

Preparation and activity research of ecological nano mineral admixture from rice husk charcoal

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Abstract: The rice husk ash (RHA) and silica (SiO_2) nanoparticles are prepared from rice husk charcoal (RHC) by the methods of ventilated calcining and chemical precipitation, respectively, to remove the residual carbon which is harmful to cement composites. The structures and morphologies of these products are investigated by the Fourier transform infrared spectroscopy, X-ray diffraction, scanning/transmission electron microscopy and N_2 adsorption-desorption analyzer. The results show that the as-produced RHA and SiO_2 nanoparticles exist in amorphous phase without residual carbon, and exhibit porous structures with specific surface areas of 170.19 and 248.67 m^2/g , respectively. The micro particles of RHA are aggregated by numerous loosely packed SiO_2 gel particles with the diameter of 50 to 100 nm. The SiO_2 nanoparticles are well dispersed with the average size of about 30 nm. Both the RHA and SiO_2 nanoparticles can significantly reduce the conductivity of saturated $\text{Ca}(\text{OH})_2$ solution and increase the early strength of the cement composites. They also exhibit high pozzolanic activity, indicating that they can be used as ecological nano mineral admixtures.

Key words: ecological nano mineral admixture; rice husk charcoal (RHC); rice husk ash (RHA); SiO_2 nanoparticles; pozzolanic activity

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The ultra-high performance concrete (UHPC) refers to the concrete with compressive strength more than 150 MPa and tensile strength more than 15 MPa. Compared with conventional concrete, UHPC requires concrete with improved performance such as high strength, high durability, low shrinkage and low abrasion, which is urgently needed in the key projects such as cross-sea bridges, subsea tunnels and marine works. Extensive re-

search has found that the introduction of SiO_2 , Al_2O_3 , Fe_2O_3 , and TiO_2 nanoparticles can effectively improve the mechanical properties and durability of cement composites^[1–5]. But the massive application of nanoparticles in cement composites is limited due to their high cost and low productivity. Therefore, exploring a low-cost technique for the industrial preparation of nanomaterials is important for the application of UHPC.

Rice husks are agricultural byproducts of which major constituents are organic materials and hydrated silica. As cheap and renewable energy, the rice husk is widely used for gasification power generation, while the remaining waste becomes rice husk charcoal (RHC). RHC contains 30% to 40% residual carbon, 40% to 50% silica and minor amounts of metallic elements^[6]. It is reported that the amorphous SiO_2 in rice husk can promote secondary hydration with calcium hydroxide producing C-S-H with high density^[7]. However, the residual porous carbon in RHC will absorb a non-negligible amount of water. Burning in air is the traditional method to remove residual carbon^[8]. Temperature is the key factor for the quality of as-produced RHA. The carbon cannot be removed thoroughly due to incomplete burning at low temperature. When the temperature is high, the crystallization process will take place, leading to the decrease of activity. Chemical precipitation is another way to purify the silica from RHC. However, the precipitated silica tends to agglomerate due to the existence of hydrophilic Si-OH groups. Therefore, the removal of residual carbon without undermining the activity of SiO_2 particles is the prerequisite for the preparation of ecological nano admixtures.

In this paper, approaches are developed to prepare ecological nano mineral admixtures from RHC and their pozzolanic activity is also investigated. This research provides benefit for the sustainable development of the ecology and environment.

1 Experimental

1.1 Materials

The raw material RHC is provided by Shanghai Sen-nong Environmental Technology Company. Fig. 1 illus-

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trates the X-ray diffraction analysis of RHC. A broad peak around 20° to 30° is observed, which can be attributed to the presence of amorphous silica. The peak at 26° is for the graphitic structure indicating the existence of residual carbon. The chemicals used in this research are sodium hydroxide, ammonium chloride and ethyl alcohol, which are all analytical grade. Polycarboxylate superplasticizer (PC, solid content 40%) is procured from Subote New Material Co., Ltd., Nanjing, China.

