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Fabrication of a High-Performance Fertilizer To Control the Loss of Water and Nutrient Using Micro/Nano Networks

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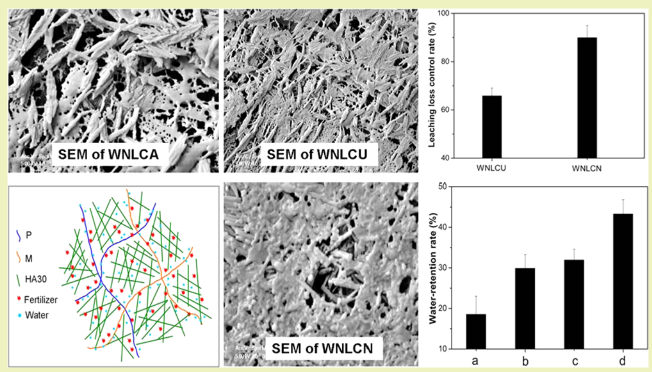
S *Supporting Information*

ABSTRACT: Nitrogen fertilizer tends to migrate into the environment through runoff, leaching and volatilization, causing severe environmental pollution. In this work, a high-performance water and nutrient loss control fertilizer (WNLCF) was developed by adding a high-energy electron beam (HEEB) dispersed attapulgite (HA)−sodium polyacrylate (P)−polyacrylamide (M) complex to traditional fertilizer. Therein, HA-P-M was used as the water and nutrient loss control agent (WNLCA), which could self-assemble to form three-dimensional (3D) micro/nano networks in aqueous phase. Thus, water and nutrient could be effectively combined and held in the networks which could be then retained in the soil via the filtering effect of soil, resulting in low loss of water and nutrient. Pot experiments of ^{15}N labeled fertilizer indicated that WNLCF could effectively improve the amounts of fertilizer nutrients in the stem of corn and facilitate the growth of corn. Therefore, this work provides a promising approach to enhance the utilization efficiency of water and nutrient, and lower the pollution risk of fertilizer.



KEYWORDS: *Attapulgite, Sodium polyacrylate, Polyacrylamide, Micro/nano networks, Loss control*

INTRODUCTION

Fertilizer and water are two fundamental factors for crops.[1] At present, nutrient deficiency and drought are still two main constraints for agriculture in many parts of the world.[2] Traditional fertilizer, owing to the low thermal stability, high solubility and small molecular weight, tends to migrate into the air and water through volatilization, runoff and leaching, causing severe environmental pollution such as acid rain, eutrophication and worsening global warming.[3−6] In addition, the severe loss of nutrient could also result in low fertilizer utilization efficiency (UE) (30−60%).[7−10] Therefore, controlling fertilizer loss, increasing the retention of nutrient in soil, improving UE and reducing the environmental pollution risk are the main developing directions of advanced fertilizers. Because of the high porosity of soil, water in soil, especially sandy soil, tends to be lost through evaporation and leaching.[11] In many arid and semiarid areas, repeated irrigation is needed to provide sufficient water for crops, contributing to water resource crisis and increase of production cost.[12] Consequently, it is important to develop water-saving agricultural technologies. In a word, loss of fertilizer and water is rather unfavorable for agricultural production. Hence, developing a high-performance water and nutrient loss control fertilizer (WNLCF) could be a promising approach to control the loss of water and fertilizer, enhance the UEs of water and nutrient, protect the environment and lower the production cost in drought areas.

During the past 20 years, various types of controlled/slow-release fertilizers have been developed using urine coatings, nitrification inhibitors, enzyme inhibitors, and urea formaldehyde, etc.[13−15] Although these products could effectively increase nutrient-use efficiency, the released unabsorbed nutrient tends to discharge to the environment. Moreover, most of them did not possess water retention capacity. Recently, several slow-release fertilizers that possessed water-retaining abilities were reported.[16−19] However, owing to the complex production procedure, high cost, and low loss control performance of the nutrient, these newly reported fertilizers were difficult to produce and apply widely. Thus, it is significant

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to develop an advanced fertilizer with simple production procedure, low cost, and high loss control performance of both water and nutrient.

Attapulgite ($(Mg,Al)_4(Si)_8(O,OH,H_2O)_{26}{\cdot}nH_2O$), a kind of hydrated magnesium aluminum silicate, is a natural nano clay formed by nano rods with average dimensions of approximately 800−1000 nm in length and 30−40 nm in width.[20−22] Attapulgite possesses a large specific surface area and high adsorption capacity and thus is suitable to be used as a carrier to control the release of fertilizer nutrient.[23] However, because of the nano scale effect and high surface activity, attapulgite rods naturally tend to aggregate with each other to form bunches, which is unfavorable for the application of attapulgite.[24,25] Hence, it is important to improve the dispersion of attapulgite, which is the dominant factor for its adsorption and carrier performance. Here, natural attapulgite (NA) was modified using high-energy electron beam (HEEB) irradiation to separate the rods from each other to form a porous structure with higher exposed surface areas so as to obtain a higher binding capacity for fertilizer.[23] In addition, to make fertilizer obtain a good performance of retaining water, sodium polyacrylate was selected to mix with the modified attapulgite because sodium polyacrylate possessed a high water retention ability,[26] and meanwhile polyacrylamide[27] was also added because polyacrylamide could strengthen the connection between rods of the modified attapulgite and thus further improve the capacity of binding fertilizer. Therefore, mixing sodium polyacrylate (P) and polyacrylamide (M) with attapulgite modified by HEEB could produce a complex with high binding abilities for both fertilizer and water.

