Carbohydrate Polymers 90 (2012) 1609–1613

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization

Jihua Li[a,b], Xiaoyi Wei[a], Qinghuang Wang[a,b,*], Jiacui Chen[a], Gang Chang[a], Lingxue Kong[c], Junbo Su[d], Yuhuan Liu[e]

[a] *Key Laboratory of Tropical Crop Products Processing of Ministry of Agriculture, Agriculture Products Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, China*
[b] *National Center of Important Tropical Crops Engineering and Technology Reseach, Haikou, 571101, China*
[c] *Institute for Frontier Materials, Deakin University, Waurn Ponds, Vic 3216, Australia*
[d] *Southern Subtropical Crops Research Institute, Chinese Academy of Tropical Agricultural Science, Zhanjiang 524091, China*
[e] *The State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang 330047, China*

ARTICLE INFO

Article history:
Received 6 February 2012
Received in revised form 14 May 2012
Accepted 10 July 2012
Available online 16 July 2012

Keywords:
Nanocellulose
Homogeneous
High pressure homogenization
Sugarcane bagasse

ABSTRACT

Nanocellulose from sugarcane bagasse was isolated by high pressure homogenization in a homogeneous media. Pretreatment with an ionic liquid (1-butyl-3-methylimidazolium chloride ([Bmim]Cl)) was initially involved to dissolve the bagasse cellulose. Subsequently, the homogeneous solution was passed through a high pressure homogenizer without any clogging. The nanocellulose was obtained at 80 MPa for 30 cycles with recovery of 90% under the optimum refining condition. Nanocellulose had been characterized by Fourier transformed infrared spectra, X-ray diffraction, thermogravimetric analysis, rheological measurements and transmission electron microscopy. The results showed that nanocellulose was 10–20 nm in diameter, and presented lower thermal stability and crystallinity than the original cellulose. The developed nanocellulose would be a very versatile renewable material.

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1. Introduction

Cellulose is one of the most abundant, renewable and biodegradable natural polymers, existing in wood, cotton, hemp, straws, sugarcane bagasse and other plant-based materials (Habibi, Lucia, & Rojas, 2010). Although it is widely used in fiber, paper, films, and polymer industries, the utilization of this natural biomass for processing of novel material applications has recently attracted growing interest due to its ecological and renewable characteristics.

One of these applications has been the development of nanocellulose in virtue of its super functionalities, such as its extremely large, active surface area, and low cost (Hubbe, Rojas, Lucia, & Sain, 2008; Yano et al., 2005). In previous studies a number of approaches for the preparation highly purified nanocellulose from cellulosic materials have been reported, such as steam explosion treatment (Cherian et al., 2010), acid or alkaline hydrolysis (Mandal & Chakrabarty, 2011; Moran, Alvarez, Cyras, & Vazquez, 2008), enzyme-assisted hydrolysis (Henriksson, Henriksson, Berglund, & Lindstrorn, 2007), as well as a combination of two or several of the aforementioned methods (Chen et al., 2011; Qua, Hornsby, Sharma, & Lyons, 2011).

High pressure homogenization (HPH) treatment is an efficient technology for biomass refining, due to its simplicity, high efficiency and the lack of a requirement for organic solvents (Keeratiurai & Corredig, 2009). Lee et al. used a high-pressure homogenizer to prepare cellulose nanofibrils from microcrystalline cellulose (MCC). After 10 passes, the diameter of most cellulose fibrils could be in the range from 28 to 100 nm (Lee, Chun, Kang, & Park, 2009). However, natural cellulose is insoluble in water and most organic solvents, due to the extensive network via numerous intermolecular and intramolecular hydrogen bonds (Liu, Sun, Zhang, & Ren, 2007). It can cause a clogging of the valve of the homogenizer, and for this reason is difficult to refine uniformly. Therefore, a pretreatment of cellulose such as steam explosion, microfluidizer processor or other method (Kaushik & Singh, 2011; Lee et al., 2009) is essential prior to homogenization. Even so, cellulose is still suspended in water after these treatments. Zimmermann et al. introduced a mechanical pretreatment to obtain the homogeneous cellulose fibril bundles (CFB) suspensions before

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[*] Corresponding author at: Agriculture Products Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang, Guangdong 524001, China. Tel.: +86 759 2212978; fax: +86 759 2208758.
E-mail address: qinghuangwang@163.com (Q. Wang).

