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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/acs.analchem.7b04376>

Analytical Chemistry, 90, 3, pp. 1547-1553, 2018-01-05

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Low-Temperature and Atmospheric Pressure Sample Digestion Using Dielectric Barrier Discharge

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Supporting Information

ABSTRACT: A new sample digestion method using a double layer and coaxial dielectric barrier discharge (DBD) digestion reactor was developed for the sensitive determination of trace elements in rice samples. All the operation parameters of the DBD microplasma and other digestion conditions were carefully optimized. Three DBD-digestion modes were investigated for real matrix samples, including H₂O-DBD-digestion, H₂O₂-DBD-digestion, and HNO₃-DBD-digestion systems. Among the three modes, the H₂O-DBD-digestion system provides a suitable digestion of sample without any additional chemicals, achieving environmental friendly sample treatment and eliminating the potential interferences. Under the optimized conditions, limits of detection for Mg, Mn, Zn, Cd, Cr, Co, and As were in the range of 0.01–0.35 ng g⁻¹ by inductively coupled plasma mass spectrometry (ICPMS). The accuracy of the proposed method was checked by analysis of a certified reference material (GBW10043) and spiked samples with satisfactory results (83–113% recoveries).

In order to alleviate the serious interferences from matrix constituents and achieve reproducible and accurate analytical results, complete digestion of sample is necessary prior to the determination of the elements in complex samples by atomic spectrometry.¹ Up to date, numerous sample digestion methods have been available for routine digestion of samples in laboratories, such as conventional electrically heated digestion, microwave digestion (MWD), and microwave-induced combustion (MIC). Conventional heated digestion and MWD generally consume large amounts of concentrated mineral acids, which inevitably introduce a relatively high blank because of acid impurities. Although MWD significantly improves digestion efficiency, minimizes analyte loss, and reduces digestion time,^{1–3} more time is needed to cool pressurized vessels to room temperature before opening the caps of digestion vessels. Furthermore, a time-consuming step is usually needed to evaporate the acids from the digestion solution prior to analysis because large amounts of mineral acids were used during sample digestion. Compared to the conventional digestion techniques, MIC combined with acid extraction was regarded as a relatively ideal digestion technique not only because of minimization of concentrated acids consumption but also due to reduction of digestion time and interference in inductively coupled plasma mass spectrometry (ICPMS) analysis.^{4,5} MIC has also been successfully used to

pretreat complex matrix containing volatile elements such as Hg and halogens with a closed system.^{6,7} Unfortunately, pressurized vessels (20 bar) with oxygen were needed in this method and might limit its further application.

Recently, significant efforts have been devoted to develop rapid and efficient methods for the digestion of complex samples aiming to reduce or even eliminate the use of concentrated acids. Advanced oxidation processes (AOPs) based on UV irradiation with/without photocatalysts and oxidizing reagents, ozone in the presence/absence of UV or ultrasound irradiation, UV photocatalysis, or Fenton reaction, which involves in situ generation of highly potent chemical oxidizing species (hydroxyl radical, ·OH etc.), have been regarded as efficient techniques for the decomposition of organic pollutants in wastewater and as a promising alternative to the conventional sample digestion techniques for the determination of trace elements by atomic spectrometry.^{8–12} Various Fenton-like catalysts were used to improve the digestion capabilities of AOPs, including Fe⁰ and Fe₃O₄ nanomaterials. These materials remarkably accelerate the

Received: October 24, 2017

Accepted: January 5, 2018

Published: January 5, 2018

purification system (Chengdu Ultrapure Technology Co., China). Nitric acid (65%, Merck, Germany) was used in this experiment. 30% hydrogen peroxide was purchased from Kelong Chemical Reagents Co. (Chengdu, China). High-purity argon (Ar) was supplied by Qiaoyuan Gas Co. (Chengdu, China). A Certified Reference Material (CRM) of rice (GBW10043) and stock solutions (1000 mg L⁻¹) of Mg, Mn, Zn, Cd, Cr, Co, and As were obtained from the National Research Center of China (NRCC, Beijing, China). Other rice samples were bought from a local supermarket in Chengdu, China. COD reagents (A: sulfuric acid 15.0–25.0%, mercuric sulfuric 1.0–10.0%; B: sulfuric acid 90.0–100.0%, silver sulfuric 0.5–3.0%, potassium dichromate <0.1%) were purchased from HACH, USA. DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, 97%, CAS: 3317-61-1) for capturing hydroxyl radical was purchased from J&K Chemical Ltd., China.

