

Extraction of Lignocellulose and Synthesis of Porous Silica Nanoparticles from Rice Husks: A Comprehensive Utilization of Rice Husk Biomass

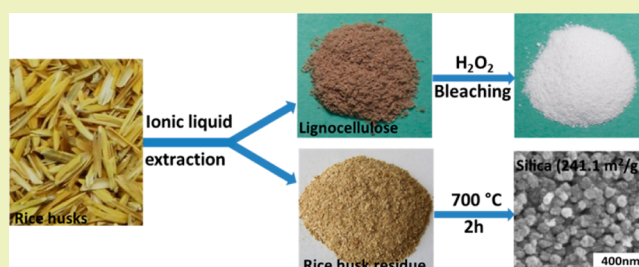
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ABSTRACT: Rice husk (RH) biomass is a massive byproduct from rice milling. Applications of RHs have been very limited. Therefore, RHs are often considered as a biowaste. RHs are mainly composed of lignocellulose (ca. 72–85 wt %) and silica (ca. 15–28 wt %). The majority of previous explorations focused on the preparation of silica or other silicon based materials from RHs, while the lignocellulose in RHs was usually burnt and thus wasted. Herein, an approach for comprehensive utilization of RHs has been developed to obtain both lignocellulose and high quality porous silica nanoparticles from RHs. Most of the lignocellulose in RHs was first extracted by dissolving in ionic liquids. The dissolved lignocellulose was subsequently separated and collected. The remaining RH residue after extraction that contains a high concentration of silica was thermally treated to synthesize amorphous porous silica nanoparticles with a high purity and surface area. It was also found that, during the extraction of lignocellulose using ionic liquids, some metal cations (e.g., K⁺) that generate negative effect for the synthesis of silica can be removed simultaneously, which generates a synergy for this comprehensive approach to make full use of RH biomass. The implication of the present findings is discussed.

KEYWORDS: Comprehensive utilization, Rice husks, Lignocellulose, Silica, Ionic liquid



INTRODUCTION

Rice husks (RHs) are a tough and bulky biomass with a high silica content from rice production.^{1–4} They contribute ca. 20–25 wt %³ of the dry weight of paddy rice. The anticipated world rice production in 2012 is 489.1 million tons,⁵ which means approximately 122–163 million tons of RH biomass will be generated globally in 2012. The density of an individual RH is ca. 735 kg/m³, whereas the bulk density of piled RHs is approximately 100–122 kg/m³.^{6,7} Studies have shown that RH contains ca. 15–28 wt % silica depending on the variety, origin, climate, and geographic location^{4,8} and about 72–85 wt % of lignocellulose (LC),^{9,10} including cellulose (ca. 35–40 wt %), hemicellulose (ca. 15–20 wt %), and lignin (ca. 20–25 wt %).^{3,10} In addition to the two main components, RH also contains a trace amount of other substances such as metal ions, chlorides, phosphates, etc.¹¹ The application of RHs has been limited because of their tough nature, low nutritional value, and great bulk.¹ Currently, the two most common RHs disposal methods are open field burning and land filling, which result in energy waste, greenhouse gas emission, air pollution, and huge landfill space occupancy due to their low bulk density.^{9,12} To address those issues, researchers have been investigating for decades to explore more economical ways to make full use of

RHs.^{8,13–16} Conventional applications of RHs include producing agriculture compost,¹⁷ making construction materials (e.g., bricks, insulation fillers, etc.),¹⁸ generating electricity (controlled burning).¹⁹ In addition, methods to derive higher values from RHs have also been explored, such as deriving various silicon based materials,^{1,4,20} which have attracted high attention in the past decades.

