This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
**Highlight:** The PVA hydrogel with high-transparency has been prepared, the 1DMSO/2H₂O network structure and the transparent mechanism were also explored.

**Colour graphics:**

Schematic diagrams of spatial structure for PVA hydrogels prepared with different concentration of DMSO aqueous solutions: deionized water (a), 40wt% DMSO aqueous solution (b), 68.5wt% DMSO aqueous solution (c), 80wt% DMSO aqueous solution (d) and pure DMSO (e).
Preparation of PVA hydrogel with high-transparency and investigations on its transparent mechanism

Yi Hou†,a Chen Chen†,a Kemin Liu,a Ying Tu,a Li Zhang*,a Yubao Li*#

Abstract: Polyvinyl alcohol (PVA) hydrogels with high-transparency were prepared by dissolving PVA powders into the dimethyl sulfoxide (DMSO) aqueous solutions with different concentration to obtain 16.7wt% PVA hydrogels followed by several freeze-thaw cycles. The transparency, crystallinity, mechanical strength and compositions of PVA hydrogels were tested and analyzed by using spectrophotometer, universal testing machine and Infrared spectroscopy (IR), indicating that when the concentration of DMSO was 80wt%, the transparency of PVA hydrogel displayed a maximum value (99.8±0.2%), close to that of natural human cornea (99.7-99.9%), which is closely related to the interaction between DMSO and H₂O molecules as well as the crystallinity of PVA hydrogel. Based on this, the interaction between DMSO and H₂O molecules and the transparent mechanism were also explored. It has been found that the viscosity of DMSO aqueous solution reaches the maximum value when its concentration is 68.5% and is prone to be affected by temperature, while the 80wt% DMSO aqueous solution endows PVA hydrogel with the highest transparency. Based on IR and DSC analysis, the spatial structures of PVA hydrogels prepared with different DMSO aqueous solutions were schemed, and it was thought that the formation of 1DMSO/2H₂O network structure contributes the most to the crystallinity and the transparency of PVA hydrogel. Such a PVA hydrogel with high transparency could have a great potential to be used as the optical core of artificial cornea.

Introduction

Corneal blindness is now the second leading cause of blindness globally[1]. It is estimated that about 2 million new cases of corneal blindness occur every year caused from trachoma trauma and corneal ulcerations[2]. Up to now, the only widely accepted treatment of diseased or damaged human corneas is corneal transplantation using human donor corneal tissue. But the donor corneas are in short supply. So, it is very urgent and necessary to create an artificial substitute able to simulate the physical characteristics of the natural cornea and to perform some of its essential functions.

From literatures we can know that, the materials and the structure design had played important roles in the development history of Keratoprosthesis (KPro)[3-5]. Especially, since Slazer[6] proposed "core-and-skirt" concept in the structure design of artificial corneas, study of artificial cornea materials have entered a stage of rapid development[7-11]. An ideal KPro should have a biocompatible porous skirt able to interlock or heal with the host cornea and, an optical core with high transparency and a suitable refractive index. Also, the KPro should be flexible and should have sufficient tensile strength to allow surgical manipulation and fixation. So far, developing a KPro has been attempted by many groups[12-17], among which, the most promising artificial cornea is the PHEMA KPro explored by Chirila group[18-24]. The PHEMA KPro had been assessed by replacing the damaged regions of the cornea of different animals, and found that the KPro could be retained longer than 3 years in some animals. And the pilot clinical trial in human patients had also been operated, but found the long-term survival was not satisfactory. Analysis demonstrated that most of the postoperative complications were caused by the low tensile strength and the bio-inert property of the porous PHEMA skirt. To solve the problem, our research group had developed an improved KPro, in which a hydrophilic polymer, poly(vinyl alcohol) (PVA) hydrogel, was used for both porous skirt (opaque sponge containing hydroxyapatite or graphite powder) and the transparent optical core, and the attachment of

† Analytical & Testing Center, Research Center for Nano-biomaterials, Sichuan University, Chengdu, 610064, P. R. China.
† These authors contribute equally to this work.
the skirt to the core was achieved through an interpenetrating polymer network, at the same time, the porous skirt permitted the ingrowth of the host cornea tissue and formed a reliable biofixation\cite{25-28}. The in vivo tests showed encouraging results, the porous PVA composite porous skirt allowed the ingrowth of cells from the host cornea tissue and their proliferation, and formed a tight fixation with the surrounding host tissue\cite{29,30}. But it was a pity that the transparency of the optical core made of PVA hydrogel was not so high and also became more and more blurred with the adsorption of proteins, finally could not fulfill its functions.

