Fabrication of Poly(acrylic acid)/Boron Nitride Composite Hydrogels with Excellent Mechanical Properties and Rapid Self-Healing Through Hierarchically Physical Interactions

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Abstract

Many living tissues possess excellent mechanical properties and self-healing ability. To mimic these living tissues, a series of novel composite hydrogels, poly(acrylic acid)/surface-modified boron nitride nanosheets (PAA/BNNS-NH2) were fabricated simply through hierarchically physical interactions: molecular-scale metal coordination interaction between –COOH of PAA and Fe3+ and nanoscale H-bond between –COOH of PAA and –NH2 of BNNS-NH2. The composite hydrogels exhibit both excellent mechanical properties (including enhanced fracture stress, elongation, toughness, Young’s modulus, and dissipated energy) and rapid healing ability without any external stimulus. Especially, the B0.5P70 (the hydrogel with BNNS concentration of 0.5 mg mL−1, the water content of 70 wt%) exhibits a fracture stress of ~ 1311 kPa and toughness of ~ 4.7 MJ m−3, almost ~ 3 times and ~ 8 times to B0P70, respectively. The excellent properties, combined with the simple preparation method, endow these composite hydrogels with potential applications.

Keywords: Self-healing hydrogel, Boron nitride nanosheets, Hierarchically physical interactions

Background

Hydrogels with three-dimensional networks formed by covalent bonds and/or physical interactions crosslinking containing a large amount of water possess high hydrophilicity, water-holding capacity and unexceptional biocompatibility [1–4], enabling to be one of the most popular biomaterials. However, most hydrogels have poor mechanical property, which largely limited the applications. It is well known that many living tissues, such as muscle, ligament, and skin, possess excellent mechanical property and significant ability to heal wounds autonomously [5–7]. Inspired by these living tissues, materials with high mechanical properties and self-healing ability have been explored for various applications [8, 9], including tissue engineering, drug release, wound dressing, contact lenses, sensors, and actuators [2, 10–12]. Ihsan et al. reported a polyampholyte hydrogel self-healed through re-forming the ionic bonds at fracture surface [7]. Zhang et al. designed a PVA self-healable hydrogel with fast self-healing process through hydrogen bonds [13]. Tao et al. prepared a cold resistance self-healing hydrogel crosslinked by dynamic catechol-borate ester bonding which enable to self-heal at both room temperature and low temperature [14]. However, all these self-healable materials have a common weakness: poor mechanical property [15–19] largely limited the applications.

In order to improve the mechanical property of the hydrogels, some inorganic nanomaterials have been introduced to the crosslinked systems. Han et al. reported
a supermolecular hydrogel by using graphene oxide nanosheets to reduce the temperature for self-healing [15]. Si et al. exploited a new ultrahigh-water-content, super-elastic, and shape-memory nanofiber-assembled hydrogels [20]. The flexible SiO2 nanofibers were introduced to enhance mechanical property and to accelerate shape memory and pressure response. Especially, Duan et al. developed poly(vinyl alcohol)/boron nitride nanosheet (PVA/BNNS) composite hydrogels with enhanced mechanical properties [21]. Gao et al. fabricated a nano-composite hydrogel filled with exfoliated montmorillonite which dramatically improved the fracture elongation [22]. Zhong et al. designed graphene oxide (GO)/poly(acrylic acid) (PAA/GO) nanocomposite hydrogels which significantly enhanced the mechanical properties [23]. Novel composite self-healing hydrogels with enhanced mechanical property are still highly pursued although exploited hydrogels have advanced significantly in recent years. Boron nitride nanosheets, “white graphene”, exhibit many excellent properties including superb mechanical properties, extraordinary chemical inertness, and remarkable non-toxicity [24–26]. Notably, surface-modified BN nanosheets served as nanofillers in the nanocomposite hydrogels enhance mechanical and thermal properties and have been reported in recent works [27, 28]. Therefore, the development of a novel composite hydrogel with surface-modified BN nanosheets is still highly pursued.

Here, the novel composite hydrogels are fabricated from poly(acrylic acid) (PAA) and amino groups surface-modified boron nitride nanosheet (BNNS-NH2) through hierarchically physical interactions: molecular-scale metal coordination interaction between –COOH of PAA and ferric ion (Fe3+) and nanoscale H-bond between –COOH and BNNS-NH2 were reported. The introduction of BNNS-NH2 enhanced the mechanical property and accelerated self-healing process of the hydrogels. This work provides a new route to prepare hydrogels with excellent mechanical properties and rapid self-healing ability.