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http://dx.doi.org/10.1016/j.carbpol.2012.07.038

high shearing in the homogenizer. This method could minimize the size of the cellulose fibers to avoiding clogging the homogenizer (Zimmermann, Bordeanu, & Strub, 2010).

Recently, room-temperature ionic liquids (ILs) have received much attention since they have excellent dissolution ability for cellulose (Brandt, Hallett, Leak, Murphy, & Welton, 2010; Swatloski, Spear, Holbrey, & Rogers, 2002). It is proved that the $[\mathrm{Bmim}]^+$ cations in ILs can attack the oxygen atoms of H—O—H bonds, and Cl^- associate with the hydroxyl proton of H—O—H bonds. These two interactions can destroy the extensive hydrogen bonding network among cellulose chains, resulting in the dissolution of cellulose (Zhu et al., 2006). Therefore, it was considered to be an appropriate homogeneous media for cellulose because of its non-volatility, thermal stability and recyclable.

In this study, the nanocellulose from sugarcane bagasse is successfully isolated by high pressure homogenization coupled with an ionic liquid pretreatment. The structural and physicochemical properties of the nanocellulose were studied by Fourier transformed infrared (FTIR) spectra, X-ray diffraction (XRD), thermogravimetric analysis (TG), rheological measurement and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials

Sugarcane bagasse was collected from local plantations in Zhanjiang, China. The ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was synthesized according to the previous work (Li et al., 2011). All other chemicals were of analytical grade, purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China).

2.2. Preparation of nanocellulose

The dried and ground bagasse was first washed with deionized water, and then bleached with 1% (w/v) sodium hydroxyl solution for 1.5 h at 90 °C to remove the lignin and hemicelluloses, respectively. The original cellulose was subsequently washed with acid and distilled water until the solution was neutral, and then airdried.

The dissolution of cellulose was carried out according to the previous work (Wei et al., 2011). Briefly, the 1% (w/w) bagasse cellulose/BmimCl solution was mixed in the microwave oven (Qpro-M, Questron Inc., Canada) at 130 °C for 2 h under magnetic stirring, until cellulose was completely dissolved to form a clear and viscous solution. Then it was homogenized by a high pressure homogenizer (AH100D, ATS Engineering Inc., Canada) at pressure levels ranging from 40 to 140 MPa and for up to 50 HPH cycles. After cooling to room temperature, cellulose was precipitated from the IL solution by the addition of water, due to the impairment of the IL solvent properties and the increased hydrogen bond of cellulose. Finally, the regenerated nanocellulose was dried in a vacuum freeze drying equipment until reaching a constant weight.

2.3. Characterization

2.3.1. Particle size measurements

Particle sizes of regenerated nanocellulose were determined by a photon correlation spectroscopy with a Nano-ZS (Malvern Instruments, UK). The nanocellulose was diluted in water with ultrasound for 10 min. The mean diameter (z average) was determined by the analysis of the intensity autocorrelation function. All measurements were conducted at room temperature. The data reported are means of three replicates.

2.3.2. Morphological analysis of nanocellulose

The morphology measurements of the regenerated nanocellulose were carried out on a TEM (JEM-100, JEOL, Tokyo, Japan) operated at 100 keV. The nanocellulose was deposited from an aqueous dilute dispersion and casted one drop onto copper grid with carbon film support. Samples were observed directly with TEM after they were dried under room temperature without further staining.

2.3.3. Infrared spectroscopy (IR) analysis

The FTIR spectra of original cellulose, IL pretreated cellulose and nanocellulose was measured using a Fourier Transform Infrared Spectrometer (Spectrum GX-1, PerkinElmer, USA). The samples were dried at 80 °C under vacuum for 12 h before analysis. Then a small quantity (approximately 1 mg) samples were blended with 300 mg of KBr powder and compressed to form a disc. The spectra for each sample were recorded as an average of 100 scans at a resolution of $1\ \mathrm{cm}^{-1}$ in the range from 4000 to $400\ \mathrm{cm}^{-1}$.