How to improve the transparency of PVA hydrogel used as the optical core is what we should firstly consider here. PVA hydrogel has been studied extensively and considered as one of the most suitable hydrogels for biomedical applications due to its biocompatibility and nontoxicity\cite{31}. In recent years, it has also been reported that PVA hydrogel has many excellent properties, such as sufficient mechanical strength, light transparency and nutrition permeability. Besides, PVA hydrogel prepared under appropriate conditions has been proved able to autonomously self-heal, exhibiting good self-healing capability. Therefore, PVA hydrogel is always being and will still be the research hotspot in the field of artificial corneas and contact lens. PVA is a representative water soluble polymer and its aqueous solution can form both chemical and physical gels depending on the preparation conditions, and the low-temperature crystallized PVA hydrogel has light transparency and nutrition permeability. In addition, PVA hydrogels with high transparency and low protein adsorption have been reported to be obtained by doping with different solvents\cite{32-36}.

So, in the present study, we prepared PVA hydrogels with different transparency by adjusting the concentration of DMSO aqueous solutions and investigated the effects of DMSO concentration on the properties of PVA hydrogels, and ultimately optimized the concentration of DMSO aqueous solution to obtain the PVA hydrogel with the highest transparency to be used as the optical core of artificial cornea. Based on these results, the transparent mechanism of PVA hydrogels was also analyzed and explored in order to provide not only some reference data for the optical core of artificial cornea made of PVA hydrogels with high transparency and excellent mechanical strength but also important theoretical guidance for the further development of biomaterials used for artificial cornea and contact lens.

**Experimental section**

**Preparation of PVA hydrogels**

PVA powder (mean degree of polymerization 1700 ± 50, hydrolysis degree 99%, residual content of acetate groups 0.13%, content of PVA more than 90.5 wt.%) was from Chongqing Beipei Chemical Co. Ltd., China, and analytical grade DMSO was purchased from Chengdu Kelong Chemical Co. Ltd., China. Both the two chemicals were used here without further purification. Firstly, PVA powders were dissolved in mixed solvents composed of DMSO and deionized water, in which the DMSO concentration was 0, 20, 40, 60, 68.5, 75, 80, 90 and 100 respectively, with continuous stirring for 3h at 90°C to obtain a 16.7 wt% PVA solution. Then, the PVA solution was poured into a mold and frozen at -18°C for 7h, subsequently taken out and thawed at room temperature for 3h. After such a freeze-thaw cycle was repeated 7 times, PVA hydrogels could be obtained. After that, the products were rinsed thoroughly with deionized water at 37.5°C to remove DMSO as clean as possible, and the PVA hydrogel samples were achieved to be used for characterization. The process can be schemed in Fig.1 in order to be understood more easily.

![Fig. 1](image)

**Characterization**

**Transparency.** Light transmittance is an important indicator of the transparency. Transmittance (T) of PVA hydrogels fully swollen by deionized water was measured by using a UV-visible spectrophotometer (754UV-visible spectrophotometer, Shanghai Spectrum Instruments). We selected the wavelengths of 425nm, 450nm, 485nm, 550nm, 590nm, 600nm and 700nm in the visible region as the incident light to measure the transmittance. According to literature\cite{37}, the thickness of artificial cornea or corneal contact lens is about 0.5mm, so here the transmittance (Ta) of PVA hydrogel films with 0.5mm thickness was calculated by the following formula based on the transmittance of the PVA hydrogel films (T) and its actual thickness (d).

\[
Ta = 100 \times \frac{(100-T)}{d} \times 0.5
\]

**Crystallinity.** PVA hydrogels were dried until the weight remained constant in a thermostatic oven at 55°C. Then, the crystal melting enthalpy of the dry gels (ΔH) was determined by differential scanning calorimetry (DSC)\cite{38}. Compared with the complete crystallization of endothermic enthalpy (ΔH*) for pure PVA powder, the relative degree of crystallinity (Xc) was calculated by the following equation: \[ Xc = \frac{ΔH}{ΔH*} \]. (Here, ΔH* was measured by using pure PVA powder, and the value of ΔH* was determined as 55.19 J/g.)