Lignocellulose (LC), a major component in RHs, is an abundant renewable carbohydrate resource that can produce sustainable energy and chemicals. Making full use of LC can help reduce CO₂ emissions and atmospheric pollution.²¹ However, during the previous explorations to prepare silicon based materials from RHs, the LC in RHs was largely ignored. They were typically burnt and thus wasted. The major challenge lies in the fact that there was no effective method to separate lignocellulose from RH. This situation has changed since the revolutionary work conducted by Rogers and co-workers²² on the dissolution of lignocellulose by ionic liquids

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(ILs).^{23–26} It has been shown that several ILs can dissolve the lignocellulose in RHs.^{27,28}

In addition to lignocellulose, RH also contains a high concentration of silica. The silicon element enters rice plants via their root in a soluble form, probably as a silicate or monosilicic acid, which undergoes biomineralization to form a lignocellulose and silica connected network in rice plant.²⁹ It is widely agreed that the silica in RHs is predominantly in inorganic linkages. A small portion of the silica might be covalently bonded to the organic compounds.²⁹ This portion of the silica cannot be dissolved in alkali and can withstand very high temperatures.²⁹ Studies have shown that the silica in rice plant is mainly localized in the tough external layer (epidermis) of RHs and it also fills in the space between the epidermal cells.¹ Harvesting silicon based materials has been the major research focus on RHs, since silicon based materials have widespread application in auto industry, information technology, fine chemistry, and material science.^{30,31} So far, various silicon based materials¹ have been derived from RHs, including silica,¹² silicon carbide,³² silicon nitride,³³ silicon tetrachloride,³⁴ zeolite,³⁵ and silicon.^{36,37}

It is of great environmental and economical importance to utilize both the lignocellulose and the silica in RHs. In this paper, to our best knowledge, for the first time, a comprehensive approach to make full use of RHs by deriving both lignocellulose and silica from RHs is reported. We first used 1-butyl-3-methylimidazolium chloride (BMIMCl), an ionic liquid, to dissolve and isolate LC from RHs. The dissolved LC in BMIMCl could be easily regenerated and is ready for applications in various fields, such as paper pulp, biofuel, etc.³⁸ After IL extraction, the RH residue can be readily thermally treated to yield high purity, amorphous, and porous silica. Through this method, both of the two major components in RHs could be utilized to yield value-added products. In addition, the IL used in this method can be recycled efficiently and be used as a solvent to extract LC from RHs multiple times, which would facilitate the commercialization of this technology.

■ EXPERIMENTAL SECTION

The RHs used in this study were obtained from Three H's LLC (Arkansas, USA). 1-Butyl-3-methylimidazolium chloride (BMIMCl, Sigma-Aldrich) and concentrated hydrochloric acid (VWR) were used as received without further purification.

RHs were first washed by deionized (DI) water three times to remove dirt and then dried in an oven at 90 °C overnight. The water rinsed and dried RHs (RH-H₂O) were chopped into powders using a regular countertop blender prior to the IL treatment to increase the surface area of RHs. The grounded RH powders were mixed with a predetermined amount of IL to extract lignocellulose. The weight ratio of IL to RHs was maintained at 15 to 1. The mixture of IL and RHs was stirred by a magnetic stirrer in an oil bath at a set temperature for a period of time (see Table 1). Immediately after the dissolution, the product mixture was centrifuged to separate the insoluble portion of RHs (namely RH residue) when the mixture was still hot to take advantage of its low viscosity. The supernatant was collected and

mixed with DI water to precipitate the dissolved lignocellulose in IL. The precipitated LC was collected, washed with DI water three times, and then dried in an oven at 90 °C overnight. A small portion of LC was bleached by 5 wt % H₂O₂ for 2 h at 100 °C, and then the bleached LC was filtered and rinsed with DI water three times for demonstration purpose. The LC after bleaching was dried in an oven at 90 °C overnight.

The separated RH residue was washed by DI water to remove the small amount of absorbed IL, and then recentrifuged. This process was repeated three times to fully remove the absorbed IL, and then, the RH residue was dried in an oven at 90 °C overnight. All the above solutions containing IL were collected and purified following a reported procedure: they were first evaporated under vacuum in a rotary evaporator (IKA-RV10) at 90 °C to remove the water as much as possible, and then the recycled IL was dried in a vacuum oven (VWR S/P Model 1430) for 24 h at 90 °C.³⁹ The recycled IL was used to extract LC in RHs following the same procedures as described above.

The degree of extraction of LC was calculated according to eq 1, where w_i is the initial weight of RHs used, w_{re} is the weight of RH residue (insoluble portion) after IL extraction. LC content was set to be 81.7 wt % in RHs in this article based on the TGA measurement, which will be discussed below.

$$\text{degree of extraction of LC (wt \%)} = \frac{w_i - w_{re}}{81.7\% \times w_i} \times 100\% \quad (1)$$

In order to compare the effectiveness of IL treatment on the removal of metal cations for the synthesis of silica, acid treated RHs were also prepared and used as a control. Acid treatment was carried out based on the water rinsed and dried RHs, which were directly refluxed in 5.0 wt % HCl in a round-bottom flask for 1 h. After that, the RHs were rinsed with DI water three times before being dried in an oven at 90 °C overnight.