In this paper, we report on the development of a novel water and nutrient loss control fertilizer (WNLCF) prepared by adding a HEEB dispersed attapulgite (HA)−sodium polyacrylate (P)−polyacrylamide (M) complex, as a water and nutrient loss control agent (WNLCA), to traditional fertilizer. To investigate the detailed microstructure and interactions inside WNLCF, and its loss control performance, urea and NH_4Cl were selected as the model fertilizers to make WNLCFs, called water and nutrient loss control urea (WNLCU) and water and nutrient loss control NH_4Cl (WNLCN). Additionally, the effect of WNLCF on corn was investigated through pot experiments using ^{15}N labeled fertilizer. Compared with traditional fertilizer (TF), this WNLCF displayed higher retaining capacity, lower loss amount, and higher UE for water and nutrient, and meanwhile possessed simple production procedure and low cost. Thus, this WNLCF could have a huge application prospect in ecological agriculture, especially in drought areas.

■ MATERIALS AND METHODS

Materials. The original attapulgite powder (100−200 mesh) with a purity of 99% was provided by Mingmei Co., Ltd. (Anhui, China). Other chemicals, analytical reagent grade, were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Deionized water was used throughout this work except in the pot experiments. Corn seeds were provided by DuPont Pioneer Co. (Liaoning, China).

HEEB Irradiation. Attapulgite samples in plastic bags (100 g each) were irradiated by a high-energy electron beam accelerator (10 MeV and 10 kW) with fluence of 10, 20, 30, and 40 kGy at room temperature (25 °C), and the resulting samples were designated as HA10, HA20, HA30, and HA40, respectively.

Preparation of WNLCF. A-P-M complexes were prepared by mixing the A, P, and M in different proportions of weight. The optimum A-P-M complex was achieved through water retention determination and selected as the WNLCA, which was added to urea (U) (or NH_4Cl (N)) to obtain WNLCU (or WNLCN).

Water Retention Performance. As for A-P-M complex, 2 g of A-P-M complex sample was mixed with 55 g of dry sand (150−200 mesh) in a Petri dish (diameter of 9 cm), and then 15 mL of deionized water was slowly added to the system that was thereafter covered by 10 g of dry sand. The initial weights of this system and the control experiment system (without A-P-M samples) were designated as W_0 and W_{C0}. These two systems were placed at 30 °C for 10 h, and the weights of the resulting systems were noted as W_{10} and W_{C10}, respectively. The water retention ratio (WRR) was calculated using the following equation:

$$\mathrm{WRR} = [(W_{C0} - W_{C10}) - (W_0 - W_{10})]/(W_{C0} - W_{C10}) \times 100\%$$

As for WNLCF, first of all, 20 g of dry sand was placed into a plastic cup, and 10 mL of deionized water was slowly sprayed onto the sand. Then 2 g of WNLCF was spread on the sand. Finally, 40 g of dry sand was placed evenly on the top. The initial weights of this system and the control experiment system (without A-P-M samples) were designated as W_0 and W_{C0}. These two systems were placed at 30 °C for 24 h and the weights of the resulting systems were noted as W_{24} and W_{C24}, respectively. The water retention ratio (WRR) was calculated using the following equation:

$$\mathrm{WRR} = [(W_{C0} - W_{C24}) - (W_0 - W_{24})]/(W_{C0} - W_{C24}) \times 100\%$$

Migrate-to-Surface (MS) Performance. First, 20 g of dry sand was placed into a plastic cup, and 10 mL of deionized water was slowly sprayed onto the sand. Then 2 g of WNLCF was spread on the sand. Subsequently, 40 g of dry sand was placed evenly on the top. Finally, the system was placed at 30 °C for 24 h. A layer of top sand (1 cm depth) of the resulting system was transferred into 50 mL of deionized water afterward, and the resulting suspension was stirred (100 rpm) for 30 min. After a centrifugation (12000 rpm), the concentration of urea (or NH_4Cl) in the supernatant was measured to get the MS amount of urea (or NH_4Cl). The MS loss control ratio (ULCR) of WNLCF was calculated through the equation: ULCR = (MS amount of TF − MS amount of WNLCF)/MS amount of TF × 100%.

Leaching Behavior Investigation. 30 g of dry sand (150−200 mesh) was put into a 50 mL centrifuge tube with a hole (diameter of 2 mm) at the bottom. Then 5 mL pf deionized water was added to keep the sand humid. Sample (1 g of WNLCU or WNLCN) was buried (cylinder shape, diameter of 2.0 and 1 cm under the top) in the sand (humidity of 30%) at 30 °C, and covered with another 10 g of dry sand. 50 mL of deionized water was sprayed over the top of the sand layer to collect the leachate, in which the concentration of urea (or NH_4Cl) was measured afterward. The leaching loss control ratio (LLCR) was calculated through the equation: LLCR = (leaching loss amount of TF − leaching loss amount of WNLCF)/leaching loss amount of TF × 100%.

Pot Experiments. WNLCU samples were prepared by mixing urea (or ^{15}N labeled urea at the abundance of 30%) and WNLCA with W_U:W_{WNLCA} of 0.09 g:0.00 g, 0.09 g:0.006 g, and 0.09 g:0.012 g, respectively. Then each WNLCU sample was mixed with 10 g of soil respectively, and the mixture was placed on the surface of 50 g of soil in a pot (cylinder shape, diameter of 4.5 cm and depth of 7 cm). After that, 200 g of soil was placed on the top of the system. Two corn seeds were planted in the resulting system (4 cm under the top soil layer), and the system was kept in a greenhouse at 20 °C. A total amount of 30 mL of water was sprayed on the top of the system every 4 days.