**IR and DSC analysis.** Pure PVA powder and PVA hydrogels prepared with different concentration of DMSO aqueous solutions were characterized by IR in order to analyze the composition changes in the molecule chains. The FTIR spectra were obtained over a wavenumber range of 500–4000 cm\(^{-1}\) using an infrared spectrometer (TENSOR27, BRUKER Co. Germany). Also, differential scanning calorimetry (DSC, NETZSCH DSC 204 F1, Germany) was used to analyze the thermal property of 68.5 wt% DMSO aqueous solution as well as PVA hydrogels prepared with different DMSO aqueous solutions.

**Mechanical strength.** The standard samples of PVA hydrogels were prepared according to the requirement of tensile strength for plastics based on the national standard GB/T 1040-1992.
Then, the tensile strength and the elongation at break of these samples were tested using a universal testing machine (AG-10TA universal testing machine, Shimadzu, Japan).

**Viscosity.** The mixture solutions composed of DMSO and H2O with different ratios were prepared at 30°C, and the densities($\rho$) of these solutions were calculated by the convention formula. Based on this, the flow time (i) of these solutions were measured using an Ubbelohde viscometer. Thus, the viscosity of these solutions could be calculated according to the following formula: $\eta=A\rho t$ (Where $A$ is the instrument constant).

### Results and discussion

**Properties of PVA hydrogels**

**Transparence of PVA hydrogels.** The transmittance of PVA hydrogels were determined using different wavelengths of incident lights in the visible region. Table1 showed that the longer the wavelength of the incident light, the higher the transmittance of PVA hydrogels. The formation mechanism of PVA hydrogel is generally considered that, freeze-thaw cycles at low temperature make crystallization of PVA occur in the action of hydrogen bonds, resulting in the formation of PVA crystallites that act as physical cross-links to hold the network structure in the PVA hydrogel. These crystallites, that is crystallized regions in PVA hydrogel, influence the direction and the intensity of the light and generate some physical phenomena, such as light scattering, refraction and reflection, and then affect the transparence of PVA hydrogels. From Table 1, it is obvious that the transparence of PVA hydrogels increases with the DMSO concentration at first, then reaches a maximum value gradually, subsequently decreases. We can find that the PVA hydrogel prepared by 80wt% DMSO aqueous solution demonstrates the highest average transmittance, about 99.8 ± 0.2%, which is higher than that reported in patent[39], and is also close to that of natural human corneas (99.7-99.9%)[40].

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average transmittance (%)</td>
<td>40.6</td>
<td>41.0</td>
<td>44.2</td>
<td>47.7</td>
<td>47.1</td>
</tr>
</tbody>
</table>

**Crystallinity.** Crystallinity is an important physical quantity to reflect the crosslinking degree of PVA hydrogel. The value of crystallinity corresponds to the total amount of crystallites, including the number of crystallites and crystallite volumes. Fig.2 (Fig. S1 and Table S1) showed that the crystallinity of PVA hydrogels increased at 20wt% of DMSO solution firstly, and kept a slight fluctuation. Then, the curve decreased dramatically when the concentration of DMSO was 68.5wt%, after that continue to increase.

Combined with the above results in Table 1, we find that the relationship between the transparence and the crystallinity of PVA hydrogels is inversely proportional, that is to say, the weaker the crystallinity, the higher the transparence of PVA hydrogels. This is consistent with the fact that when the crystallinity gets to a higher value, it would increase the scattering of visible light, thus results in a decreased transparence.

