Preparation and characterization of silicon nanomaterials with different morphologies

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Abstract. Coal combustion produces a large number of pollutants, leading to serious air pollution. The development of efficient ash removal technology from coal is imminent. Coal is a mixture of carbonaceous organic matter and inorganic mineral ash. Usually, the clean coal and inorganic mineral ash are separated by flotation according to the Hydrophobicity of carbonaceous organic matter and the hydrophilicity of inorganic mineral ash. Hydrophilic silica nanorods we prepared have high surface energy and chemical activity, which is easy to adsorb inorganic mineral ash, and then be floatated by flocculation. In this paper, a series of silicon nanomaterials with different morphologies were prepared by microemulsion method. On the basis of hydrophobic difference between coal and mineral ash, The inorganic ash minerals are adsorbed on the nanomaterials, and then separated by conventional flotation. At the same time, we used XRD and SEM to characterize the silicon nanomaterials.

1. Introduction

Coal occupies a dominant position in China's energy structure. The total amount of energy consumption in China was 44.9 million tons, and the consumption of coal accounted for 60.4% in 2017. Coal is a mixture of carbonaceous organic matter and inorganic mineral ash. Through the existing coal flotation technology, the inorganic mineral ashes, which have good natural dissociation in the raw coal, can only be separated. However, the inorganic ash minerals embedded in the carbonaceous organic matter can not be selected. The high ash content of coal will cause technical difficulties in coal utilization, accompanied by lower efficiency and higher cost. In addition, high ash in the coal will result in larger transportation and more pollutants. In recent years, serious air pollution and haze weather have become the most important environmental pollution problems in our country. Therefore, it is very urgent to use the clean and efficient coal, and it is necessary to develop efficient deashing technology.

The deashing technology can be divided into chemical methods and physical methods. The chemical method is to remove inorganic mineral ash by acid or alkali leaching. The disadvantage is the high cost, the strong corrosion, and the waste pollution. Physical method is divided into oil agglomeration[1], selective flocculation flotation[2]and hydrophobic flotation[3]. The principle of physical method is to add one or several reagents which can increase the hydrophobicity between the carbonaceous organic matter and the inorganic mineral ashes, so that the inorganic mineral ashes are

clustered together, and then the coal and minerals are separated by sieving or conventional flotation. Commonly used agents include pentane, kerosene, diesel and polyacrylamide. The separation performance and efficiency of the ash is a major factor affecting the ash content of clean coal. Therefore, developing a new type of high efficiency ash removal agent is the key to improve the deashing technology.

Hydrophobic silica nanomaterials have high surface energy and chemical activity. They are easy to adsorb inorganic mineral ash, and then be floatated by flocculation. In 1995, Nakamura et al[4-5]synthesized square silicon nanotubes and a small amount of cylindrical particles by sol-gel methods at room temperature. They also changed tartaric acid into citric acid and prepared a new type of insect shaped silica gel hollow tube. The cross section of the worm shaped hollow tube was round and the inner area was square, whose specific surface area was between 250 m^2/g and 350 m^2/g. Subsequently, Fumiaki et al. [6]used ammonium oxalate instead of racemate tartarate to synthesize hollow silica nanotubes with triangular or rectangular cross sections, and suggested that the acicular organic salts could form nucleation, used as templates for sol-gel reaction, and then formed a few of hollow silicon fiber and filaments. In 2002, Chengzh Yu et al.[7]used three block copolymers as structural guide, KCl as an additive and hydrothermal treatment at 130^0C to prepare highly ordered mesoporous silicon tube materials with a length of 1~2um and a diameter of 700 to 900nm. In 2004, Abdelhamid et al.[8]synthesized a monodispersed hexagonal SBA-15 silicon rod by hydrothermal method. The diameter of the silicon rod was between 0.4um and 0.5um, and the length was between 1.0um and 1.5um. There are hexagonal channels on the surface of silicon rods with a wall thickness of 5nm to 9nm. Subsequently, Supratim et al.[9] reported the synthesis of a MCM-41 type mesoporous silicon nanorod using co-condensation method. The average size of the synthesized silicon nanorods was 200nm x 80nm , and the average diameter of the nanorods was 3.0nm. In 2007, Zhenk Zhang et al. [10]reported that the filamentous wild type fd virus was used as a template for the first time. The silica precursor was first produced by acid catalyzed tetraethoxysilane, and then the silicon dioxide precursor was added into the dispersions of the fd virus to prepare the silicon nanorods. In 2008, Jianh Zhang et al. prepared polyvinyl pyrrolidone modified with gold nanoparticles as a structural directing agent, and prepared hollow nanocrystalline silicon rods.[11]. After three years, Kuijk[12]added ethanol, water, sodium citrate and ammonia to the dissolved pentol solution of polyvinylpyrrolidone (PVP) to prepare a cartridge silicon rod by one pot method. Subsequently, there were related reports[13] on the effects of different factors on the growth of silicon rods.