**Method/Experimental Materials**

Potassium persulfate (KPS; 99.0%) and FeCl3·6H2O (99.0%) were purchased from J&K Chemical Technology, and acrylic acid (AA; 98.0%) was purchased from Sigma-Aldrich. All these chemicals were used as received without any purification. Rhodamine B (95.0%) was purchased from Sigma-Aldrich. BNNS-NH2 was obtained by our previous work [24]. Deionized water was used throughout the experiments.

**Preparation of BNNS-NH2 Dispersion**

BNNS-NH2 was prepared according to our previous work [24]. In order to make BNNS-NH2 steadily dispersed in the polymer network, it is indispensable to prepare the BNNS-NH2 water dispersions. To obtain the stable BNNS-NH2 dispersions, magnetic stirring and ultrasound bath were utilized at room temperature. The BNNS-NH2 dispersions with concentration of 1.0, 0.8, 0.5, and 0.1 mg mL−1 were obtained by the following procedure. The 100 mg, 80 mg, 50 mg, and 10 mg of BNNS-NH2 were added in 100 mL of deionized water, respectively, under magnetic stirring (1000 rpm) for 24 h at room temperature in air ambient to obtain mixtures, and then the mixtures were sonicated (20 kHz) at room temperature for 2 h in air ambient to get stable dispersions. For prohibiting loss of the water solution, the obtained dispersions were preserved in sealed vessels with different marks for following preparation of self-healing hydrogels.

**Preparation of Self-Healing Hydrogel**

PAA as the common polymer with abundant –COOH groups enables to establish the amount of intrachain and interchain hydrogen bonds which endow the polymer to possess superior elasticity and favorable strength [29]. In addition, metal coordination interactions are set up between –COOH of PAA and ferric ion (Fe3+). The two kinds of reversible non-covalent bonds equipped the hydrogel with self-healing property. The hydrogels cross-linked by non-covalent bonds always possess inferior mechanical properties. In order to enhance the strength of the hydrogel, BNNS-NH2 was introduced to the polymer three-dimensional network, which established hydrogen bonds between –NH2 of BNNS-NH2 and –COOH of PAA. Here, the composite PAA/BNNS-NH2 hydrogels were abbreviated as B_xP_y, in which B represents BNNS-NH2, x is the content of the BNNS-NH2 (mg mL−1), P means PAA/BNNS-NH2 composite hydrogel, and y refers to the water content of the PAA/BNNS-NH2 composite hydrogel (mass fraction, wt%). The hydrogels were prepared according to a procedure described below. Typically, 10 mL of AA, 0.25 g of FeCl3·6H2O (1.05 mol% of AA), and 0.1 g of KPS (0.25 mol% of AA) were dissolved in BNNS-NH2 dispersions with different concentrations or deionized water under magnetic stirring (1000 rpm) at room temperature for 10 min under air ambient to form a homogeneous mixture. After that, N2 was bubbled into the mixture to remove oxygen (10 min), and then polymerization was carried out at 25°C in water bath for 6 h to form hydrogels. Hydrogels prepared as aforementioned procedure and parameters from BNNS-NH2 dispersions with the concentration of 1.0, 0.8, 0.5, and 0.1 mg mL−1 were denoted as B1P00, B0.8P00, B0.5P00, and B0.1P00, respectively, while hydrogels prepared from deionized water was named as B0P00.

It is well known that the hydrogels with different water contents possess entirely different mechanical properties.
In order to characterize the influence of water content to the mechanical properties of the hydrogels, the hydrogels with different water contents were prepared as follows. Firstly, the B₈P₉₀ hydrogels were prepared as the aforementioned procedure and parameters. Then, the as-prepared B₈P₉₀ hydrogels were exposed in air at room temperature for different times depending on the final water content of the hydrogels. Thereinto, the obtained drying hydrogels with different water contents were labeled as B₈P₇₀, B₈P₅₀, and B₈P₂₅, respectively. The water content was calculated by the formula: water content = \( W_w/W_t \) where the \( W_w \) is the weight of the water and \( W_t \) is the whole weight of the hydrogel. On the other hand, the crosslinking densities of B₈P₉₀ hydrogels were calculated from the results of rheological measurements, and it is well known that the higher crosslinking density leads to the more robust mechanical property. To verify the theory, it is indispensable to carry out the tensile tests. However, the B₈P₉₀ hydrogels were so soft that the electrical universal material testing machine cannot recognize the sample exhibiting no load, so the composite hydrogels with lower water content were highly required to fabricate. The hydrogels with different water contents were cut into different shapes or sizes for the following various tests.