Characterization. The morphology was observed with scanning electron microscopy (SEM) (Sirion 200, FEI Co., U.S.A.). The elemental mapping was carried out with scanning transmission electron microscopy (STEM, JEM-ARM200F, JEOL Co., Japan). The structure and interaction were analyzed using X-ray diffraction (XRD, TTR-IIIRigaku Co., Japan) and Fourier transform infrared (FTIR) spectrometry (Bruker Co., Germany). The concentration of urea (or NH_4Cl) in aqueous solution was determined using UV−vis spectrophotometry (UV 2550, Shimadzu Co., Japan) at a wavelength of 422 nm (or 420 nm). The ^{15}N abundance and total nitrogen in the

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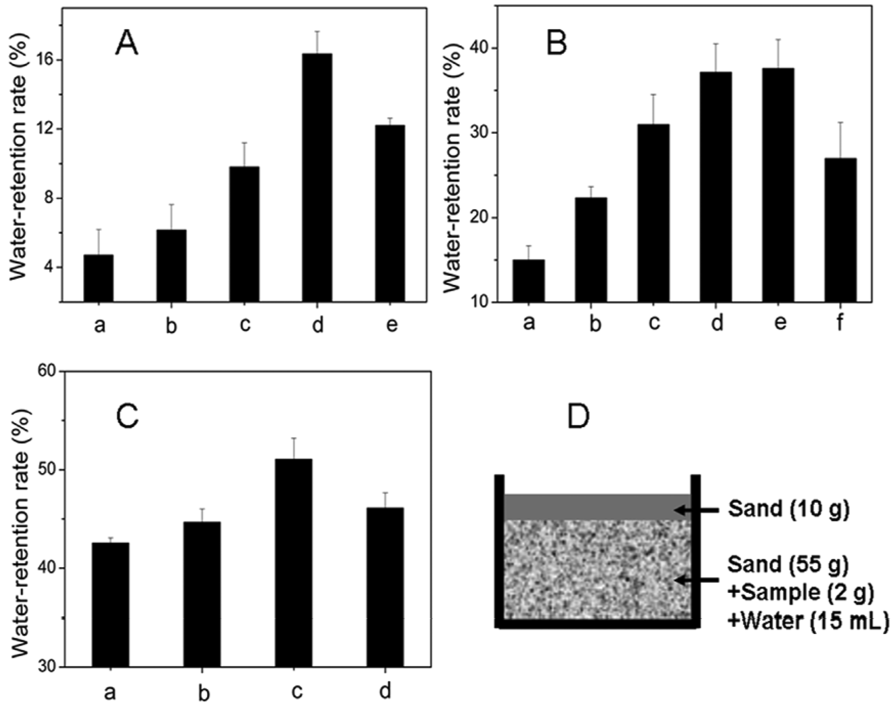

Figure 1. Water retention ratios of different samples with same weight of 2 g. (A) NA (a), HA10 (b), HA20 (c), HA30 (d), and HA40 (e); (B) HA30-P with W_{HA30}/W_P of 9:0 (a), 9:0.4 (b), 9:0.6 (c), 9:0.8 (d), 9:1 (e), and 9:1.2 (f), respectively; (C) HA30-P-M with W_{HA30}:W_P:W_M of 9:1:0 (a), 9:1:0.1 (b), 9:1:0.4 (c), and 9:1:0.8 (d), respectively; (D) schematic diagram of the experiment system.

root, stem, and leaf of corn were detected on an isotope mass spectrometer (Isoprime 100, Elementar Trading Co., Germany). The micronutrient element contents in the corn were detected using inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 7300 DV, PerkinElmer Co., U.S.A.).

RESULTS AND DISCUSSION

Microstructure Modification. Attapulgite has poor thermal and electrical conductance.[24,28] When NA rods are bombarded by HEEB with high energy and density, the thermal stress caused by the inhomogeneous distribution of heat along the NA axis can make the aggregated rods separate from each other. In addition, the poor electrical conductance of NA is favorable for plenty of electrons to accumulate on the rods surface during the irradiation process of HEEB, so that the charges on the surface of NA rods and then electrostatic repulsions among NA rods increase. Besides the thermal and charge effects, the physical impact effect resulting from HEEB with high momentum might be another factor for dispersing NA. After HEEB irradiation at fluences of 10 and 20 kGy, these three effects could contribute to transform the originally compact NA bunches to loose ones (Figure S1a-c of the Supporting Information). With the increase of fluence, plenty of the loose bunches of HA30 and HA40 were further transformed to single rods that cross-linked each other to form porous networks (Figure S1d,e of the Supporting Information, and the inset in Figure 5a). This result indicates that HEEB treatment played a key role in the dispersion of attapulgite (schematic diagram is shown in Figure S1f of the Supporting Information), and the dispersion degree increases with the fluence. The main mechanism can probably be attributed to the thermal, charge and impact effects of HEEB treatment.