Digestion and Analytical Procedure. The operation process of sample digestion is described and shown in Figure S1. In order to evenly mix rice powder with the digestion solution and avoid settling of the sample in the vial, all of the rice samples were ground to less than 150 mesh, except the certified reference material of rice powder (GBW10043), sealed in polyethylene bags, and stored in a refrigerator at 4 °C prior to their analysis. 0.0240 g of CRMs or rice powder was weighed into a vial in which 4 mL of digestion solution was added. For the rice samples obtained from local supermarkets, Cr, Co, As, and Cd stock solutions were spiked to certain concentrations before their digestion. The mixture was digested using three different DBD-digestion systems, respectively, including the H₂O-DBD-digestion system, H₂O₂-DBD-digestion system, and HNO₃-DBD-digestion system. Samples were diluted 50 times for the determination of Mg because of its high concentration in the analyzed samples, while the samples were diluted 5 times for the determinations of other elements. The operation conditions of ICPMS are shown in Table S2. A AS14 column was used to separate nitrite with a flow rate of 1.2 mL min⁻¹. The details of the EPR experimental procedure used for the identification of oxidative radicals in the DBD plasma are available in Section 4 of the Supporting Information.

RESULTS AND DISCUSSION

Feasibility and Improvement of DBD-Digestion Technique. Although low temperature atmospheric pressure plasma has been widely used for the degradations of organic pollutants in wastewater, the research on utilizing it in sample digestion has not been reported so far. The feasibility of the DBD-digestion technique was thus undertaken using a rice powder obtained from a local supermarket. 0.0240 g of this rice powder was added into a vial together with 4 mL of DIW and subsequently digested in the DBD plasma. As the digestion time increased, the digested solution gradually became clear. However, it was observed that a small amount of yellow-white solid was still left on the inner wall of the quartz tube. To gain insight into this effect, an infrared thermometer was used to measure the temperature of the solution in the DBD chamber. The temperature was found to be above 60 °C, suggesting that a solvent (DIW) evaporation occurred at this temperature and thus resulting in inefficient digestion to cause solids adhesion to the quartz tube wall, as well as possible loss of elements. An ice box was thus used to avoid the above problem by cooling the solution from the digestion tube. As shown in Figure 2a, the turbid solution became clear after 6 h of digestion. In previous work,²⁰ digestion efficiency was evaluated through the

Figure 2. Pictures of H₂O-DBD-digestion of rice powder. (a) Effect of digestion time: 0, 2, 4, and 6 h. (b) COD values of digests obtained under different digestion times.

determination of residual carbon content (RCC) by using ICP-OES. However, the rice powder in the sample solution usually blocked the nebulizer of ICP-OES, and thus, it was not easy to use ICP-OES to evaluate the digestion efficiency of the developed system. COD is a traditional chemical method to measure the amount of material that needs to be oxidized in a water sample. This index is also one of the comprehensive indicators of relative content of organic matter in the solution. Therefore, COD was applied to characterize digestion efficiency of the developed system. Figure 2b shows that the COD value of digested solution gradually decreased with increasing digestion time. These results agree well with the phenomenon presented in Figure 2a and indicate that the organic compounds contained in the sample solution have been degraded efficiently by the DBD plasma after 6 h of digestion. In order to improve sample throughput, simultaneous discharge of four coaxial DBDs was designed and the goal of batch digestion was achieved, as shown in Figure 1a,d.