**Mechanical Test**

In order to characterize the mechanical properties of the hydrogels, the as-prepared hydrogels were cut into a flaky shape (50 mm × 2 mm × 2 mm) and tested by the electrical universal material testing machine with a 200 N load cell (Instron 2360). Firstly, the as-prepared hydrogels were exposed in air at room temperature for different times depending on the final water content of the hydrogels. Then, the obtained hydrogels with different water contents were labeled as B₈P₇₀, B₈P₅₀, and B₈P₂₅, respectively. The water content was calculated by the formula: water content = \( W_w/W_t \), where \( W_w \) is the weight of the water and \( W_t \) is the whole weight of the hydrogel. On the other hand, the crosslinking densities of B₈P₉₀ hydrogels were calculated from the results of rheological measurements, and it is well known that the higher crosslinking density leads to the more robust mechanical property. To verify the theory, it is indispensable to carry out the tensile tests. However, the B₈P₉₀ hydrogels were so soft that the electrical universal material testing machine cannot recognize the sample exhibiting no load, so the composite hydrogels with lower water content were highly required to fabricate. The hydrogels with different water contents were cut into different shapes or sizes for the following various tests.

**Characterization**

The Fourier-transform infrared (FTIR) spectra was carried out to record the samples’ FTIR characters, which were recorded on a Thermo Scientific Nicolet 6700 spectrometer in attenuated total reflection (ATR) mode, with a resolution of 4 cm⁻¹ within the range 400–4000 cm⁻¹. The morphology of the hydrogels after the frozen drying process was observed on scanning electronic micrographs (SEM, Carl Zeiss AG, ZEISS EV0 MA15). In order to analyze the viscoelasticity of the hydrogels and calculate the crosslinking density, the rheological measurements were carried out by using a rheometer (HAAKE MARS III Thermo Fisher Scientific Limited, China) to measure the storage moduli (\( G' \)) and loss moduli (\( G'' \)). The tensile tests were carried out to analyze the mechanical properties of the samples, which were conducted using an electrical universal material testing machine with a 200 N load cell (Instron 2360).

**Results and Discussion**

The PAA/BNNS-NH₂ composite hydrogels were simply formed by in situ polymerization of AA, with the presence of Fe³⁺ and the BNNS-NH₂. The as-formed PAA macromolecular chains were crosslinked by hierarchically physical interactions: metal coordination interaction between carboxyls (–COOH) of the PAA and Fe³⁺ in molecular scale, and hydrogen bond interaction between –COOH of the PAA and –NH₂ of BNNS-NH₂ in nanoscale, resulting in the formation of three-dimensional networks (Scheme 1).

The two different types of physical interactions within the PAA/BNNS-NH₂ composite hydrogels were revealed by FTIR spectroscopy firstly. From the results in Fig. 1, PAA shows a characteristic stretching (–C=O stretching) at 1690 cm⁻¹, which has shifted to 1620 cm⁻¹ in the PAA/BNNS-NH₂ composite hydrogel. This shift indicates the existence of hydrogen bond interactions between –COOH of PAA and –NH₂ of BNNS-NH₂ [30, 31]. The presence of hydrogen bond can be verified by the fact that the characteristic peaks at 3400 cm⁻¹ for –COOH became less obvious in the composite hydrogel [32, 33]. The peak at 3230 cm⁻¹ can be assigned to N–H stretching vibration in the composite hydrogel. Metal coordination interaction was revealed by the peak at 620 cm⁻¹ in both PAA hydrogel and composite hydrogel, demonstrating that metal coordination interaction between Fe³⁺ and –COO⁻ was formed in the network system [34]. The in-plane B–N stretching at 1388 cm⁻¹ and the out-of-plane B-N-B bending vibrations at 1780 cm⁻¹ can be seen from composite hydrogel (Fig. 1a), confirming the presence of BNNS-NH₂.