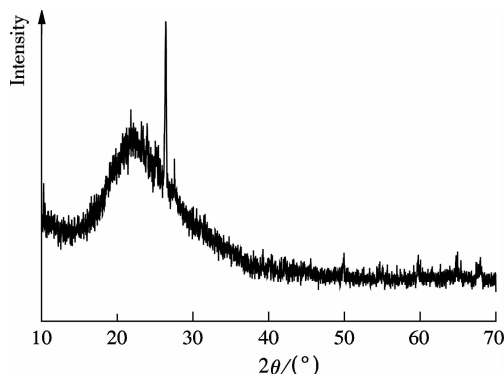


Fig. 1 XRD pattern of rice husk charcoal

1.2 Experimental procedures

In order to obtain highly purified ecological nano admixtures, the pretreatment process of leaching in H_2SO_4 acid (20%) at the temperature of 100°C for 2 h was carried out.

The preparation process of ecological nano admixtures from RHC is illustrated in Fig. 2. RHA was obtained by calcining the pretreated RHC at 600°C for 2 h in a well-ventilated tube furnace. The chemical precipitation method included the following procedures: the pretreated RHC and NaOH solution were mixed and subjected to boiling at 100°C for 2 h in a reaction still. Then the sodium silicate solution and residual carbon were separated through filtering. Subsequently, ammonium chloride solution was added

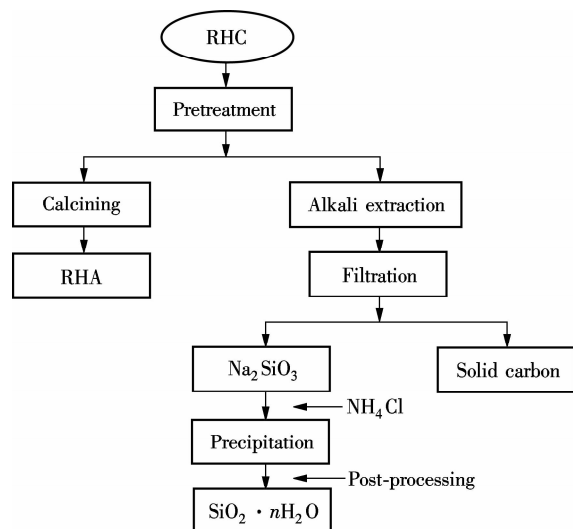


Fig. 2 The preparation process for RHA and SiO_2 nanoparticles

very slowly in small amounts to the flask containing sodium silicate, ethyl alcohol and PC at the temperature of 40°C . Meanwhile, white colloidal precipitation slowly appeared. The as-produced SiO_2 was purified by water before being filtrated and dried under vacuum at 60°C for 24 h.

1.3 Characterization

The crystalline phase was analyzed using a X-ray diffractometer. The presence of functional groups was clearly proved by the Fourier transform infrared spectroscopy (FTIR) analysis. A transmission electron microscope (TEM) and scanning electron microscope (SEM) were utilized to visualize the morphology of samples. The specific surface areas and pore structures were characterized by a N_2 adsorption-desorption analyzer.

2 Results and Discussion

2.1 Structure

The FTIR spectra of precipitated SiO_2 and RHA are shown in Fig. 3. The characteristic peak around 470 cm^{-1} is assigned to the bending vibration of $\text{Si}-\text{O}-\text{Si}$. The peaks at 807.09 and 1043.78 cm^{-1} refer to the symmetric stretching and anti-symmetric stretching of $\text{Si}-\text{O}$, respectively. The peak for $\text{H}-\text{OH}$ bending vibration is observed at 1629.44 cm^{-1} , showing the presence of absorbed water. The peak at 3432.61 cm^{-1} is characteristic of the presence of $\text{O}-\text{H}$ anti-symmetric bending vibration in OH groups. A tiny peak at 958.67 cm^{-1} in the spectra of precipitated SiO_2 shows the presence of $\text{Si}-\text{OH}$ groups, albeit they fail to appear in the spectra of RHA due to the conversation of silanol groups ($\text{Si}-\text{OH}$) to siloxane bridges ($\text{Si}-\text{O}-\text{Si}$) when RHC is calcined in air^[9].