Water Retention Behavior Investigation. Each rod of attapulgite possessed many nano channels along the direction of the rod's axis, and there were plenty of −OH and $-OH_2$ on the inner surface of the nano channels and the rod surface.[29] Therefore, attapulgite could adsorb much water on the rods' surface and these nano channels. However, the adsorption of water on attapulgite was also related to the specific surface area (SSA) of attapulgite. NA illustrated a relatively low adsorption capacity on water because of low dispersion and SSA. After HEEB treatment, the dispersion of attapulgite significantly increased, so HA possessed a higher water retention performance. Furthermore, with the increase of the HEEB fluence, the dispersion and the SSA of HA increased, so that HA30 and HA40 displayed higher WRR compared with HA10 and HA20 (Figure 1A) after a water retention behavior investigation (Figure 1D). However, because of the rather large mean diameter of the pores formed among the rods, HA40 possessed a relatively low SSA and WRR compared with HA30. That is to say HA30 had the highest water retention capacity and thus was selected as one of the components of WNLCA. Moreover, after addition of P with plenty of −COOH, HA30 displayed a much higher WRR, and HA30-P illustrated the highest WRR at W_{HA30}/W_P of 9:1 (Figure 1B). Moreover, in order to further improve the WRR of HA30-P, M was added to HA30-P to form HA30-P-M. It could be seen clearly from Figure 1C that HA30-P-M displayed a significantly increased WRR compared with HA30-P, and the optimal W_{HA30}:W_P:W_M was 9:1:0.4. The reason was probably that HA30-P-M could form three-dimensional (3D) micro/nano networks easily through the colloid destabilization and netting effect.[11] Hence more water could be adsorbed in the 3D networks of HA30-P-M wherein HA30 rods were acting as the skeleton in the molecular penetrating networks of P and M. Based on the preceding analysis, HEEB treatment could effectively improve the dispersion and the WRR of attapulgite, wherein HA30 possessed the highest WRR. Moreover, P and M could further increase the WRR of HA30, and the HA30-P-M with

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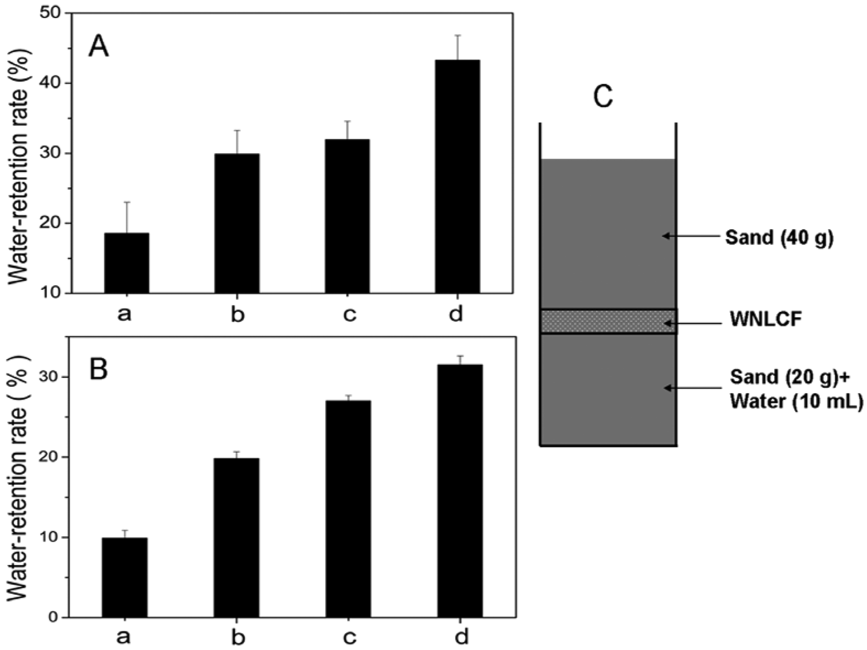

Figure 2. (A) Water retention ratios of 2 g of WNLCU (A) and 2 g of WNLCN (B) with W_F/W_{WNLCA} of 9:0.6 (a), 9:0.8 (b), 9:1 (c), and 9:1.2 (d); (C) schematic diagram of the experiment system.

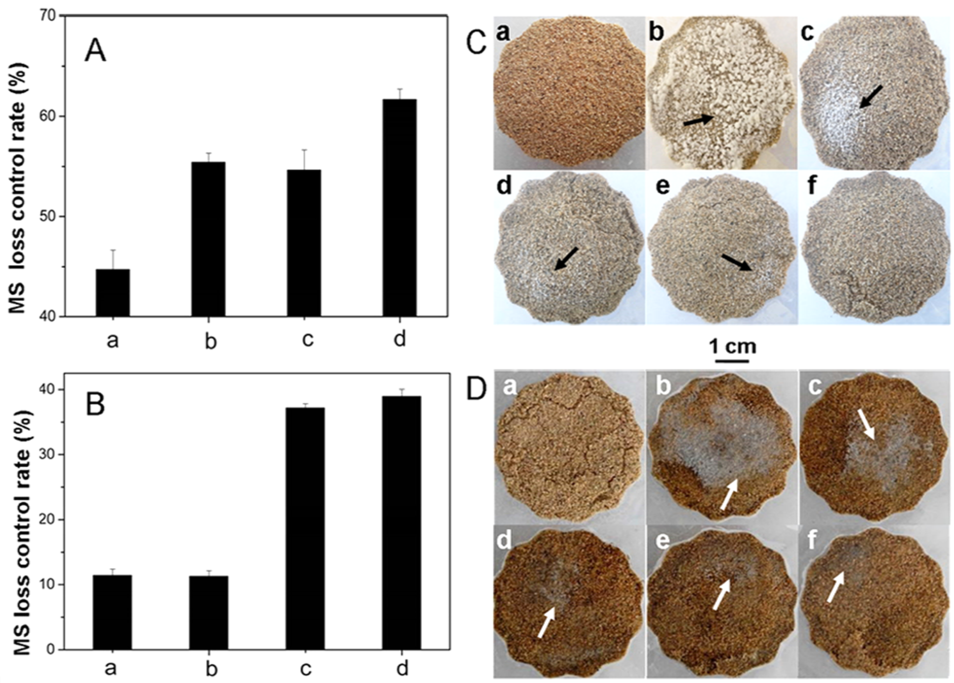

Figure 3. MS loss control ratios of 2 g of WNLCU (A) and 2 g of WNLCN (B) with W_F/W_{WNLCA} of 9:0.6 (a), 9:0.8 (b), 9:1 (c), and 9:1.2 (d); (C) digital photos of the experiment systems of sand (a), U (b), WNLCU samples (2 g) with W_U/W_{WNLCA} of 9:0.6 (c), 9:0.8 (d), 9:1 (e), and 9:1.2 (f) after MS process; (D) digital photos of sand (a), N (b), WNLCN samples (2 g) with W_N/W_{WNLCA} of 9:0.6 (c), 9:0.8 (d), 9:1 (e), and 9:1.2 (f) after MS process. The black and white arrows noted the U and N migrated to the surface of sand, respectively.