Both the RH residue after IL extraction and the acid treated RHs were pyrolyzed at 700 °C for 2 h to prepare silica nanoparticles.

Scanning electron microscopy images were acquired on a LEO 1530 VP field emission scanning electron microscope (FE-SEM). All samples were sputter-coated with a thin layer (ca. 3 nm) of Au/Pd prior to SEM imaging. The purity of silica was measured on a PANalytical AXIOS X-ray Fluorescence (XRF) Spectrometer. The surface area of silica nanoparticles was measured on a TriStar II 3020 Surface Area and Porosity System. The samples for surface area measurement were dried at 250 °C over 8 h prior to the measurement. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 diffractometer with Bragg–Brentano θ - 2θ geometry (40 kV and 30 mA), using a graphite monochromator with Cu K α ($\lambda = 0.1540$ nm) radiation. Thermogravimetric analysis (TGA) was conducted on a TA Q50 analyzer (TA Instruments) at a heating rate of 10 °C/min in air atmosphere.

■ RESULTS AND DISCUSSION

RHs are mainly composed of lignocellulose (cellulose, hemicellulose, and lignin), hydrated silica, and a trace amount of various metal ions, chlorides, and phosphates.^{1,11} Researchers have managed to synthesize various silicon based materials from RHs¹ while silica has been the major product. Earlier research has proved that metal cations, particularly potassium ions, in RHs are responsible for the melting of silica nanoparticles at relatively low temperatures during pyrolysis,^{12,40–44} which leads to the aggregation of silica nanoparticles and increase of crystallinity. Studies have shown that acid treatment is an effective way to remove the K⁺ ions in RHs. Pyrolysis of acid treated RHs yielded silica nanoparticles with high purity and surface area and low crystallinity.^{12,45,46} However, acid leaching is demanding on reaction equipment and may generate potential pollution issues, thus is highly undesirable for commercial production. Moreover, few of the

Table 1. Results on IL Extraction of LC^a

sample ID	temperature (°C)	time (h)	degree of extraction of LC (%)	IL recovered (%)
RH-IL-1	100	12	21.4	98.9
RH-IL-2	150	12	46.6	97.9
RH-IL-3	130	36	51.1	96.8

^aThe weight ratio of IL to RHs was 15 to 1 for all the samples.

approaches to prepare silicon based materials reported so far have taken the lignocellulose into consideration. During the conventional processes, the lignocellulose in RHs was simply burned and wasted, which also leads to severe CO₂ emission and potential pollution.

ILs have been found to be a group of effective and green solvents for dissolving LC.²³ It has also been reported that LC can be used in renewable energy⁴⁷ and the paper industry^{48,49} and be converted into biofuel (particularly ethanol).^{14,15} Therefore, using IL to extract LC from RHs before harvesting silica (or other silicon based materials) would lead to a comprehensive utilization of the two major valuable components in RHs. At the same time, during the IL extraction of LC, it is expected that the metal impurities, particularly potassium which is typically soluble in water, can be effectively removed simultaneously, which can bring synergistic benefits for the later stage of harvesting silicon based materials. In our study, the characterization results support this hypothesis, which will be discussed below. The detailed conditions for IL extraction are listed in Table 1. These conditions (temperature, time, and weight ratio of RHs to IL) for IL extraction of LC were chosen since they are representative and were most typically used in the previous research.^{24,28,39} The results showed that either a higher extraction temperature or a longer duration is needed to improve the degree of extraction. At 130 °C, ca. 51.1% of LC was extracted after 36 h of reaction. This degree of extraction is comparable to the previous reports which is approximately 30–50 wt %.^{28,39}

The used IL can be easily recovered by a rotary evaporator (Table 1), and the IL dissolution efficiency after recycling was also studied. Table 2 shows that after 3 recycles of IL, the