2.3.4. X-ray diffraction (XRD) analysis

X-ray diffraction studies of the samples were carried out by high resolution X-ray Diffractometer (X'Pert, Philip, Germany) with nickel filtered Cu Kα radiation at 45 kV and 30 mA. Scattered radiation was detected in the range $2\theta = 10–75^\circ$, at a speed of 3°/min. The crystallinity index (CI) was measured by Segal's empirical method (Segal, Creely, Martin, & Conrad, 1959), with the equation as follows:

$$C_{\mathrm{Ir}}\ (\%) = \frac{I_{200} - I_{\mathrm{am}}}{I_{200}} \times 100\% \qquad (1)$$

where I_{200} is the intensity value for the crystalline cellulose ($2\theta = 22.5^\circ$), while I_{am} the intensity value for the amorphous cellulose ($2\theta = 18^\circ$).

2.3.5. Thermogravimetric analysis (TG)

Thermogravimetric analysis measurements (TG) were carried out with a Synchronous Thermal Analysis (STA449C/4/G, Netzsch, Germany). Original cellulose, IL treated cellulose, and nanocellulose were dried and ground into powder using a mortar and pestle before analysis. Then approximately 3 mg of each sample was loaded into a platinum pan and heated from 30 °C to 750 °C at a heating rate of $10\ ^\circ\mathrm{C\ min}^{-1}$. All of the measurements were performed under a nitrogen atmosphere with a gas flow of $20\ \mathrm{ml\ min}^{-1}$ in order to prevent any thermoxidative degradation.

2.3.6. Rheological characterization

Rheological measurements were carried out using a DHR-3 (TA Instruments, USA) with a 40 mm aluminum plate-and-plate geometry and a Peltier temperature controller. The gap was fixed at 0.6 mm. A mechanical spectrum (G' and G'' as a function of angular frequency) was obtained at 25 °C in the range of $100–0.1\ \mathrm{rad\ s}^{-1}$.

3. Results and discussion

3.1. Solubility of cellulose in ionic liquid

The individual cellulose chains between sugarcane bagasse are joined by a network of inter- and intra-molecular hydrogen bonding and van der Waals forces, causing insolubility in conventional solvents. In the present study, ionic liquid ([Bmim]Cl) was employed to dissolve the SCB cellulose. It was found that it could disrupt the hydrogen interaction network in cellulose, and dissolve cellulose as a homogeneous solution. Conventionally solubility of cellulose using ILs was carried out by conductive heating with an external heat source for a comparatively long time (Lin, Zhan, Liu, Fu, & Huang, 2010). To improve the method, cellulose was treated

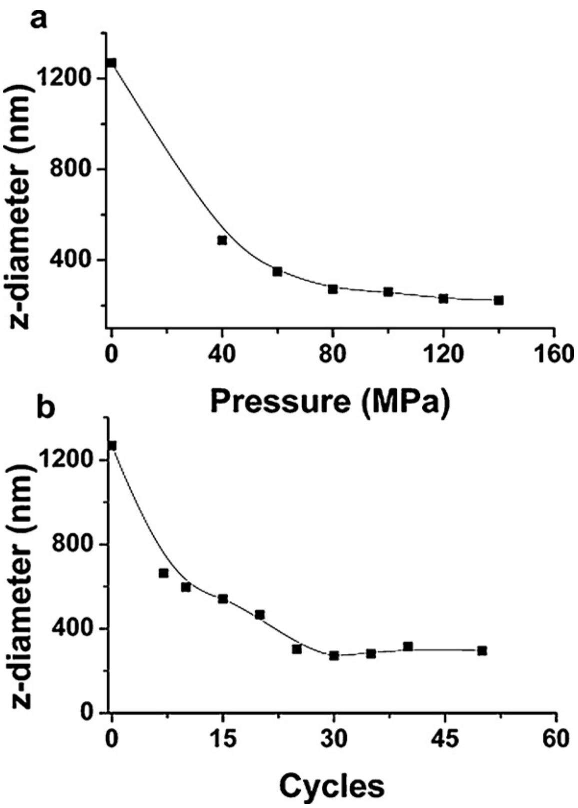

Fig. 1. The mean particle sizes on different conditions (a, pressure; b, cycles).

with ILs under microwave (MW) irradiation using an MW oven with mechanically stirring. The reaction time was only 2 h, which is much shorter than the time required without microwave treatment (24 h).

