxyl type A and few reports are found about the surface hydroxyl type B and C [22,23]. In the present study, the intensity of bands at 3130 (IES) and 3111 cm<sup>-1</sup> (ATR) have a significant decrease in intensity with temperature increase and the intensity approaches zero when temperature is over 400 °C. Therefore, the two bands are assigned to bulk hydroxyl units in agreement with previous reports.

As for IES, seven sub-divided vibrational bands are obtained and the peak at  $3652 \text{ cm}^{-1}$  splits into two peaks as goethite is heated to 200 °C. This is in agreement with the report of Russell et al. [22]. These researchers suggested that three types of surface hydroxyl



Fig. 4. Resolved band between 3800 and 2200 cm<sup>-1</sup> based on the results of IES.



Fig. 5. Resolved band between 3800 and 2200 cm<sup>-1</sup> based on the results of ATR.

Table 2				
Resolved band between 3800–2200 cm <sup>-1</sup>	and	their	assignmen	t.

	Thermal treatment temperature (°C)									Assignment	H bond distance (Å)	
	25	100	150	200	250	300	400	500	600			
		2892	2919	2930						Molecular water	2.627-2.635	
		3137	3153	3191	3141	3130				Bulk hydroxyl		
		3279	3285	3337	3381	3389	3300			Nonstoichiometric hydroxyl		
IES		3416	3407	3414						Molecular water	2.803-2.81	
		3524	3521	3501	3490	3496	3498			Surface hydroxyl A	2.882-2.935	
		3652	3652	3634	3631	3626	3622			Surface hydroxyl B		
				3670	3662	3658	3653	3649		Surface hydroxyl C		
		3708	3710	3728	3721	3718	3717	3715		Fe-OH without H bond		
ATR	2894	2913	2868	2889	2946	2953	3060	3017	3010	Molecular water	2.623-2.664	
	3116	3114	3115	3111	3093	3111				Bulk hydroxyl		
	3241	3222	3213	3202	3271	3284	3262	3210	3235	Molecular water	2.705-2.736	
	3425	3406	3395	3409	3427	3432	3427	3407	3430	Molecular water	2.795-2.822	
	3544	3536	3518	3544	3550	3551	3550	3537	3560	Reversed hydroxyl		

groups existed at sites A, B and C on the (001) plane. The hydroxyl groups at sites A, B and C are coordinated to one, three and two Fe<sup>3+</sup>, respectively. The report revealed that the band of goethite surface hydroxyl at 3660 cm<sup>-1</sup> splits into two peaks (3671 and 3646 cm<sup>-1</sup>) after adsorbing phosphate. In addition, type B and C hydroxyl groups could not participate in hydrogen bond interactions with adjacent groups, but type A could. This feature is observed in this present study. Therefore, the resolved peaks at 3524, 3652 and 3670  $\text{cm}^{-1}$  are assigned to type A with a hydrogen bond distance between 2.828 and 2.935 Å, B and C, respectively, which is not found in the ATR measurements. All the hydrogen are calculated from bond distances the formula: wavenumbers =  $3592 - 304 \times 10^9 \cdot e^{\frac{-d(0-0)}{0.1312}}$ . Libowitsky [41] revealed that the regression formula can be employed relating the hydroxyl stretching wavenumber with regression coefficient better than 0.96 using infrared spectroscopy. In IES, the weak vibration peak at 3708 cm<sup>-1</sup> is interesting, which has not been previously reported. However, to the best of our knowledge, some hydroxyl groups cannot be removed in the hematite structure until the thermal treatment temperature reaches 900 °C [13,42], in this study is 600 °C. Thereby, the peak at 3708  $\text{cm}^{-1}$  is assigned to hydroxyl group coordinated to one Fe<sup>3+</sup> without hydrogen bonding labeled FeO–H. These broad bands at 3416 and 2892 cm<sup>-1</sup> disappear after heating at 250 °C due to the strong hydrogen bonding as shown in Table 2. The last stretching band at 3279 cm<sup>-1</sup> is retained till the thermal treatment temperature up to 500 °C. It is proposed that this band should be assigned to nonstoichiometric hydroxyl due to stability at the high dehydration temperature.