**Mechanical strength.** The tensile strength and the elongation at break of PVA hydrogels were tested after being fully swollen in deionized water at 37.5°C. Fig.4a showed that the tensile strength of PVA hydrogel prepared with 80wt% DMSO aqueous solution was 3.36±0.14MPa, higher than that of PVA hydrogels prepared with other concentrations of DMSO aqueous solution, and similar to the average tensile strength of natural cornea (3.81Mpa)[41], could endure the normal
intraocular pressure of human (about 1.95 KPa)[42]. Elongation at break of PVA hydrogel prepared with 80 wt% DMSO aqueous solution was over 600%, as shown in Fig. 4b, demonstrating that such a PVA hydrogel with high transparency could still keep excellent mechanical strengths which could endure the normal intraocular pressure of human.

Characterization of DMSO aqueous solutions

Viscosity. Viscosity of DMSO aqueous solutions with different concentrations were measured at different temperatures. Fig. 5 showed that the viscosity curves at different temperatures displayed a similar changing trend, going up firstly and then falling down with the increase of DMSO concentrations. And the maximum value of viscosity showed up when the DMSO concentration was about 70 wt%, corresponding to the molar ratio of around 1:2 for DMSO/H$_2$O (the theoretical value is about 68.5 wt%). It suggests that DMSO aqueous solution might have the strongest intermolecular action when the molar ratio of DMSO/H$_2$O is 1:2. Also it implies that the intermolecular force between DMSO and H$_2$O molecules is much stronger than that in single molecules such as pure H$_2$O or pure DMSO. In addition, it is obvious that the viscosity for all the samples shows a declined tendency along with the increase of temperature, hinting that the interaction between DMSO and H$_2$O molecules is inversely proportional to the temperature.

DSC. It can be seen from Fig. 6 that the freezing point of 68.5 wt% DMSO aqueous solution (1DMSO/2H$_2$O) is -139.1°C, far below that of pure water (0°C) and pure DMSO (18.4°C), indicating that the 1DMSO/2H$_2$O system becomes more difficult to solidify because of the strong interaction between molecules. The thermodynamics of 68.5 wt% DMSO aqueous solution kept stable in the range of -100°C~100°C without significant endothermic peak presence. Besides, it can also be observed that two endothermic peaks appeared at 140.0°C and 199.0°C respectively, higher than that of pure water (100°C) and pure DMSO (189°C), implying that two or more types of strong intermolecular actions have occurred between DMSO and H$_2$O. It is further testified the fact that the intermolecular actions in 1DMSO/2H$_2$O solution is limited by temperature.

Interaction between DMSO and H$_2$O molecules in 1DMSO/2H$_2$O network structure. The above results confirmed that strong interaction between DMSO and H$_2$O molecules had occurred compared to that in pure H$_2$O or pure DMSO molecules, so it can be concluded that a new structure of 1DMSO/2H$_2$O network might be formed in DMSO aqueous solution. As we know, the two lone pair electrons of oxygen atom in DMSO molecule do not participate in any bonding in pure DMSO, but they are entirely possible to bond with hydrogen atom of H$_2$O through hydrogen bonds. The molecule clusters of H$_2$O and DMSO existed in DMSO aqueous solution had been proved using mass spectrometer by Dong, et al[43]. While Cabral, et al[44] had proved that the hydrogen atom on methyl group (-CH$_3$) did not participate in the formation of hydrogen bonds. Therefore, a network structure as schemed in Fig. 7 might be very likely formed between DMSO and H$_2$O molecules.

There are two major types of the six membered rings in Fig. 7(c), one is composed of two DMSO and four H$_2$O molecules connected by hydrogen bonds, as shown in Fig. 7(a), and the other is composed of six H$_2$O molecules connected by hydrogen bonds shown in Fig. 7(b). The network structure we described could be well coincident with the relationship between 1DMSO and 2H$_2$O, in which H$_2$O molecules still remain their tetrahedral structure and the hydrogen bonds generate from the interaction between the hydrogen atom and the lone pair electrons of O atom. While, -CH$_3$ groups in DMSO are gathered in clusters, reducing the repulsion between H$_2$O molecule and the polar group of S=O.
Transparent mechanism of PVA hydrogel