Several factors could influence the efficiency of solubilisation, such as the mass ratio of cellulose to ionic liquid, the power of the microwave, the reaction temperature, as well as the dissolution time. Finally, we found experimentally that the best solubilisation could be achieved in 1% (g/g) cellulose/[Bmim]Cl during 130 °C for 2 h at 400 W of microwave. The cellulose could be transformed into a gel or be carbonized, when the cellulose ratio was above 5% (g/g) or the reaction temperature was over 150 °C.

3.2. *Preparation of nanocellulose*

After ionic liquid pretreatment, the SCB cellulose was dissolved in [Bmim]Cl to form a homogeneous solution. Then the solution was passed through high pressure homogenizer to prepare the nanocellulose.

The energy delivered by HPH into the homogenous cellulose system is directly proportional to the homogenization pressure and the number of homogenization cycles (Donsi, Wang, Li, & Huang, 2010). Fig. 1a shows the effect of the pressure on the mean particle sizes of regenerated cellulose solution under an operating pressure from 40 MPa to 140 MPa with 30 cycles at room temperature. The mean particle size of cellulose was 1300 nm after ionic liquid pretreatment, and it exhibited a sharp reduction to 300 nm with the increasing of the pressure during HPH process. Fig. 1b shows the diameter of HPH-treated nanocellulose at a fix pressure of 80 MPa with different cycles. It can be seen that the particle sizes were also significantly reduced with repeated times. Considered the particle sizes and economical factor, the optimum of HPH process condition was at a pressure of 80 MPa with 30 cycles. Under the same condition, the polydispersity of nanocellulose dispersion reached a steady value of 0.4, indicating that HPH-treated cellulose had a narrow particle size distribution.

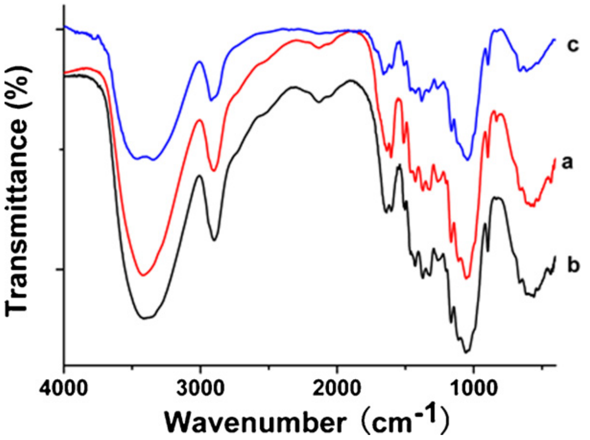

Fig. 2. IR spectra of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

After homogeneous refining by HPH, the nanocellulose was regenerated by water, and the final recovery of cellulose was more than 90%. In addition, the ionic liquid could be recycled and reused for several times. Therefore, it was concluded that homogeneous HPH process was an efficiency method to isolate nanocellulose from SCB cellulose.

3.3. *Characterization*

The morphological and chemical characteristics of nanocellulose were analyzed by TEM, FTIR spectroscopy, XRD, TG, and rheological measurements.

FT-IR spectra of original cellulose, IL treated cellulose and nanocellulose was carried out in Fig. 2. The dominant peaks of OH-stretching and CH-stretching at approximately 3400 cm^{-1} and 2800 cm^{-1} were observed in the entire spectra. Other peaks, such as the peak at 1371 cm^{-1} and 897 cm^{-1} were attributed to the O—H bending vibration, and C—H deformation vibration contribution of cellulose. Interestingly, no difference was found between the spectrum of nanocellulose and IL treated cellulose. This result suggests that no other chemical reaction occurred during the processes of dissolution and refining.