As for ATR, five resolved vibrational bands are obtained and the peak at 3116 cm<sup>-1</sup> has been assigned to the bulk hydroxyl as above. However, this spectrum does not show the sharp peaks over 3580 cm<sup>-1</sup> arising from surface hydroxyl units. Another four peaks still be retained despite the temperature up to 600 °C. The results of IES denote that all the vibrations related to hydroxyl or water disappears as the thermal treatment temperature comes to 600 °C. So, the existing peaks should be assigned to surface adsorbed water which is reversed after heating. Although little research on characterization goethite using ATR technique has been reported; the results of the present study is consistent with those previously reported. Tejedor-Tejedor and Anderson [24] revealed the difference in the infrared spectra of goethite between the diffuse reflectance transmission and attenuated internal reflection spectra. What is more important, Tejedor and his co-workers also did not find the vibration absorption peaks at 3660 and 3488 cm<sup>-1</sup> and they ascribed the peak broadening at 3140 cm<sup>-1</sup> to the presence of residual water. In addition, it has been reported that the proposed interface stoichiometry is  $(H_2O)-(H_2O)-OH_2-$ OH-Fe-O-O-Fe-R, which indicates the existence of two layers of absorbed water and two types of terminal hydroxyls, a hydroxo group and a aquo groups. The later hydroxyl probably is a kind of chemisorbed water because Parfitt et al. [25], Busca et al. [29], Van Der Kraan and Medema [31] has demonstrated the existence of chemisorbed water by thorough evacuation. Therefore, the further confirmation on the assignment of the vibration peaks at 2894, 3241 and  $3425 \text{ cm}^{-1}$  is obtained and identified as the molecular water with different hydrogen bond distances as shown in Table 2. The assignment of peaks at 2894 and 3425 cm<sup>-1</sup> also agrees well with the analysis of IES. Additional evidence for the peak at 3241 cm<sup>-1</sup> derived from the report of Frost et al. [43] which showed water molecules are very tightly bound to the mineral surface and the bands occurs in the 3250–3200 cm<sup>-1</sup>spectral region. The last peak at 3544 cm<sup>-1</sup> is assigned to the hydroxyl groups due to the weak hydrogen bonding; and is in agreement with the report of Ruan et al. [44] which indicated goethite can absorb hydroxyl units from the atmosphere. In the present study, all the resolved bands results and their assignment are exhibited in Table 2.

## Conclusions

ATR-FTIR and FT-IES were utilized to characterize synthetic goethite. FT-IES has great advantage to be used as a tool for an in situ study of thermally treated goethite which can avoid errors arising from re-absorbing water onto goethite. ATR-FTIR was restricted by the penetration depth of the beam and the effective thickness would increase with increasing  $\lambda$  which can provide more information about interface groups. Therefore, the combination of ATR-FTIR and FT-IES gives abundant information about the vibrational modes of hydroxyl/water units in/on goethite. Finally, seven kinds of hydroxyls, involving three surface hydroxyls, a bulk hydroxyl, a FeO-H without hydrogen bond, a nonstoichiometric hydroxyl and a reversed surface hydroxyl were observed, and three kinds of adsorbed water were found in/on goethite. These vibration peaks vary with different thermal treatment temperatures. Furthermore, a new vibration peak at 3708 cm<sup>-1</sup> was observed and identified as Fe-OH without hydrogen bond owing to the 500 °C dehydroxylation temperature. In addition, this study also provides a good way for characterization some minerals structure especially for minerals containing structure hydroxyl and surface hydroxyl groups.

## Acknowledgments

This study was financially supported by Natural Science Foundation of China (41130206, 41172048 and 41072036) and Ph.D. Programs Foundation of Ministry of Education of China (No. 20110111110003). The authors appreciate the financial and infrastructure support of the School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, for this research.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.06.102.

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