IR. The IR spectra in Fig.8 showed that the well-defined characteristic bands assigned to PVA were present at 3442, 2903, 2903, 2835 and 849 cm\(^{-1}\) for all samples, and the changes in peak intensity and location might be caused by hydrogen bonding between PVA chains which was influenced by the solvents containing different DMSO content. Fig.8a, 8b, 8c and 8d, the intensity of absorption peaks at 2835 cm\(^{-1}\) belonging to O-H stretching vibration (intramolecular H-bond) has changed, indicating that PVA chains might interact with H\(_2\)O or DMSO molecules through hydrogen bonds in different circumstances with the change of DMSO concentration. The adsorption peak assigning to C=C stretching vibration appeared at 1652 cm\(^{-1}\) obviously in Fig.8a-d compared with that of PVA powder in Fig.3(a), suggesting that the existence of DMSO and H\(_2\)O molecules could affect the interaction between PVA molecular chains.

Fig. 8 IR spectra of PVA hydrogels prepared with different concentration of DMSO aqueous solutions: 0wt% (a), 40wt% (b), 68.5wt% (c), 80wt% (d) and 100wt% (e) DMSO aqueous solutions.

DSC. The DSC curve of PVA hydrogel prepared with pure water (0wt% DMSO) was shown in Fig.9a, it could be seen that there were two endothermic peaks, the one appeared at 102.6°C, close to the boiling point of pure water (100°C), contributing to the fact that a large number of H\(_2\)O molecules in the form of free water existed in PVA hydrogel; and the other appeared at 123.4°C, much higher than 100°C, implying that large amount of hydrogen bonds formed between H\(_2\)O molecules and PVA chains. In Fig.9c, it can be found that endothermic peak appeared at 114.7°C, between the boiling points of pure water and pure DMSO (189°C), meaning that 1DMSO/2H\(_2\)O network structure was formed in 68.5wt% DMSO aqueous solution, which is exactly agreed with the proposed configuration in Fig.7. Therefore, the two endothermic peaks at 107.8°C and 119.3°C in Fig.9b confirmed the fact that part of H\(_2\)O molecules bonded with PVA chains through hydrogen bonding, while the rest combined with DMSO molecules, forming 1DMSO/2H\(_2\)O network structure. In Fig.9e, two endothermic peaks appeared at 123.6°C and 182.5°C, close to the boiling point of pure DMSO, indicating that large amount of DMSO molecules might combine with PVA chains through hydrogen bonding, and the rest of DMSO molecules existed freely in PVA hydrogel. Based on the above analysis, it can be easily explained that the endothermic peak at 105.8°C and 160.7°C in Fig.9d might be caused by DMSO molecules hydrogen-bonded with H\(_2\)O molecules (or PVA molecule chains) and the freely existed DMSO molecules respectively.

Fig. 9 DSC curves for PVA hydrogels prepared with different concentration of DMSO aqueous solutions: 0wt% (a), 40wt% (b), 68.5wt% (c), 80wt% (d) and 100wt% (e) DMSO aqueous solutions.

Transparent mechanism. It was considered that the physical cross-linked points including microcrystalline zones and hydrogen bonds in molecular chains contributed to the formation of three-dimensional structures during the freezing process. Compared with hydrogen bonds, microcrystalline zones are relatively stable in cross-linked structures due to their tightly arranged molecular chains and strong interaction. Therefore, hydrogen bonds play a more important role in the crystallization of PVA hydrogel, which in turn influences the transparence of PVA hydrogel.

Fig. 10 Schematic diagrams of spatial structure for PVA hydrogels prepared with different concentration of DMSO aqueous solutions: deionized water (a), 40wt% DMSO aqueous solution (b), 68.5wt% DMSO aqueous solution (c), 80wt% DMSO aqueous solution (d) and pure DMSO (e).

When the solvent to prepare PVA hydrogel was just composed of pure water, hydrogen bonds formed between PVA molecular chains. What’s more, plenty of H\(_2\)O molecules could provide H atoms to combine with polar groups of –OH in PVA molecular chains by hydrogen bonds, which in turn promoted the cross-linking degree of PVA and made the cross-linked structure grow tightly along three-dimensional directions. Consequently, the volume of crystalline regions became larger. But these larger crystalline regions are prone to blocking the penetration of the light, thus leading to the lower transmittance, schemed in Fig.10(a).