The application of silicon nanorods as a new field is rarely reported. Yi et al. prepared hydrophobic silicon rods by co-precipitation of silicone and tetraethoxysilane and successfully developed super hydrophobic coating[14].It is also reported that silicon rods can be used as reinforcing agents for porous silica networks. Silicon rods can improve the flexural strength of the composites. The length of silicon rods is conducive to the flexural strength of the composites[15]. Byranvanda et al. reported that using silicon rods can make the thin film solar cells with a higher conversion efficiency instead of spherical silicon particles[16]. Daware et al. used the silicon bar to stabilize the Pickering emulsion. Even if the solvent evaporated, the silicon rod remained stable on the Pickering surface. The study also showed that the two affinity silicon rod could stabilize the emulsion better than the hydrophilic rod, and the long rod had better stability than the short rod. The thermo reversible gel can be synthesized by the short range ordered arrangement of silicon rods[17]. In addition, the bar biosensor composed of silicon rods coated with gold nanoparticles has been used for visual inspection of micro RNA, they fixed DNA on the surface of the biosensor, and then added micro RNA. The micro RNA was further hybridized with the DNA chain on the gold nanoparticles deposited on the silicon rod. Because of the large amount of gold nanoparticles on monocrystalline silicon rods, the detection signal is highly amplified by compared with the gold nanoparticles alone[18]. However, no silicon nanorods have been reported for the separation of carbonaceous organic matter and the inorganic mineral ashes.

2. Experimental Section

2.1. Chemical Reagents

Pentyl alcohol ($C_5H_{12}O$, Aladdin), polyvinylpyrrolidone (PVP, MW=40000, Aladdin), ethanol, two sodium citrate, ammonia and tetraethoxysilane (TEOS, Aladdin). All of them are analytical reagents.

2.2. Preparation and characterization of silicon nanomaterials

We prepared silica nanomaterials by microemulsion method[19]. Firstly, dissolve 30g polyvinylpyrrolidone in pentyl alcohol of 300mL for two hours in 500mL flask, then 30mL anhydrous ethanol, 8.4mL water and 2mL 0.18mol/L of sodium citrate solution were added, and the mixture was mixed. Finally, 6.75mL ammonia and 3mL tetraethoxysilane were added to stay overnight. The reaction mixture was centrifugally separated and washed with ethanol for three times and dried at 100^0C. The structure was characterized by X ray diffractometer and scanning electron microscope (Zeiss Merlin).

3. Results and Discussions

3.1. Characterization of silicon nanomaterials

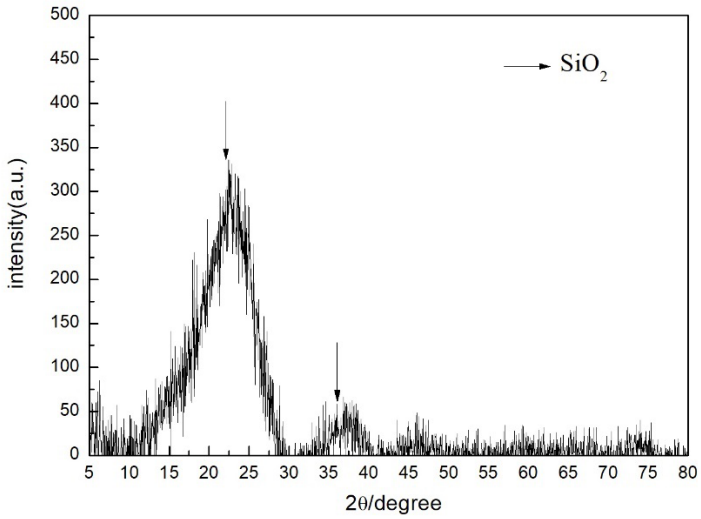

Figure 1. XRD spectra of silicon nanomaterials.