Table 2. Effect of BMIMCl Recycling on the Extraction Efficiency^a

sample ID	temperature (°C)	degree of extraction of LC (wt %)	IL recovered (wt %)	IL recycle times
RH-IL-3	130	51.1	96.8	0
RH-IL-4	130	44.2	97.1	1
RH-IL-5	130	40.0	98.5	2
RH-IL-6	130	37.2	97.9	3

^aThe weight ratio of RH and IL was 1:15 for all samples, and the extraction times were kept at 36 h.

degree of extraction of LC under the same conditions decreased from ca. 51.1 to ca. 37.2%. The decrease in IL efficiency is probably caused by several factors. First, a small portion of the IL was decomposed during the RH extraction. Li et al. revealed that during the extraction, part of IL (as high as 15%) would undergo degradation depending on the temperature and duration.³⁹ Second, there is always residual water remaining in the recycled IL after recovery, and water is a poor solvent for LC.³⁹ Since hydrophilic BMIMCl and water molecules could form weak interactions with each other,⁵⁰ it is hard to completely remove the water content during recycling. Third, after the LC regeneration, there is always a tiny amount of LC remaining in the IL. The residual LC will interact with IL, and this interaction would negatively affect the recycled IL to accommodate new LC from RHs and, thus, affect the performance of the recycled IL in the new cycle of extraction.³⁹ Li et al. studied this phenomenon, and based on the color of the recycled IL and ¹³C NMR results, they found that a low concentration of LC, presumably the ones with low molecular

weights, could still remain dissolved during the LC regeneration process.³⁹ Nevertheless, on the basis of our study, even after 3 recycles, the IL still remains to be efficient in terms of isolating LC from RHs with a degree of extraction of 37.2 wt %. Overall, the IL efficiency data on LC extraction are in good agreement with earlier reports.^{39,51}

The collected LC from RH is shown in Figure 1. The LC can readily be used in various applications such as renewable



Figure 1. Regenerated LC from RHs before (left) and after bleaching (right).

energy, biofuel, etc.^{14,15,38,47} After bleaching, the LC exhibits white color, thus potential for paper industry applications. It was reported that the LC after IL extraction typically possesses a lower crystallinity compared to the original LC in plants, and such LC with a lower crystallinity is a better candidate for widespread application.⁵²

Figure 2 shows the TGA results for the water rinsed RH (RH-H₂O), HCl treated RHs (RH-HCl), and RH residue after

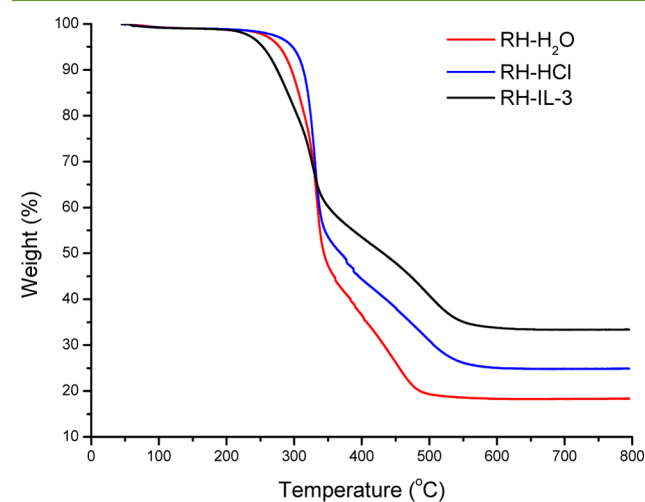


Figure 2. TGA thermograms of the water treated RHs (RH-H₂O), acid treated RHs (RH-HCl), and RH residue after BMIMCl extraction (RH-IL-3).

IL extraction (RH-IL; which is RH-IL-3 in Table 1). On the basis of Figure 2, the RH-H₂O used for this study contains ca. 18.3 wt % RH ash (RHA), most of which is silica. The ash content for RH-HCl and RH-IL is 24.8 and 33.4 wt %, respectively. This shows that after either HCl or IL treatment, the silica content in RH residue was increased. For RH residue after IL treatment, the increase of silica content is simply owing to the partial dissolution of LC in RHs by BMIMCl. For the HCl treated RHs, the increase of silica content can be explained

by the fact that the HCl treatment can help hydrolyze the organic components in RHs, especially hemicellulose.^{14,53} Hemicellulose is hydrogen-bonded to the surface of cellulose microfibrils. Under acid pretreatment, part of hemicellulose could be depolymerized by acid assisted hydrolysis and this will also release some lignin which is indirectly associated with cellulose via linkage to xylan.⁵³