With the DMSO concentration in the solvent increasing to 40wt%, O atoms in DMSO preferentially combined with the active H atoms in H\(_2\)O, showing a tendency to form
1DMSO/2H₂O network structure. Hydrogen bonds in PVA hydrogel could be formed not only between PVA molecular chains but also between PVA molecular chains and H₂O. However, since part of active H atoms of H₂O had combined with O atoms in DMSO yet, the number of hydrogen bonds between PVA and H₂O would be reduced. Thus, the density and the strength of cross-linked structure in three-dimensional direction would correspondingly decrease. Meanwhile, the presence of the 1DMSO/2H₂O network structure might affect the growth of PVA crystals in spite of its incompleteness and fragmental shapes. Under such a growth circumstance, the volume of PVA crystalline regions would decrease and show a growth trend along two-dimensional direction gradually. Consequently, the transparence of PVA hydrogel became higher and higher. This process was schemed in Fig.10(b).

According to the intermolecular action between DMSO and H₂O molecules, a schematic diagram shown in Fig.7 was made. When the concentration of DMSO in aqueous solution was 68.5%, a precise 1DMSO/2H₂O network structure would be formed. The crystallization of PVA hydrogel was restricted by such a structure, and presented a growth trend along the two-dimensional direction. Finally, a flat-shaped crystal structure of PVA could be obtained, as shown in Fig.10(c). Despite the PVA crystalline region was long and thin, its volume was still large, so the light couldn’t pass through smoothly all the same. That is why we has not got PVA hydrogel with the highest transmittance when the concentration of DMSO is 68.5wt%. In addition, the plane of PVA crystallites were parallel each other, resulting in the relative shift happened easily, therefore, a maximum value of elongation at break have been obtained at such circumstances. However, we have not got the maximum value of tensile strength due to the weaker interaction between PVA molecular chains in the two-dimensional direction compared with that in the three-dimensional direction.

When the concentration of DMSO increased to 80wt%, we got a PVA hydrogel with a maximum value of transmittance. Under this condition, excessive DMSO molecules outside of 1DMSO/2H₂O network structure might affect or even destroy this complete structure into fragments. Thus, a three-dimensional crosslinking structure of PVA hydrogel appeared, as shown in Fig.10(d). Besides, hydrogen bonds formed between excessive DMSO molecules and -OH on PVA chains limited the crystallization of PVA hydrogel and also hindered the growth of crystalline regions along the two-dimensional direction, resulting in the smallest volume of PVA crystallites. Also, the tensile strength was improved with the increase in number of PVA crystallites formed in two-dimensional or three-dimensional space.

Finally, 1DMSO/2H₂O network structure disappeared when the concentration of DMSO aqueous solutions was up to 100wt%. Crystallization of PVA hydrogel grew along three-dimensional direction because most of DMSO molecules bonded with PVA chains by hydrogen bonds. The volume of crystalline region in PVA hydrogel prepared by pure DMSO became smaller compared with that prepared by pure water due to the weaker crosslinking within molecules, as schemed in Fig.10(e). Therefore, the transparence for such a PVA hydrogel could keep higher, but was still slight lower than that of the PVA hydrogel prepared with 80wt% DMSO solution.

Conclusion

We have prepared highly transparent PVA hydrogels with different concentrations of DMSO aqueous solution in the experiment. And the optimum concentration of DMSO was also determined by a series of tests. The results showed that the average transmittance of PVA hydrogel prepared with 80wt% DMSO aqueous solution reached a maximum value (99.8 ± 0.2%). According to investigations on the properties of DMSO aqueous solution with different concentrations, the network structure of 1DMSO/2H₂O existed in the mixed solution was put forward at the DMSO concentration of 68.5wt%. And the influencing mechanism of such a network structure on the transparence and mechanical strength of PVA hydrogels was analyzed thoroughly. Based on this, why the highest transparence of PVA hydrogel was obtained at the 80wt% DMSO was explained clearly. The PVA hydrogel with highly transparence prepared in this study might have a great potential to be applied in the fields of artificial corneas and contact lens.

Acknowledgements:

This work was supported by the National Basic Research Program of China (973 Program, 2012CB933902) and the National Natural Science Fundation of China (No.31370971).

References