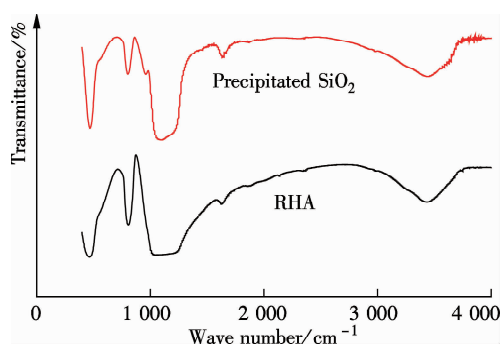


Fig. 3 FTIR spectra of RHA and precipitated SiO_2

Fig. 4 shows the X-ray diffraction analysis of precipitated SiO_2 and RHA. All the samples exhibit an amorphous form. A broad peak is observed between 15° and 30° , which can be attributed to the presence of disordered cristobalite. The disappearance of the peak at 26° as shown in Fig. 1 demonstrates that the residual carbon has been removed. A low temperature (600°C) is sufficient to ox-

idize the residual carbon completely during ventilated calcining, which is advantageous for saving energy and protecting activity.

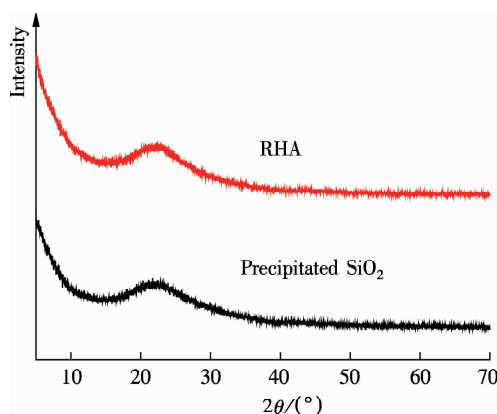


Fig. 4 XRD patterns of RHA and precipitated SiO_2

2.2 Morphology

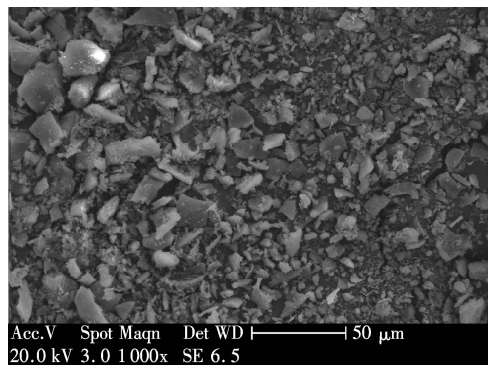
The SEM images of RHA at different magnifications are shown in Fig. 5. The microstructure of as-produced RHA is coincident with the three-layer model (The 1st layer: 1 μm to 1 mm; the 2nd layer: 0.05 to 1 μm ; the 3rd layer: <50 nm) proposed by Ouyang et al.^[10]. It is observed that the 2nd layer of RHA particles are aggregated of numerous loosely packed SiO_2 gel particles with the diameter of 50 to 100 nm, leaving considerable nanopores, which are in favour of increasing specific surface area and pozzolanic activity.

Dispersion of precipitated SiO_2 nanoparticles is crucial to fulfill their function as an active admixture for cement composites. However, dispersion of them is very difficult due to the large surface areas. In this research, PC was used to improve dispersion of SiO_2 by creating a layer of common charge over particles and also by reducing the surface energy. Moreover, as the precipitant, NH_4Cl slowly releases H^+ in case of the agglomeration of SiO_2 nanoparticles.

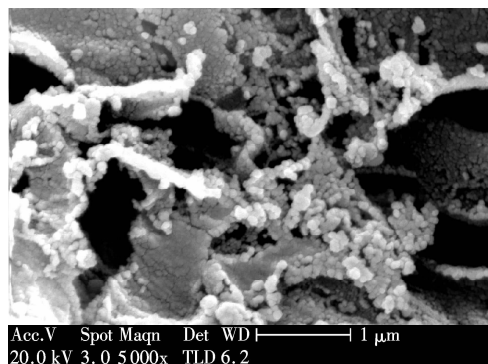
TEM images of as-produced SiO_2 nanoparticles at different magnifications are shown in Fig. 6. The diameter of SiO_2 nanoparticles is about 30 nm, lower than that of 50 to 100 nm reported in Ref. [11]. The SiO_2 nanoparticles are well dispersed without sever agglomerates.