W_{HA30}:W_P:W_M of 9:1:0.4 displayed the highest water retaining performance (51.1%) and thus was selected as the WNLCA.

To further investigate the water retention performance of WNLCF, WNLCA was added to U and N with different weight ratios to obtain different WNLCU and WNLCN samples. As shown in Figure 2A,B, with the increase of WNLCA amount, the WRR of both WNLCU and WNLCN increased. Considering the cost of WNLCF, the highest mixing ratio of fertilizer and WNLCA was set as 9:1.2 (W_F/W_{WNLCA}), and at such a ratio, the WRRs of WNLCU and WNLCN reached the values of 43.30% and 31.53%. The results indicated that WNLCF displayed a significantly higher water retaining ability compared with TF.

Fertilizer Nutrient Loss Control Performance of WNLCF. Besides the water loss control performance, the fertilizer nutrients loss control capacity of WNLCF was also

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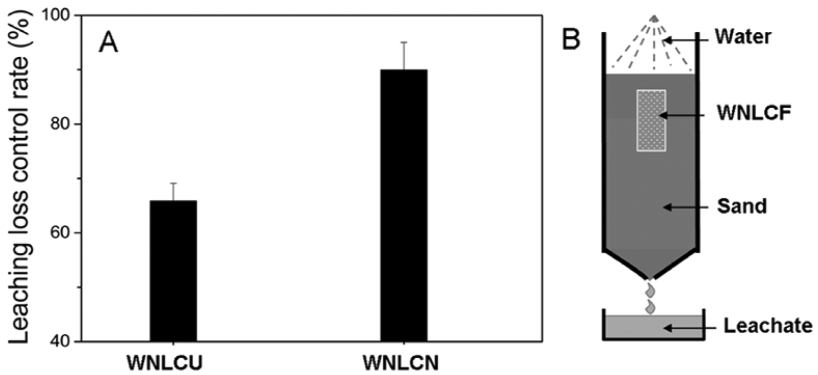

Figure 4. Leaching loss control ratios of WNLCU (1 g) and WNLCN (1 g) with W_F/W_{WNLCA} of 9:1.2 (A), and the schematic diagram of the leaching system (B).