Effects of Operation Conditions on the Sample Digestion. From the above experiments, it is evident that organic substances could be degraded efficiently by DBD plasma with DIW only, but the digestion time is very long using the H₂O-DBD-digestion method. In order to gain insight into the H₂O-DBD-digestion and improve its digestion efficiency, the effects of the type and flow rate of discharge gas and the speed of the peristaltic pump on the digestion efficiency were investigated. As shown in Figure S2a, although both argon and air can be used as discharge gas to digest the rice sample to some certain extent with 6 h of digestion, it is evident that air as carrier gas had better efficiency compared to argon. This may be because oxygen contained in air can generate oxidative radicals or compounds with DBD excitation, thus accelerating digestion. Meanwhile, argon is much more expensive than air; thus, air was selected as the discharge gas in subsequent experiments. When the flow rate of air increased to above 40 mL min⁻¹, complete digestion was achieved as indicated by clear solutions, as shown in Figure S2b. Thus, flow rate was maintained at 40 mL min⁻¹ for all subsequent experiments. The residence time of sample in the DBD device was dependent on the speed of the peristaltic pump. Figure S2c shows the effect of pump speed on the digestion; it was found that optimum digestion efficiency was obtained at 5 mL min⁻¹ and digestion efficiency decreased at higher or lower pump speeds. Thus, 5 mL min⁻¹ was selected for all subsequent experiments.

According to previous works, addition of oxidizing reagents, such as H₂O₂ and HNO₃, can significantly accelerate the speed

of sample digestion. Therefore, the H_2O_2 -DBD-digestion system and HNO_3 -DBD-digestion system were also applied to improve the performance of sample digestion by DBD plasma. Subsequently, the concentration of oxidizing chemicals, output power, and digestion time were optimized for these two systems, respectively. For the H_2O_2 -DBD-digestion method, concentrations of H_2O_2 in a range of 4–30% were tested. As shown in Figure S2d, the clarity of the solution increased as the H_2O_2 concentration increased. Complete clear solution was obtained with the use of 30% H_2O_2 whereas the same output power (50 W) and digestion time (40 min) were used. Thus, 30% H_2O_2 was chosen as the optimal concentration of H_2O_2 . Figure S2e shows the effects of output power on the digestion efficiency when concentration of H_2O_2 and digestion time were kept at 30% H_2O_2 and 40 min. With the increase of output power from 10 to 50 W, digestion solutions became gradually clear and became completely transparent at 50 W. Figure S2f shows that digestion efficiency was also influenced by digestion time. A clear solution could be obtained at 40 min. Finally, 30% H_2O_2 , 50 W of output power, and 40 min of digestion time were chosen as the optimized conditions for the H_2O_2 -DBD-digestion method.

For the HNO_3 -DBD-digestion method, the concentration of HNO_3 in a range of 6–33% was tested. As shown in Figure S2g, the digestion efficiency increased with the increase of concentration of HNO_3 solution at 55 W of output power and 40 min of digestion time. The higher the concentration of HNO_3 , the better digestion efficiency and the less stable DBD discharge were obtained. The HNO_3 concentration was found to be an important factor influencing the stability of DBD. The DBD device could not discharge stably and efficiently when the concentration of HNO_3 was higher than 33%. Consequently, 33% HNO_3 was chosen for all subsequent experiments. Figure S2h shows the effect of output power on the digestion efficiency at 33% of HNO_3 and 40 min of digestion time. With the increase of output power from 15 to 55 W, the digestion solutions gradually became much clearer and became transparent at 55 W. The DBD plasma could not be generated when the output power was lower than 10 W. The relation between output power and input voltage can be found in Table S2. Figure S2i shows the effect of digestion time on the digestion efficiency. A clear solution could be obtained at 40 min. Thus, 33% HNO_3 , 55 W of output power, and 40 min of digestion time were selected as the optimized conditions for the HNO_3 -DBD-digestion method.

In acidic solutions, $\text{Cr}_2\text{O}_7^{2-}$ oxidizes reducing substances (both organic and inorganic). When Ag_2SO_4 is used as the catalyst, the majority of organic matters, including linear organic matter, can be oxidized in acidic solutions. This is an important basis of COD for the indication of digestion efficiency. Unfortunately, COD could not be applied to indicate the digestion efficiency of sample obtained using H_2O_2 -DBD-digestion and HNO_3 -DBD-digestion systems because $\text{Cr}_2\text{O}_7^{2-}$ not only oxidizes organic compounds but also oxidizes inorganic reducing substances under these conditions. In the H_2O_2 -DBD-digestion system, the residual H_2O_2 could react with $\text{Cr}_2\text{O}_7^{2-}$, which would lead to interferences of reaction between organic matters and $\text{Cr}_2\text{O}_7^{2-}$.^{2–21}