2.3 Specific surface area and pore structure

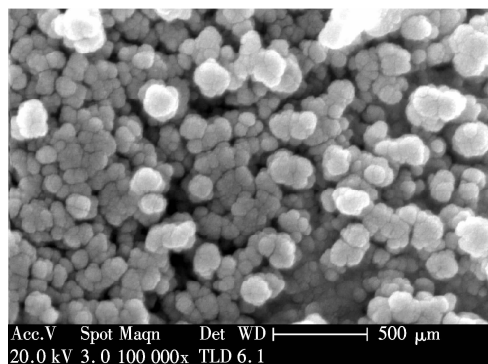
Tab. 1 summarizes the results of specific surface areas and pore structures of RHA, SiO_2 nanoparticles and silica fume (SF). The statistics of the pore volume exhibit that the as-produced RHA and SiO_2 nanoparticles are highly porous materials in accordance with the morphology analysis in section 2.2. The specific surface area of RHA is 170.19 m^2/g , which is much higher than that of 50 to 100 m^2/g reported by Ouyang et al.^[10]. Meanwhile, the



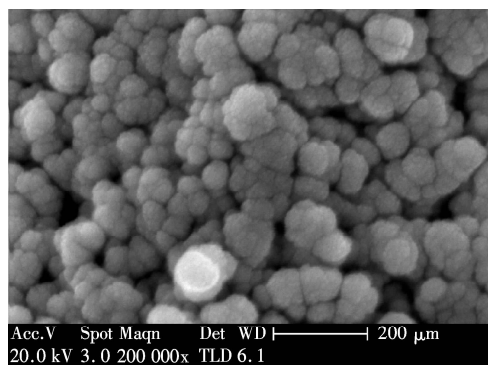
(a)



(b)



(c)



(d)

Fig. 5 SEM images of RHA at different magnifications. (a) $\times 1\,000$; (b) $\times 5\,000$; (c) $\times 10\,000$; (d) $\times 20\,000$

surface area of SF is 53.30 m^2/g , which is mainly due to the aggregation of fine particles. For SiO_2 nanoparticles, the nano-sized SiO_2 particles with well dispersion contribute to the high surface area of 248.67 m^2/g .

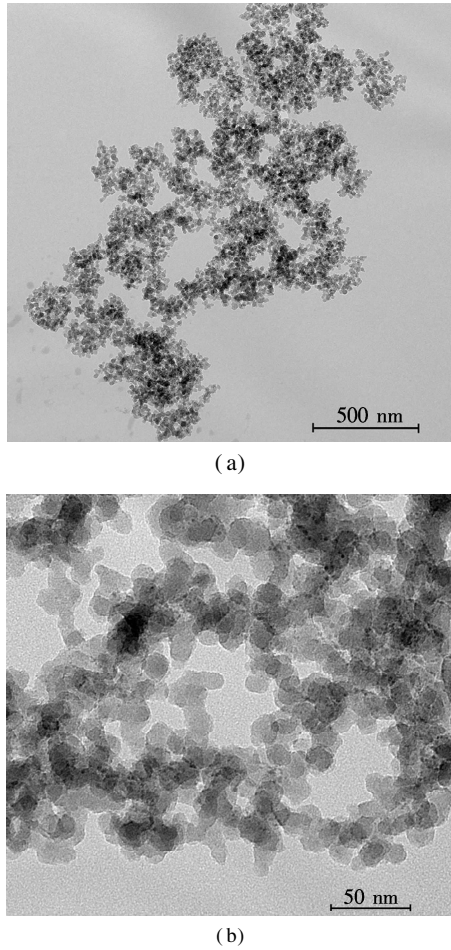


Fig. 6 TEM images of precipitated SiO_2 . (a) At low magnification; (b) At high magnification

Tab. 1 The specific surface areas and pore structures of RHA, SiO_2 nanoparticles and SF

Sample	Specific surface area/($\text{m}^2 \cdot \text{g}^{-1}$)	Total pore volume/($\text{mL} \cdot \text{g}^{-1}$)	Maximum pore volume/nm
RHA	170.19	0.269	361.7
SiO_2	248.67	0.323	418.0
SF	53.30	0.102	339.6

2.4 Pozzolanic activity

Conductivity tests^[12] were carried out to investigate the pozzolanic activity of as-produced RHA and SiO_2 nanop-

articles with SF as reference. The particles with pozzolanic activity will hydrate with Ca^{2+} leading to a lowering of the conductivity of the saturated $\text{Ca}(\text{OH})_2$ solution. Therefore, the difference of conductivity (ΔE) can be measured as the pozzolanic activity of particles. Test results are plotted in Fig. 7. The activity of RHA and SiO_2 nanoparticles is superior to that of SF encompassing all ages. The high specific surface areas of SiO_2 nanoparticles and RHA can promote chemical reactivities and accelerate nucleation growth^[13]. In the early stages, the activity of SiO_2 nanoparticles is slightly lower than that of RHA. This is because the hydration reactions are temporarily retarded by PC.