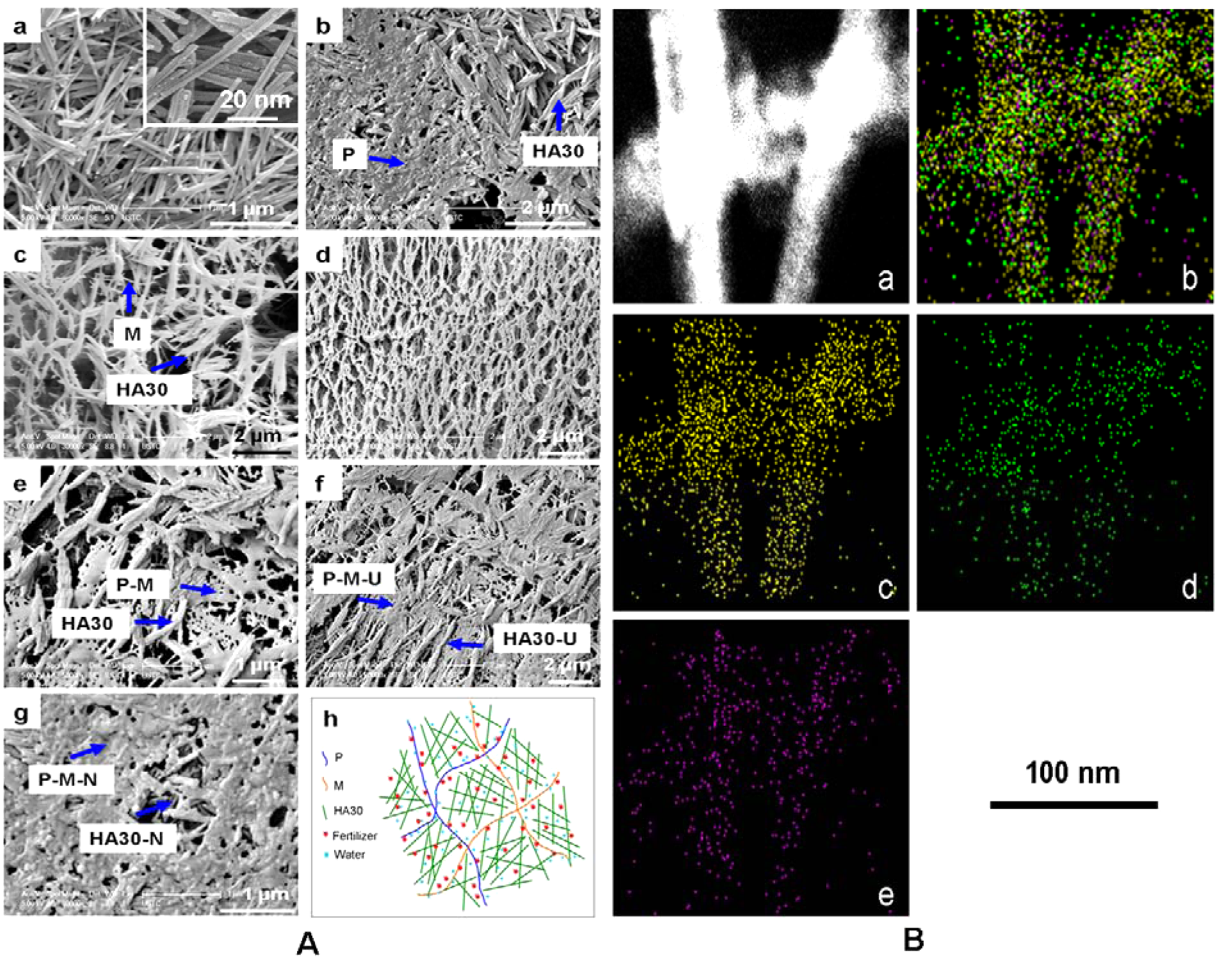

Figure 5. (A) SEM images of HA30 (a) (inset of panel a is the magnified image of HA30), HA30-P (W_{HA30}/W_P = 9:1) (b), HA30-M (W_{HA30}/W_M = 9:0.8) (c), P-M (W_P/W_M = 1:0.8) (d), WNLCA (e), WNLCU (W_U/W_{WNLCA} = 9:1.2) (f), and WNLCN (W_N/W_{WNLCA} = 9:1.2) (g), and the schematic diagram of the WNLCF structure (h). (B) TEM image of WNLCA (a), merged image (b) of the distribution maps of Si (c), Mg (d), and Al (e) in WNLCA.

investigated. In a drought area, fertilizer nutrients in soil tend to be lost through MS and leaching, causing reduction of UE. During the MS process, the dissolved U and N in soil could easily migrate to the soil surface with water and stay on the soil surface owing to the high evaporation effect in drought areas, and this part of nitrogen was hard to be absorbed by crops. Meanwhile, this phenomenon could contribute to the runoff and volatilization of nitrogen. Therefore, controlling the MS amount of nitrogen was significant to improve the UE of fertilizer. Herein, the MS performance of WNLCU and WNLCN was investigated, as shown in Figure 3A,B, and it was found that both WNLCU and WNLCN possessed obviously higher MS loss control abilities compared with U and N. Moreover, their MS loss control ratios increased greatly with the WNLCA amount and reached the value of 61.7% (WNLCU) and 38.95% (WNLCN) at W_F/W_{WNLCA} of 9:1.2. The results were in accordance with that of WRR (Figure 2A,B), indicating higher water retention ability caused lower

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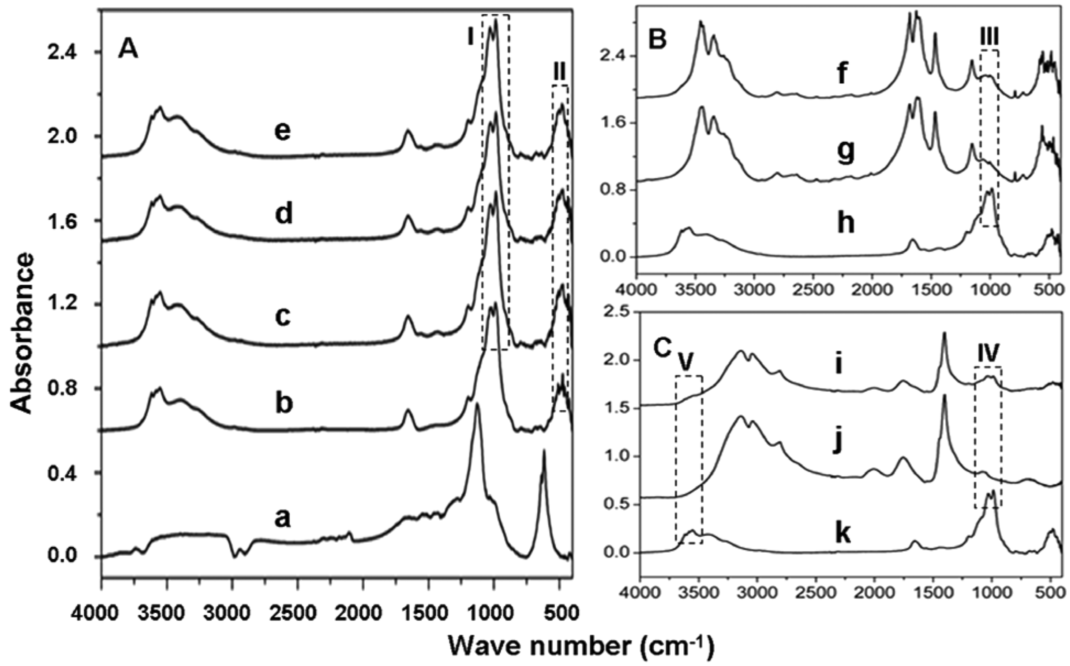

Figure 6. FTIR spectra. A: (a−e) M, HA30, HA30-M (W_{HA30}:W_M = 9:0.8), HA30-P (W_{HA30}:W_P = 9:1), and HA30-P-M (W_{HA30}:W_P:W_M = 9:1:0.8, actually WNLCA). B: (f−h) WNLCU W_U:W_{WNLCA} = 9:1.2), U, and WNLCA. C: (i−k) WNLCN (W_N:W_{WNLCA} = 9:1.2), N and WNLCA.

water evaporation, and thus lower MS loss. In addition, it could also be seen clearly in Figure 3C,D that the amounts of U and N (noted by the arrows) on the sand surface decreased obviously with the increase of WNLCA amount. This result indicated that WNLCF could effectively control the MS loss of nitrogen, which was beneficial for retaining more fertilizer nutrients in soil, reducing their runoff and volatilization loss, and improving the UE of nitrogen.