After drying, the morphologies of these hydrogels were observed by SEM. Porous structures have been observed in PAA hydrogel (Fig. 2a, b) and B₈P₇₀ composite hydrogel (Fig. 2c). The larger pores have an average diameter of around dozens of micrometers and the smaller pores have an average diameter in nanoscale. The presence of pores might provide high stretchability and squeezability to the hydrogels [35]. Compared to PAA hydrogels, the
Scheme 1: Scheme illustrating the formation of a PAA/BNNS-NH$_2$ composite hydrogel with self-healing ability.

**Fig. 1** FTIR spectra of a, b composite hydrogel and b, a PAA hydrogel.

**Fig. 2** SEM images of a, b PAA hydrogel and c, d composite hydrogel. The BNNS-NH$_2$ was pointed out by arrows in (d), and the inserted image in (d) is the zoomed-in image of the BNNS-NH$_2$. 
pores within the composite hydrogel are more isolated and uniform in sizes (Fig. 2c). And the BNNSs-NH2 can be observed in a SEM image (Fig. 2d) of hydrogel containing BNNSs-NH2 and were pointed out by arrows, and the insert image further verified the presence of the BNNS-NH2 [34]. To understand the effects of the two-type interactions, tensile tests of composite hydrogels with different BNNS-NH2 concentrations were conducted, and results from these hydrogels with different water contents are shown in Fig. 3a–c. Without BNNS-NH2, the fracture stress of B0P70 hydrogel was about 406 kPa, and the facture stress of B0.1P70 increased to 526 kPa by introducing a small amount of BNNS-NH2. The B0.5P70 exhibits a fracture stress of 1311 kPa, almost three times to B0P70 and two times to B0.1P70, as shown in Fig. 3a. The result far exceeded previous composite hydrogels in published work [34]. This means that the hydrogen bond formed between –COOH of PAA and –NH2 of BNNS-NH2 significantly enhanced the mechanical properties [36]. However, the fracture stress decreased when the BNNS-NH2 concentration continued to increase. The fracture stress becomes even lower than that of B0P70, which indicated that a prime balance of metal coordination interactions and hydrogen bonds was achieved at the BNNS-NH2 concentration of 0.5 mg mL\(^{-1}\). Correspondingly, the greatest fracture stresses were also realized at the same BNNS-NH2 concentration (0.5 mg mL\(^{-1}\)) within composite hydrogels with the water content of 50 wt% and 25 wt% (Fig. 3b, c) which was an important factor to affect the mechanical properties of the hydrogel [37, 38]. The fracture stresses of the composite hydrogels were remarkably improved (Additional file 1: Figure S1-S5) when water content decreased to 50 wt% and to 25 wt%, attributed to the narrow space between chains at low water content [35]. Notably, the B\(_x\)P\(_y\) hydrogels were able to withstand tensile, knotting, bending, and torsion even under high degree of deformations (Fig. 3d–g, Additional file 1: Figure S6). The addition of BNNS-NH2 might slightly change the pH of the solution due to the presence of −NH2 groups, leading to a change in association constant between −COOH and Fe\(^{3+}\). The balance between metal coordination interactions and hydrogen bonds was dependent on the BNNS-NH2 concentration with the

![Figure 3](image-url)

**Fig. 3** Tensile stress-strain curves of the composite hydrogels: **a** B\(_x\)P\(_{70}\), **b** B\(_x\)P\(_{30}\), and **c** B\(_x\)P\(_{25}\). The digital photograph of composite hydrogels: **d** original, **e** stretched, **f** bent, and **g** stretched after being knotted.
constant content of Fe$^{3+}$. The excellent mechanical behaviors of the composite hydrogel stemmed from the optimum balance between the metal coordination interaction in molecular scale and the hydrogen bond interactions in nanoscale [36].