Figure S3a shows that very little hydrogen peroxide in 4 mL of solution could cause significant interference to COD

detection. For the HNO_3 -DBD-digestion method, because of the interference of reaction between NO_2^- and $\text{Cr}_2\text{O}_7^{2-}$, COD detection could not be applied in solutions after digestion. As shown in Figure S4a,b, no NO_2^- could be detected before DBD digestion in nitric acid solution and the mixture of rice powder dissolved in nitric acid, respectively. However, NO_2^- could be detected after DBD digestion in the mixture of rice powder and nitric acid by the ion chromatogram (Figure S4c). The concentration of nitrite in solutions after digestion (2597 mg L^{-1}) is above the COD detection range (Figure S3b). As a strong reducing group, NO_2^- could react with $\text{Cr}_2\text{O}_7^{2-}$, which would lead to interferences.

Possible Mechanism of DBD Digestion. In this work, a series of physical and chemical effects generated in DBD discharge were used to achieve complete sample digestion. A series of light and acoustic phenomena, such as ultrasonic holes, shock waves, and ultraviolet light, occur during the DBD discharge, which are called physical effects. In the process of discharge, a plasma channel will be formed, along with the shock wave and ultrasonic cavitation.^{22,23} Then, local hot spots are formed and transient supercritical water was formed eventually. Organic compounds and oxygen are completely miscible with supercritical water, allowing organic compounds to undergo spontaneous oxidation. UV light generated during the DBD discharge process allows photolysis reactions during the entire digestion process:

Various active radicals and oxidizing groups generated in the DBD discharge could react with organic compounds in the solution and result in complete digestion. A variety of high-energy electrons could be obtained in the plasma generated in the DBD discharge process. These high-energy particles bombard molecules in aqueous solution, which leads to ionization and excitation of water molecules. Ions, excited molecules, and secondary electrons are generated to facilitate stronger reactions of substances, such as $\cdot\text{OH}$, $\cdot\text{H}^+$, $\cdot\text{O}$, $\text{HO}_2\cdot$, H_2O_2 , and O_3 . These highly reactive oxidants can effectively oxidize and degrade organic compounds.

The spectroscopic technique was performed to measure optical emission spectra of the three DBD-digestion methods between 200 and 600 nm. As shown in Figure 3a, several peaks could be clearly identified according to previous studies.^{24,25} Peaks were observed at 299 nm corresponding to O_3 , in addition to a peak observed at 440 nm, corresponding to the oxygen atom. Moreover, peaks were observed at 319 and 407 nm, corresponding to OH radical and OH^+ , respectively. Furthermore, the EPR/DMPO experiments were carried out to confirm the identity of the involved reactive intermediates. As shown in Figure 3b, no peaks were identified before DBD digestion. After DBD digestion, four typical peaks in the spectra with intensity ratio of 1:2:2:1 could be assigned to DMPO- OH adducts (with $a\text{N} = a\text{H} = 14.9$ G), confirming the existence of $\cdot\text{OH}$ in mixtures.

$\cdot\text{OH}$ is the most important and active oxidizing species among these active species. The oxidation potential of $\cdot\text{OH}$ is 1.80 V, higher than O (2.42 V), O_3 (2.07 V), H_2O_2 (1.77 V),

Figure 3. (a) Optical emission spectrum for H_2O -DBD-digestion, H_2O_2 -DBD-digestion, and HNO_3 -DBD-digestion systems, respectively. (b) EPR spectra of DMPO–OH adduct.

and O_2 (1.23 V). Attributed to $\cdot\text{OH}$, the organics are converted into easily degradable small molecular substances, carbon dioxide and water, by reactions of direct ring opening, breakage, addition, substitution, or electron transfer.²⁶ In addition to the direct effect of refractory macromolecular organic matter, $\cdot\text{OH}$ can react with H_2 , $\cdot\text{OH}$, H_2O_2 , or OH^- in the solution to further form strong oxidizing groups and promote the digestion.