Previous work has shown that in order to prepare high quality silica nanoparticles from RH, metal cations, particularly K^+ , must be removed. Acid treatment has proved to be effective to remove metal cations.^{44,45} In this work, it is expected that metal cations, particularly the ones soluble in water, can be removed during IL extraction and achieve a similar effect as HCl treatment. To compare the metal removal effect, the silica samples prepared from both the RH residue after IL extraction and HCl treated RHs are systematically evaluated.

Table 3 shows the XRF results of the silica samples from the water, IL, and HCl treated RHs. Among the three samples, the

Table 3. XRF Data of the Silica Made from the Pyrolysis of RHs at 700 °C for 2 h^a

compound	silica from RH-H ₂ O (wt %)	silica from RH-IL-3 (wt %)	silica from RH-HCl (wt %)
SiO ₂	96.89	99.52	99.80
CaO	1.22	0.05	
Cr ₂ O ₃	0.61		
P ₂ O ₅	0.31	0.02	0.03
MgO	0.25		
SO ₃	0.19	0.04	0.06
Fe ₂ O ₃	0.18	0.30	0.06
K ₂ O	0.11		
MnO	0.10		
ZnO	0.08		
NiO	0.04	0.05	0.03
CuO	0.02	0.02	0.02

^aThe RHs were treated by H₂O, IL, and HCl, respectively.

silica from the HCl treated RHs exhibits the highest purity of 99.80 wt %; the silica from the IL treated RHs exhibits a slightly lower purity of 99.52 wt %; while the silica from the H₂O treated RHs possesses a much lower purity of 96.89 wt % compared to the above two. Overall, the XRF results support that the IL treatment is much more effective than the water rinse and is comparable to the HCl treatment in terms of metal and nonmetal impurities removal. This is probably because during the dissolution of LC, the impurities in the dissolved LC were removed together with this portion of LC. Meanwhile, the partial dissolution of LC disrupted the overall structure of the husk, allowing for better contact between the ILs and the RH residue, which helps further remove the impurities in RH residue via an ion exchange process. In particular, IL treatment can effectively remove potassium cations, whose absence has proved to be very critical for the synthesis of high quality silica nanoparticles from RHs.^{44,45} This in turn is consistent with the high purity silica samples from the HCl and IL treated RHs, which will be discussed in detail below. As such, the results support our initial expectation that the IL treatment, whose major purpose is to extract LC, can lead to a synergistic effect to remove critical metal cations, facilitating the subsequent synthesis of silica nanoparticles from RH residue.

The XRD patterns of the silica samples from HCl and IL treated RHs are shown in Figure 3. The two patterns are very

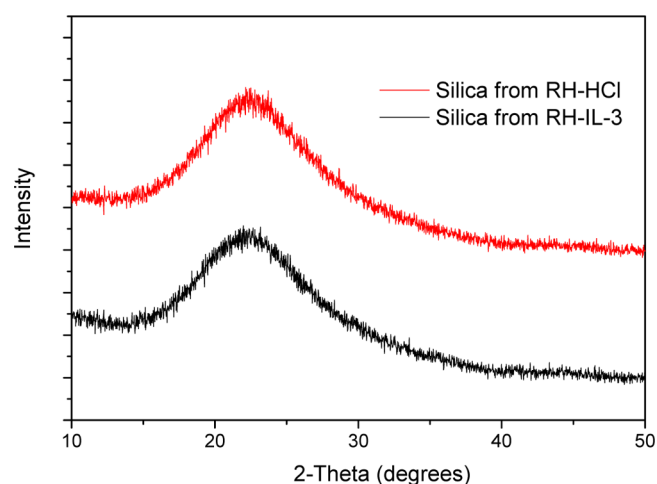


Figure 3. XRD patterns of the silica samples prepared from RH-HCl and RH-IL-3, respectively.

close to each other and suggest that the silica samples are amorphous. This again suggests that the IL extraction process has effectively removed K^+ cations, which is consistent with the above XRF results.