Fig. 3 shows the TEM micrograph of a dilute suspension of nanocellulose. The nanoparticles had a circular shape. Although some of the particles aggregated the independent particles had sizes in the diameter range of 10–20 nm. Therefore, it suggested that the diameter of the SCB cellulose could be refined to the nano-level by HPH in homogenous media.

The XRD patterns of original cellulose, IL treated cellulose as well as nanocellulose was shown in Fig. 4. It is clear that the original cellulose (Fig. 4a) shows typical cellulose I structure with a wide peak between 22.5° and 18° (Wu, Wang, Wang, Bian, & Li, 2009). After dissolution in IL (Fig. 4b) and subsequently refined by HPH (Fig. 4c), both of the regenerated cellulose presented typical cellulose II structure with peaks at 12°, 20° and 22° (Mansikkamaki, Lahtinen, & Rissanen, 2005). This indicated that the crystal structure of cellulose was transformed from cellulose I to cellulose II after the dissolution and refining processes. On the other hand, the crystallinity index of three kinds of cellulose (original, ionic liquid treated and homogenised) was 60%, 52% and 36% respectively using Segal's empirical method. The crystallinity index significantly decreased because the cellulose became amorphous region after treatment by IL and HPH (Zhao et al., 2012). It was indicated that the

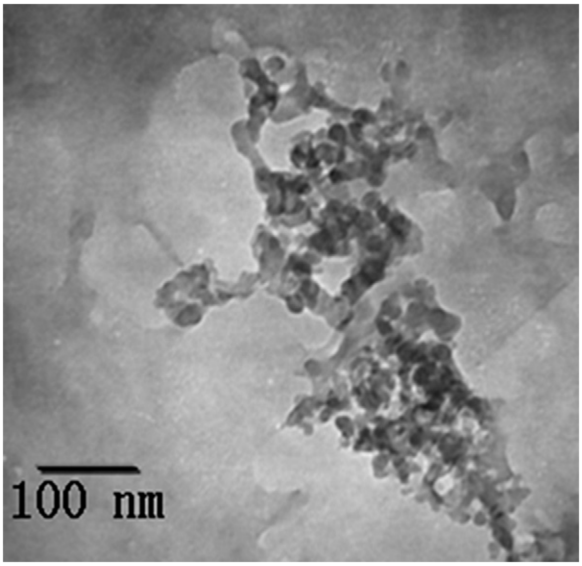

Fig. 3. TEM of nanocellulose.

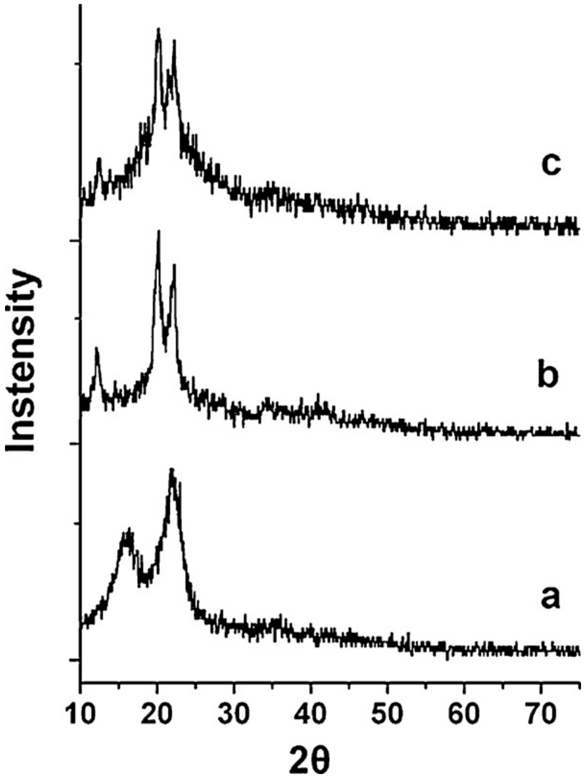

Fig. 4. X-ray diffraction pattern of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

intermolecular hydrogen bonds of cellulose were broken, causing the collapse of crystal structure during the whole process.