O_3 in the ultraviolet light can be decomposed to produce secondary oxidants such as $\cdot\text{OH}$ to oxidize organic compounds.^{27–29} In the acidic solution, ozone, which has a high oxidation potential (2.07 V), can carry out an electrophilic attack of organic compounds. In the acidic medium (H^+), the presence of hydrogen ions could accelerate decomposition of ozone and promote digestion of samples, which makes digestion efficiency higher.

In the hydrogen peroxide system, peroxone reaction could occur between ozone and hydrogen to generate $\cdot\text{OH}$.^{30,31}

Hydroxyl radicals, superoxide radical, and ozone could react with organics rapidly. Also, the synergistic effect of ozone, UV, and hydrogen peroxide could accelerate the production of $\cdot\text{OH}$ ³² and promote the digestion. As a result, the DBD- H_2O_2 -digestion method provides better digestion efficiency than that of the DBD- H_2O -digestion method.

Analytical Performance. Under the optimized conditions, three DBD-digestion methods can be applied for the suitable digestion of real matrix sample. Since reagent impurities could contribute to process blanks, the intensities of digestion blanks of the three DBD-digestion systems were measured by ICPMS. As shown in Figure S5, intensities of digestion blanks of the H_2O -DBD-digestion method were the lowest than those of the other two digestion methods. Compared with intensities of

blanks of microwave digestion, the intensities of the three DBD-digestion methods were all lower, making the sensitive and accurate determination of elements by the three DBD-digestion methods possible. The analytical performance of the three DBD-digestion methods was all evaluated under the optimum conditions. Linear coefficients (R^2) of external calibration curves were better than 0.99. The precisions [relative standard deviations (RSDs), $n = 9$] were both better than 7% for analysis of the 0.0240 g of rice power sample spiked with or without 25.00 ng g^{-1} Cr, 25.00 ng g^{-1} Cd, 30.00 ng g^{-1} As, and 30.00 ng g^{-1} Co, respectively. Table 1 shows

Table 1. LODs of These Digestion Methods Detected by ICPMS^a

method	Mg	Mn	Zn	Cr	Co	As	Cd
H_2O	0.01	0.005	0.01	0.005	0.004	0.006	0.002
H_2O_2	0.12	0.03	0.35	0.03	0.01	0.02	0.03
HNO_3	0.16	0.02	0.13	0.02	0.01	0.01	0.01

^a ng g^{-1} .

limits of detection (LODs) of seven elements in samples obtained by three DBD-digestion systems and detected by ICPMS. The obtained low LODs of the three DBD-digestion systems are evident, making them suitable for the determination of these analytes in rice samples. It is worth noting that, although the digestion time obtained by the H_2O -DBD-digestion system is longer than those achieved by H_2O_2 -DBD-digestion and HNO_3 -DBD-digestion systems, it provides the lowest LODs due to its low blanks and most stable baselines. A comparison of the performance of the proposed method with other digestion methods is summarized in Table S3. The aim of digestion without any chemicals except H_2O was achieved by extending the DBD- H_2O -digestion method to 6 h.

Sample Analysis. The accuracy of the three proposed methods was evaluated by analyzing a certified reference material (GBW10043) of rice. For the H_2O -DBD-digestion method and the H_2O_2 -DBD-digestion method, Mg, Mn, and Zn in the CRM could be detected, while for the HNO_3 -DBD-digestion method, only data of Mg and Zn could be obtained. Table 2 shows that the determined values of GBW10043 are in good agreement with the certified values, confirming the accuracy of the three proposed methods. The utility of the proposed digestion techniques was further demonstrated by the determination of Cr, Cd, Co, and As in two real rice samples from a supermarket. It was necessary to spike these samples with 25.00 ng g^{-1} Cr, 25.00 ng g^{-1} Cd, 30.00 ng g^{-1} Co, and