Figure 4 shows the SEM images of the silica samples from the pyrolysis of HCl and IL treated RHs. The SEM images show that the diameter of the silica nanoparticles from the HCl leached RHs is ca. 50 nm, which is slightly lower than that of the silica nanoparticles (ca. 70 nm) from the IL treated RHs (RH-IL-3). Such a minor dimensional difference might be owing to the slightly higher concentration of metal cations in the IL treated RHs, particularly Ca^{2+} and Fe^{3+} . It has been reported that Ca^{2+} can promote the melting of silica, although its promoting effect is much less significant compared to K^+ cations.^{54,55} In addition, both silica nanoparticle samples exhibit a narrow particle size distribution, which is very valuable for their future applications.

While the two silica samples differ slightly in particle size, both of them exhibit a porous structure. The surface area of the silica nanoparticles from the HCl treated RHs is 283.3 m²/g according to the BET characterization, which is slightly higher than that of the silica nanoparticles from the IL treated RHs (241.1 m²/g). Assuming all the particles are solid (nonporous) and perfectly spherical and the density of silica is 2.22 g/m³,⁴⁴ then based on the particle size of the two samples in Figure 4 (~50 and ~70 nm), their specific surface areas should be ca. 54.1 and 38.6 m²/g, respectively. Thus, the BET surface area measurement showed that those silica nanoparticles were actually porous. The porous structure is probably because the silica retained its cellular skeleton structure in RHs,⁵⁶ which is originated from the loose aggregation of primary silica nanoparticles. The porous silica structures observed here are consistent with our previous work.⁴⁴

While this work focuses on silica, other silicon based materials can also be synthesized after IL extraction. On the other hand, this comprehensive utilization approach can be applied to other biomass containing silica such as wheat, sorghum, etc.² or other valuable inorganic materials which cannot be dissolved in ILs.

CONCLUSIONS

Our study has shown that ionic liquid BMIMCl is an effective solvent to extract lignocellulose in RHs. The LC in RHs can be

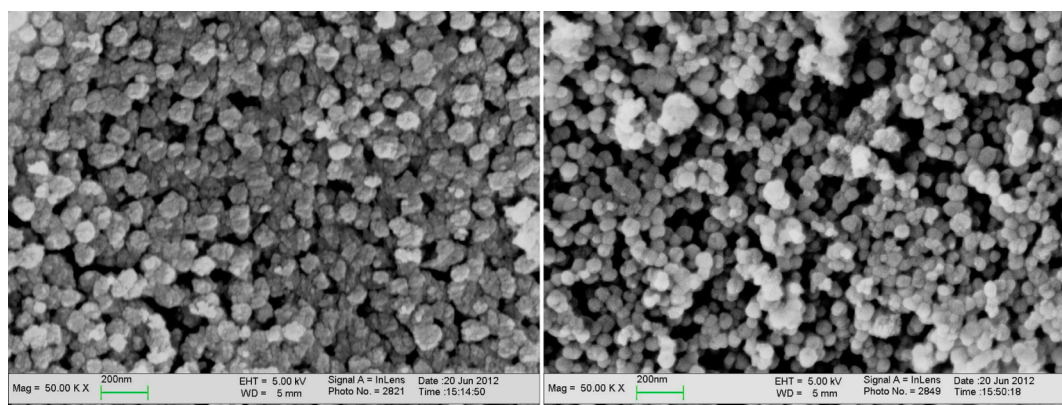


Figure 4. (left) Silica nanoparticles from the pyrolysis (2 h @ 700 °C) of the IL treated RHs (RH-IL-3). (right) Silica nanoparticles from the pyrolysis (2 h @ 700 °C) of the HCl treated RHs (RH-HCl).

easily isolated and collected. The degree of extraction of LC by using BMIMCl reached 51.1 wt %, and the BMIMCl can be collected and reused for the extraction of LC. The IL treatment of RHs leads to a synergistic effect to effectively remove K^+ cations, which has been conventionally achieved by HCl leaching of RH. Amorphous silica nanoparticles with a high purity, high surface area, and narrow particle size distribution were synthesized by the pyrolysis of RH residue after IL extraction. This work represents a fine first example of comprehensive application of RHs, which is expected to promote effective utilization of RH biomass globally in the near future.

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Notes

The authors declare no competing financial interest.

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