The TGA and DTG curves of three kinds of cellulose were shown in Fig. 5. As can be seen, the onset decomposition temperature was 288 °C for original cellulose (Fig. 5a), and 251 °C for IL treated bagasse cellulose (Fig. 5b). The nanocellulose exhibited the lowest thermal stability with the decomposition temperature of 238 °C (Fig. 5c). The decreased of decomposition temperature was due to the damages in crystal region between cellulose, as verified by XRD results in Fig. 4.

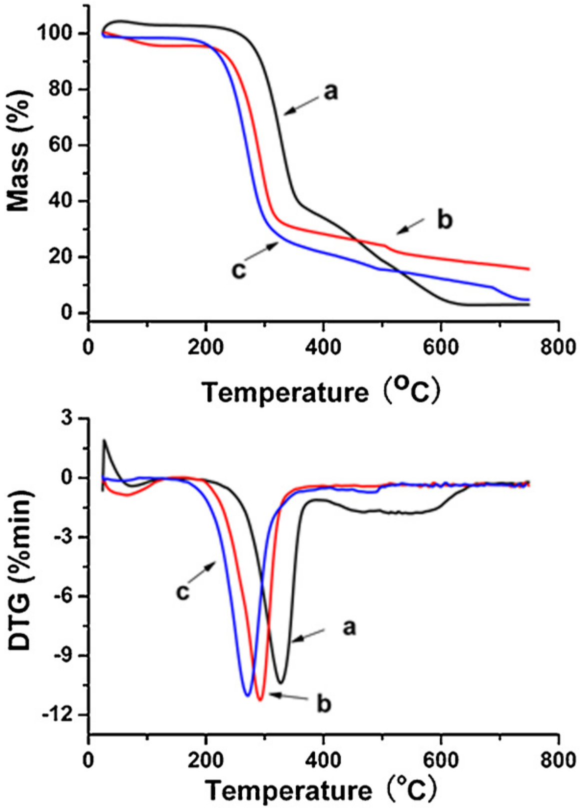

Fig. 5. TG and DTG curves of original cellulose (a), IL treated cellulose (b) and nanocellulose (c).

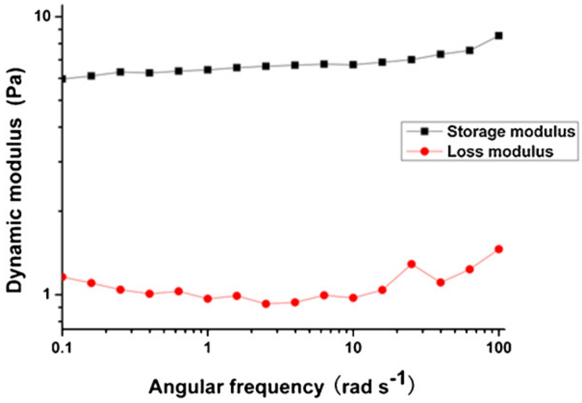

Fig. 6. Mechanical spectra of nanocellulose.

The rheological measurement of nanocellulose was shown in Fig. 6. The mechanical spectra showed the storage modulus G' to be higher than the loss modulus G'' within all the angular frequency range, evidencing a gel-like behavior (Agoda-Tandjawa et al., 2010). Moreover, the obtained mechanical spectra presented an almost smooth shape, indicating the strong temporary network as a result of interactions between the nanocellulose particles.

4. Conclusion

In this study, the nanocellulose from sugarcane bagasse was prepared by high pressure homogenization coupled with an ionic liquid pretreatment. The HPH process resulted in nanocellulose with a diameter range of 10–20 nm. Chemical morphology and structural analysis of nanocellulose were measured by TEM, IR, XRD, TG and the suspension rheology determined. The nanocellulose exhibited a lower thermal stability and crystallinity, which was attributed to the breakage of hydrogen bonds between celluloses by ionic liquid homogenous treatment and the high pressure shearing of HPH. Further studies will explore the applications of this form of nanocellulose.

Acknowledgements

We gratefully acknowledge the financial support from Hainan Natural Science Foundation (no. 211019) and National Non-profit Institute Research Grant of CATAS (nos. 1610032012021 & SSCRI200907). The work is also partially supported by Chinese Central Government 948 Research program (2012-Z10), and Chinese National Engineering Research Center building program (2011FU125Z09).

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