The effects of BNNS-NH$_2$ concentration on mechanical properties of B$_x$P$_{90}$ were studied by rheological measurement (Fig. 4a). For all the samples, their storage moduli ($G'$) are always higher than the corresponding loss moduli ($G''$) in the frequency range from 0.1 to 100 rad s$^{-1}$, indicating the formation of three-dimensional networks [34, 36]. With the increase of frequency, both $G'$ and $G''$ increased, but the increase in $G''$ is more sharp, showing their shear-thin behaviors [34]. B$_{0.5}$P$_{90}$ exhibited the highest $G'$, which is consistent with the results from the tensile tests. From the equilibrium shear modulus ($G_e$), crosslinking density ($N$) of these hydrogels can be calculated by using formula 1 [39–41].

$$N = G_e/(RT)$$

Here, $G_e$, $R$, and $T$ are the terrace value of $G'$, gas constant, and absolute temperature, respectively. The crosslinking density is shown in Fig. 4b. With increase in the concentration of BNNS-NH$_2$, the crosslinking density increased, which demonstrates that BNNS-NH$_2$ also served as a crosslinker in the composite hydrogels through hydrogen bond interactions between –COOH of PAA and –NH$_2$ of BNNS-NH$_2$. However, the crosslinking density decreased when the BNNS-NH$_2$ concentration is over 0.5 mg mL$^{-1}$ which corresponded with the results of the mechanical properties [40]. It is illustrated that the excess BNNS-NH$_2$ leads to reunion of the nanosheets which impairs the enhancement to the composite hydrogels such as B$_{0.8}$P$_{70}$ and B$_{1.0}$P$_{70}$ [41, 42].

To obtain hydrogels with excellent mechanical properties, the optimal balance of hydrogen bond interactions and metal coordination interactions can be achieved by adjusting the BNNS-NH$_2$ concentrations while the content of Fe$^{3+}$ is constant. Toughness and Young’s modulus representing stiffness are shown in Fig. 5a and Fig. 5b, respectively [24, 36, 37]. From Fig. 5a, hydrogels became stiff with decreasing water content or increasing BNNS-NH$_2$ concentration till 0.5 mg mL$^{-1}$ consistent with the results of tensile test (Additional file 1: Figure S7).

The toughness is observed in Fig. 5b. It is clear that toughness increases with decreasing water content, similar to the trend of Young’s modulus. Without BNNS-NH$_2$, the toughness of B$_{0.7}$P$_{70}$ was about ~0.5 MJ m$^{-3}$, and with BNNS-NH$_2$, the toughness of B$_{0.5}$P$_{70}$ increased to ~4.7 MJ m$^{-3}$, almost eight times to that of B$_{0}$P$_{70}$. The B$_{0.3}$P$_{25}$ exhibited the highest Young’s modulus of ~17.9 MPa, highest tensile strength of ~8491 kPa, and highest toughness of ~10.5 MJ m$^{-3}$, which is far higher than that of B$_{0}$P$_{25}$.

The stiffness of most polymer hydrogels decreases with increase in the corresponding toughness. According to the Lake-Thomas model [42, 43], toughness increases but stiffness decreases with decreasing crosslinking density. In this work, a novel type hydrogel with both high stiffness and high toughness (B$_{0.5}$P$_{70}$) (Fig. 5) has been fabricated, which is different from the conventional hydrogels (high stiffness/low toughness or low stiffness/high toughness). The exceptional properties can be ascribed to the existence of hierarchical interactions: metal coordination interactions in molecular scale and hydrogen bonds in nanoscale.

Cyclic tensile tests of B$_{x}$P$_{70}$ and B$_{x}$P$_{50}$ were conducted at the strain of 200% (Fig. 6a, b). Obvious hysteresis loops were observed for B$_{x}$P$_{70}$ and B$_{x}$P$_{50}$, and B$_{x}$P$_{50}$ showed much larger hysteresis loops, indicating the water content determining energy dissipation owing to more hydrogen bonds being established between polymer chains because of the shrunken networks [37]. The dissipated energy increased with increasing BNNS-NH$_2$ concentration.
Fig. 5  
(a) Young’s modulus and (b) toughness of composite hydrogels with different water contents and BNNS-NH$_2$ concentrations.

Fig. 6  
Cyclic tensile of loading-unloading curves of (a) $B_xP_{70}$ and (b) $B_xP_{50}$; the dissipated energy of (c) $B_xP_{70}$ and (d) $B_xP_{50}$. 