Table 2. Analytical Results of a Certified Reference Material (GBW10043)

method	element	found ^a ($\mu\text{g g}^{-1}$)	certified ($\mu\text{g g}^{-1}$)	recovery (%)
H_2O	Mg	387 ± 27	420 ± 20	92.0 ± 6.2
	Mn	11.6 ± 0.7	10.6 ± 0.6	110.0 ± 6.3
	Zn	14.7 ± 0.7	13.0 ± 0.6	113.0 ± 5.5
H_2O_2	Mg	462 ± 19	420 ± 20	110.0 ± 4.4
	Mn	8.8 ± 0.3	10.6 ± 0.6	83.0 ± 2.5
	Zn	14.1 ± 0.7	13.0 ± 0.6	109.0 ± 5.6
HNO_3	Mg	475 ± 25	420 ± 20	113.0 ± 6.0
	Mn	9.8 ± 0.5	10.6 ± 0.6	92.0 ± 4.5
	Zn		13.0 ± 0.6	

^aMean and standard deviation ($n = 3$).

30.00 ng g⁻¹ As because their endogenous concentrations were below the detection limits of ICPMS. As shown in Table 3, good recoveries (83–115%) were obtained.

Table 3. Analytical Results of Spiked Elements

method	sample	element	added (ng g ⁻¹)	found (ng g ⁻¹)	recovery (%)
H ₂ O	S-1	Cr	25.00	20.82 ± 0.60	83.0 ± 2.4
		Cd	25.00	24.47 ± 0.54	98.0 ± 2.2
		Co	30.00	29.27 ± 0.50	98.0 ± 1.7
		As	30.00	29.46 ± 0.97	98.0 ± 3.2
	S-2	Cr	25.00	20.80 ± 0.51	83.0 ± 2.0
		Cd	25.00	26.43 ± 0.36	106.0 ± 1.4
		Co	30.00	26.79 ± 0.32	89.0 ± 1.1
		As	30.00	29.21 ± 0.92	97.0 ± 3.1
	S-1	Cr	25.00	24.10 ± 0.69	96.0 ± 2.8
		Cd	25.00	28.61 ± 0.60	114.0 ± 2.3
		Co	30.00	30.60 ± 0.54	102.0 ± 1.8
		As	30.00	31.16 ± 1.16	104.0 ± 3.8
H ₂ O ₂	S-2	Cr	25.00	24.11 ± 0.41	96.0 ± 1.6
		Cd	25.00	28.81 ± 0.73	115.0 ± 2.9
		Co	30.00	30.04 ± 0.33	100.0 ± 1.1
		As	30.00	31.07 ± 1.21	104.0 ± 4.0
	S-1	Cr	25.00	23.46 ± 0.42	94.0 ± 1.7
		Cd	25.00	23.80 ± 0.40	95.0 ± 1.6
		Co	30.00	25.94 ± 0.34	86.0 ± 1.1
		As	30.00	25.61 ± 1.05	85.0 ± 3.5
	S-2	Cr	25.00	26.51 ± 0.82	106.0 ± 3.2
		Cd	25.00	24.64 ± 0.67	99.0 ± 2.7
		Co	30.00	25.91 ± 0.29	86.0 ± 1.0
		As	30.00	26.30 ± 1.05	88.0 ± 3.5

CONCLUSION

It is demonstrated, for the first time, that microplasma generated by DBD discharge at atmospheric pressure can be used for suitable digestion of rice samples. All operation parameters of discharge and conditions of digestion were optimized. As a result, three different DBD-digestion methods including the H₂O-DBD-digestion method, the H₂O₂-DBD-digestion method, and the HNO₃-DBD-digestion method were established. Any DBD-digestion method of the three could obtain efficient digestion under their optimized conditions. The H₂O-DBD-digestion method has the advantage of not using any chemicals, which realizes one-step, environmental friendly, and interferences free sample digestion. Compared to conventional sample digestion methods, the proposed method retains advantages for sample analysis by requiring extremely low reagent blank and may accomplish sample digestion for field analysis because of low power and no chemical consumption.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b04376.

Power, voltage, and frequency of AC voltage; diagram of digestion and analytical procedure; instrumental parameters of ICPMS and in EPR experiments; effects of operation conditions on the sample digestion; effects of COD detection; ion chromatograms for solutions of the HNO₃-DBD-digestion method; comparison of intensities

of elements of digestion blanks of the methods; comparison of performance with other similar digestion methods (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Nature Science Foundation of China (Nos. 21529501, 21622508, and 21575092) for financial support.

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