In drought areas, there is mainly sandy soil, so the fertilizer could easily be leached off with irrigating and rainwater. Hence, it is important to control the leaching loss of fertilizer nutrients. The performance of WNLCU and WNLCN (W_F/W_{WNLCA} of 9:1.2) to control the leaching loss of nitrogen was investigated through the sand column (Figure 4B), and the results shown in Figure 4A indicated that both WNLCU and WNLCN showed good leaching loss control ratios (65.87% and 89.96%) compared with those of U and N alone. Obviously, based on the preceding analysis, WNLCF could effectively control both MS and leaching loss of fertilizer nutrients.

Mechanism Study. The morphology of the WNLCF system was observed, as seen clearly in Figure 5A(a,b), P could attach to the surface of HA30 rods to form HA30-P, and M could contribute to make HA30 or HA30-P self-assembly to form three-dimensional (3D) micro/nano networks (Figure 5A(c,e)) through the polymer bridging and netting effects.[11] As shown in Figure 5A(c), the aggregates of polymer M could form plenty of nano fibers and bind to the surface of HA30, which was probably beneficial for the dispersion of HA30 and the formation of the 3D networks through the crystallization of M. The 3D networks, as the skeleton of WNLCA, could be proved by the elements (Si, Mg, and Al) mapping shown in Figure 5B. Additionally, P-M formed molecular penetrating networks (Figure 5A(d)), which could also be seen in WNLCA (Figure 5A(e)). That was to say, HA30-P-M possessed two kinds of networks, one was the 3D networks made up of HA30 rods, and the other was the molecular penetrating networks of P-M. This micro/nano networks structure endowed HA30-P-M with high porosity, SSA, and hydrophilicity attributing to the −OH, −COOH and $-CONH_2$. As a result, more nitrogen could be adsorbed and retained in the networks of HA30-P-M (Figure 5A(f−h)), and then tend to be retained in the soil, resulting in high retaining capacity and low loss amount for fertilizer nutrients. Additionally, because of the high adsorption capacities of P and M,[26,27] HA30-P-M possessed a high performance of retaining water.

To investigate the interactions in WNLCF system, FTIR measurements were carried out. As displayed in Figure 6A, the comparative strength of the two peaks (488 cm^{-1} for the translation and 509 cm^{-1} for the stretching vibration of −OH) of HA30 was different from that of HA30-M, HA30-P, and HA30-P-M (rectangular region I). In addition, the comparative strength of the two peaks (988 and 1018 cm^{-1} for the stretching vibration of Si—O—Si) of HA30 was also different from that of HA30-M, HA30-P, and HA30-P-M (rectangular region II). This was probably owing to the physical interactions among HA30, P, and M, which could probably contribute to the formation of HA30-P-M networks. As shown in Figure 6B,C, the main characteristic peaks of HA30 (988 and 1018 cm^{-1} for Si—O—Si stretching vibration (rectangular regions III and IV), 3551 cm^{-1} for $-OH_2$ stretching vibration (rectangular region V)) and U (3447 cm^{-1} for $-NH_2$, 1721 cm^{-1} for C═O and 1466 cm^{-1} for C—N stretching vibration) or N (3140 and 3038 cm^{-1} for −NH stretching vibration, and 1400 cm^{-1} for −NH bending vibration) could be found in the spectrum of WNLCU or WNLCN, indicating that WNLCA successfully bound fertilizer. In addition, new peaks or peak shifts were not found in WNLCU or WNLCN compared with U or N, which indicates that no obvious chemical reaction occurred in the fabrication process of WNLCF. In other words, the fabrication of WNLCF was mainly a physical process.

XRD measurements were performed to investigate the crystal structure information on WNLCF. As shown in Figure S2A of the Supporting Information, no obvious new peaks or peak shifts were found in HA30-P, HA30-M, and HA30-P-M