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concentration, and the maximum value was obtained at the concentration of 0.5 mg mL\(^{-1}\) due to the establishment of numerous hydrogen bonds between BNNS-NH\(_2\) and PAA chains [34]. However, the dissipated energy decreased when BNNS-NH\(_2\) concentration increased to 0.8 and to 1.0 mg mL\(^{-1}\), owing to the high concentration of BNNS-NH\(_2\) leading to aggregation of the nanosheets [41, 42]. This explanation is also suitable for specific stress-strain curves and rheology results of the B\(_x\)P\(_y\) hydrogels.

The rapid self-healing process can be realized without any external stimulus based on the abundant physical interactions: metal coordination interactions and hydrogen bonds. As shown in Fig. 7a–c, the original hydrogel was cut to three parts (two parts were dye to red by Rhodamine B to distinguish the scars of the damaged hydrogel) and then they were contacted at the damaged surfaces. Without any external stimulus, the cut hydrogel contacted for 10 min at room temperature, the healed hydrogel can be stretched to certain strain. Self-healing efficiency can be calculated from the ratio of fracture stress of the healed hydrogels and the original hydrogels. Original B\(_0\)P\(_{70}\) exhibited fracture stress of \(~410\) kPa, and the corresponding healed hydrogel exhibited a fracture stress of only \(~37\) kPa, indicating that the self-healing efficiency was only 9%. In comparison, the fracture stress of original and healed B\(_1\)P\(_{70}\) were about \(~203\) kPa and \(~166\) kPa, respectively, and the self-healing efficiency is about 81%, which is significantly higher than the hydrogels without the BNNS-NH\(_2\). Similarly, as shown in Fig. 7e, the self-healing efficiency of B\(_0\)P\(_{50}\) hydrogel was 31.8%, while the B\(_1\)P\(_{50}\) hydrogel was 94.6%. This result indicates that the presence of nanoscale hydrogen bonds between BNNS-NH\(_2\) and PAA polymer chains in nanoscale enhanced the self-healing ability ascribing that the content of reversible bonds is the key influencing factor of the self-healing efficiency, and it is well known that the self-healing efficiency is proportional to the content of the reversible bonds [16, 21, 36, 42]. However, while the water content was reduced to 25 wt% (Additional file 1: Figure S8), the self-healing efficiency declined sharply, because the movement of Fe\(^{3+}\) was...
impeded at such a low water content. This assumption was confirmed by the fact that healing efficiency of B$_x$P$_{90}$ was much better than other water content, with only 10 min required attributed to the reason that higher water contents make the Fe$^{3+}$ to migrate easily and re-establish hydrogen bonds readily [36].

Conclusions

In summary, the novel composite hydrogels have been fabricated through hierarchically physical interactions: the metal coordination interaction in molecular scale and hydrogen bond in nanoscale. The hydrogels exhibit enhanced stiffness (about 17.9 MPa), toughness (about 10.5 MJ m$^{-3}$), extension, and self-healing ability. The reversibility of metal coordination interaction and hydrogen bond interaction is responsible for the enhanced mechanical properties and self-healing efficiency. Combined with facile preparation, enhanced mechanical properties and self-healing ability make these composite hydrogels suitable for many potential applications.

Additional file

Additional file 1: Figure S1. Tensile stress-strain curves of B$_x$P$_y$ hydrogels with different water contents. Figure S2. Tensile stress-strain curves of B$_x$P$_y$ hydrogels with different water contents. Figure S3. Tensile stress-strain curves of B$_x$P$_y$ hydrogels with different water contents. Figure S4. Tensile stress-strain curves of B$_x$P$_y$ hydrogels with different water contents. Figure S5. Tensile stress-strain curves of B$_x$P$_y$ hydrogels with different water contents. Figure S6. The digital photograph of torsion hydrogel. Figure S7. Young’s modulus of hydrogels of B$_x$P$_{50}$ and B$_x$P$_{70}$. Figure S8. The fracture stresses of B$_x$P$_y$ hydrogels and healed B$_x$P$_y$ hydrogels with different BNNS-NH$_2$ concentrations (the healing time was 1 h). (DOCK: 783 kb)

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Availability of Data and Materials

The datasets supporting the conclusions of this article are available in the [repository name] repository [unique persistent identifier and hyperlink to datasets in http:// format].

Authors’ Contributions

In this work, YW designed the experimental strategy. YW, SX, and MG performed the experiment. SX and MG did the tests. TZ, WL, and DL guide the theoretical analysis for the results of the tests. SX, YW, and TZ accomplished the whole manuscript. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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