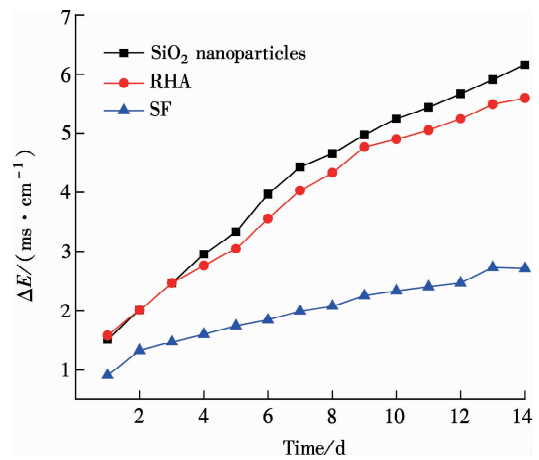


Fig. 7 Influences of RHA, SiO_2 nanoparticles and SF on the conductivity of $\text{Ca}(\text{OH})_2$ solution

The effects of as-produced RHA and SiO_2 nanoparticles on the mechanical performance of cement composites were also characterized. PI 52.5R cement and China ISO standard sand were used in this experiment. The details of the mix design and compressive strengths of the test specimens are shown in Tab. 2. The strengths of cement composites incorporating RHA and/or SiO_2 nanoparticles outperform their plain-cement counterparts at all ages. The results indicate that the addition of RHA and/or SiO_2 nanoparticles with high pozzolanic activity has a positive impact on the process of hydration, which directly transforms into mechanical properties.

Tab. 2 The reinforcement of RHA and nano- SiO_2 in early strength of cement composites

Sample	$\frac{m_{\text{water}}}{m_{\text{cement}}}$	$\frac{m_{\text{sand}}}{m_{\text{cement}}}$	$w(\text{RHA})/\%$	$w(\text{SiO}_2)/\%$	$w(\text{PC})/\%$	Compressive strength/MPa		
						1 d	3 d	7 d
Plain cement	0.42	3	0	0	0.11	27.66	42.58	52.81
RHA cement	0.42	3	1	0	0.40	31.23	48.69	58.46
Nano- SiO_2 cement	0.42	3	0	1	0.48	30.56	50.45	59.71
Compound cement	0.42	3	1	1	0.77	31.89	54.52	63.77

3 Conclusions

1) The as-produced RHA and SiO_2 nanoparticles exist in an amorphous phase without residual carbon.

2) The micro particles of RHA are composed of numerous loosely packed SiO_2 gel particles with the diameter of 50 to 100 nm. The SiO_2 nanoparticles are well dispersed with the average size of about 30 nm.

3) RHA and SiO_2 nanoparticles exhibit porous structures with large specific surface areas of 170.19 and 248.67 m^2/g , respectively.

4) Both the RHA and SiO_2 nanoparticles exhibit high pozzolanic activity, indicating that they can be used as ecological nano mineral admixtures.

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稻壳炭生态纳米矿物掺和料的制备及活性研究

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摘要:为了去除稻壳炭中对水泥基材料有害的残留炭,分别采用通风煅烧和化学沉淀的方法得到稻壳灰(RHA)和纳米 SiO_2 ;采用红外、X射线衍射、扫描/透射电子显微镜和氮吸附-脱附研究了2种产物的结构和形貌.结果表明:RHA和纳米 SiO_2 均为无定形结构,残留炭已基本去除;它们呈多孔结构,比表面积分别为179.19和248.67 m^2/g ;RHA微米级颗粒是由50~100 nm的 SiO_2 凝胶粒子疏松聚集而成;纳米 SiO_2 平均粒径为30 nm,分散良好;RHA和纳米 SiO_2 可显著降低饱和氢氧化钙溶液的电导率,增强水泥基复合材料的早期强度,显示出较高的火山灰活性,可作为生态纳米矿物掺和料.

关键词:生态纳米矿物掺和料;稻壳炭;稻壳灰;纳米 SiO_2 ;火山灰活性

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