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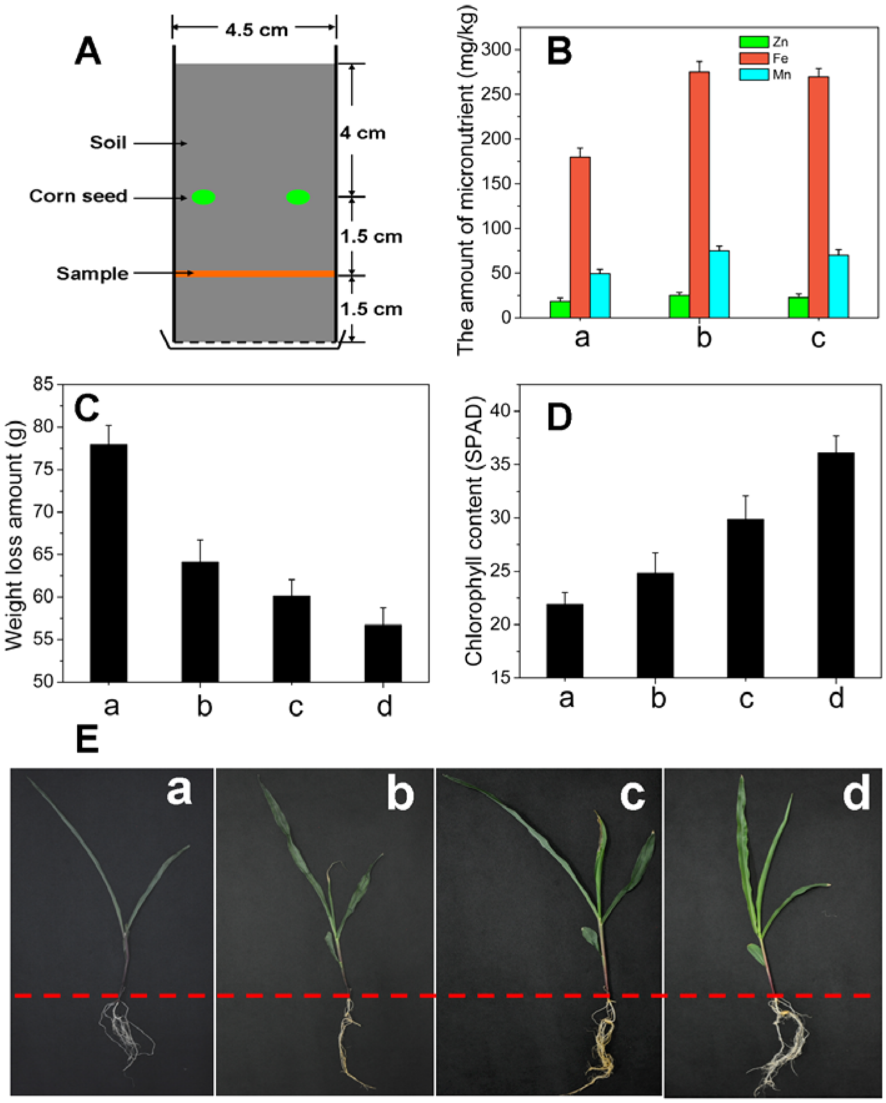

Figure 7. (A) Schematic diagram of the pot experiment system; (B−E) Micronutrient contents in the corn, weight loss amounts of the systems, chlorophyll contents in the corn, and digital photographs of the corn (25 days after seeding) treated with different samples: (a−d) blank, U (0.09 g), WNLCU (W_U:W_{WNLCA} = 0.09 g:0.012 g), and WNLCA (0.09 g).

compared with HA30, implying that no new substance was generated and no obvious chemical reaction occurred after addition of P or M. That is to say, HA30-P-M was fabricated mainly through physical effect, which was consistent with the preceding FTIR analyses. As shown in Figure S2B of the Supporting Information, the main diffraction peaks of U (22.32°, 35.5°, 37.1°) appeared in WNLCU, implying the successful binding of WNLCA and U, which was in accordance with the FTIR results. Moreover, those peaks (22.32°, 35.5°, 37.1°) in WNLCU were weakened compared with U alone, which was probably attributed to the lower crystallization of urea in some directions after addition of WNLCA in aqueous phase. It could be seen clearly in Figure S2C of the Supporting Information that the main diffraction peaks of N (42.32°, 46.84°, 58.28°) were found in WNLCN, which indicated WNLCA and N bound together. Compared with N alone, the peaks at 23.5° and 46.84° in WNLCN were enhanced, while the other peaks were weakened, which was probably because the crystallization of NH_4Cl increased in two directions (23.5° and 46.84°), but decreased in other directions after binding with WNLCA in aqueous phase.

Based on the preceding analyses, HA-P-M could self-assemble to form two kinds of 3D micro/nano networks and thus hold plenty of water and nutrients in the networks contributing to control the loss of urea, water and NH_4Cl, so that more water and nutrients could be retained in soil when such fertilizer was applied.

Effects of WNLCF on Corn. The influence of WNLCF on corn was investigated through a pot experiment of ^{15}N labeled fertilizer. In this work, ^{15}N labeled U was mixed with WNLCA to obtain two ^{15}N labeled WNLCU samples (W_U/W_{WNLCA} of 9:0.6 and 9:1.2), and the total nitrogen (TN) amount, ^{15}N abundance, C amount, and C/N ratio in root, stem and leaf of corn were measured on the 25th and 40th day after seeding (fertilizing at the same time). It could be seen clearly that U alone and WNLCU made the corn possess almost same ^{15}N abundance, TN, and C/N in root, stem and leaf during the seeding stage (25 days) (Figure S3a,c,g of the Supporting Information). However, on the 40th day, the corn fertilized with these two WNLCU samples, compared with U alone, possessed an obviously higher ^{15}N abundance and TN and thus lower C/N in the stem, and those were still almost the same in

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ACS Sustainable Chem. Eng. 2015, 3, 645−653

the root and leaf (Figure S3b,d,h of the Supporting Information), which indicated the WNLCA could effectively control the loss of nutrients in WNLCF, making WNLCF able to continuously supply sufficient nutrients for the growth of corn, whereas TF alone was not. Thus, the height and stem diameter of corn fertilized with WNLCF clearly improved (Figure S3i,j of the Supporting Information).

Besides, the influence of the WNLCU on the micronutrient element and chlorophyll contents in corn, and the water loss behavior of the pot system were investigated (Figure 7A). As shown in Figure 7B, the contents of Zn, Fe, and Mn in the corn with WNLCU and U were nearly the same on the 25th day after seeding, indicating that WNLCA displayed little effect on the absorption performance of corn on Zn, Fe, and Mn. While, both the water retaining ability of the soil and chlorophyll contents in the corn leaves showed an order of WNLCA > WNLCU > U > blank, suggesting that WNLCU and WNLCA could effectively increase the water retaining ability of soil and the antidrought capacity of corn (Figure 7C−E). In a word, the pot experiment indicated that WNLCF could effectively improve the retaining ability and utilization efficiency of fertilizer nutrients and water, and significantly contribute to the growth of crop.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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ACS Sustainable Chem. Eng. 2015, 3, 645−653