The XRD spectrum of the silicon nanomaterials is shown in figure 1. As can be seen from the diagram, the atlas has two distinct characteristics of the diffraction peak, indicating that the synthetic material is a typical amorphous silica material, which is in perfect agreement with the reported spectra[20]. No other impurity peaks were observed in the diagram, indicating that silica materials contained almost no other impurities.

3.2. Effect of PVP dosage on the morphology of silicon nanomaterials

We studied the effect of different PVP dosage on the morphology of silicon nanomaterials, as shown in Figure 2. It is known from the diagram that when the amount of PVP is 0.5g, the silicon nanomaterials present a needle shape in the head. When the amount of PVP is more than 1g, the silicon nanomaterials present a round bullet shape. The diameter distribution first gradually widens and gradually narrower, and the length distribution becomes narrower and narrower. When PVP is added to 5g, the silicon nanomaterials appears bending and tail irregularities, diameter and length distribution is the narrowest and particle size is the most homogeneous.

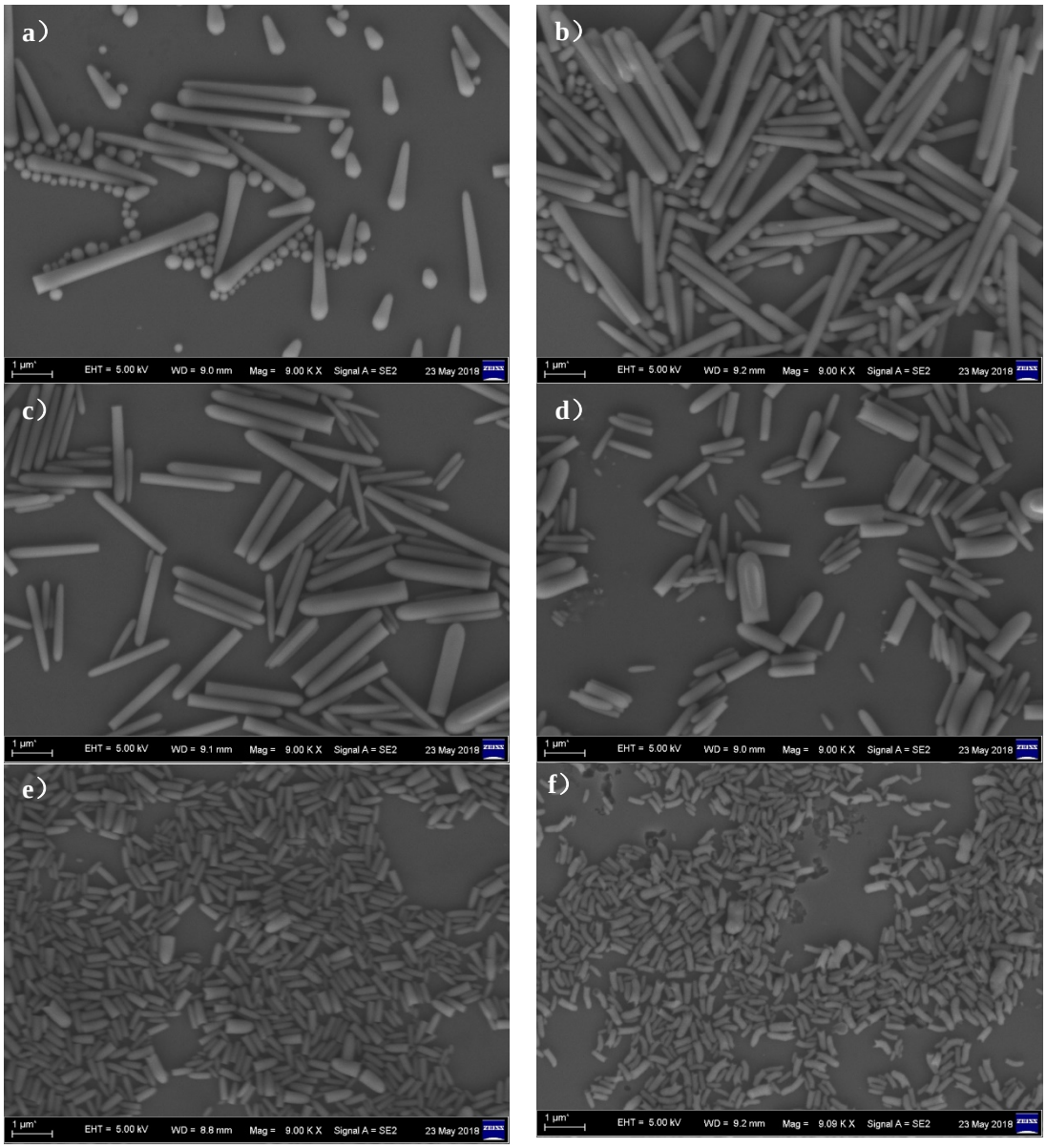

Figure 2. SEM of silicon nanomaterials prepared by different PVP dosage, (a)0.5g，(b)1g，(c)2g，(d)3g，(e)4g，(f)5g.

3.3. Effect of water dosage on the morphology of silicon nanomaterials

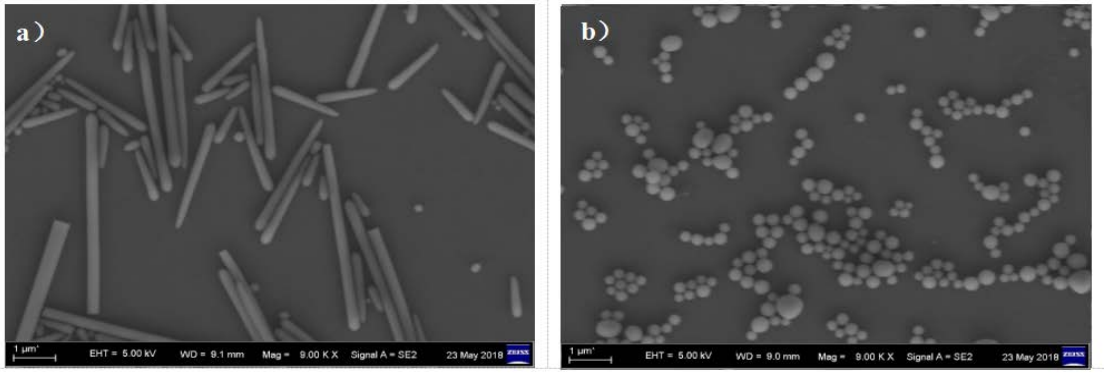

Figure 3. SEM of silicon nanomaterials prepared by different water dosage, (a)250uL，(b)500uL.

We studied the effect of different water consumption on the morphology of silicon nanomaterials, as shown in Figure 4. It is found that when the amount of water is 250uL, the silica material has a bar shape. while the added water is 500uL, the prepared silica is spherical. The amount of water can change the morphology of silica. The reason for this change is that the diameter of the water droplets in the microemulsion is too large and the concentration of $Si(OH)_4$ in the form of the hydrolysate is reduced in the droplet, and the condensation reaction is not easy to produce SiO_2, so the nucleation is not easy to occur.

We also studied the effect of the ammonia amount on the morphology of silicon nanomaterials. The results show that the increase of ammonia will reduce the length of silicon nanomaterials and continue to increase the amount of ammonia, we may eventually get spherical silicon particles. We also researched the effect of the concentration of sodium citrate on the morphology of silicon nanomaterials. The particle size of silicon nanomaterials increased with the increase of sodium citrate concentration. If the concentration of sodium citrate was increased further, it was possible to get a longer silicon rod.

4. Conclusion

In this work, we focus on the preparation of silicon nanomaterials, and studied the effect of different factors on the morphology of silicon nanomaterials. The factors include PVP dosage, water dosage, ammonia amount, the concentration of sodium citrate, and so on. The structure and morphology of the silicon nanomaterials were characterized. The application of silicon nanorods as a new field is rarely reported. Subsequently, we will research about silicon nanorods for the separation of carbonaceous organic matter and the inorganic mineral ashes.

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