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Full Length Article

Synthetic magnesium silicate hydroxide nanoparticles coated with carbonaceous shell in subcritical water condition

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ABSTRACT

Under subcritical water condition, the synthesis process of magnesium silicate hydroxide (MSH) and the decomposition process of oleic acid were simultaneously carried out, and the MSH nanoparticles coated with a carbonaceous shell on the surface were prepared. The characterization results of scanning electron microscopy (SEM) and high-resolution transmission electron microscope (HRTEM) indicate the formation of the carbonaceous shell and both granular and schistose shape of nanoparticles. This shell is characterized by using the Raman spectroscopy, Fourier transform infrared (FTIR) spectrum, and X-ray photoelectron spectroscopy (XPS). The results indicate the non-existence of C—C sp^3 bond and the high content (up to 72%) of C—H sp^3 bond. Besides, the carbonaceous shell is composed of amorphous and turbostratic carbon, which could be attributed to the decomposition of oleic acid, then followed by polymerization and aromatization of decomposition products.

1. Introduction

Serpentines, as one kind of natural 1:1 trioctahedral phyllosilicate consisted by Si—O tetrahedron sheets and Mg—O octahedral sheets [1–3], have attracted a lot of attentions owing to its excellent anti-wear property as the lubricant additive. Many studies have shown that the serpentine micro-powder in mineral oil [4–6] or paraffin [7] can form a protective layer on the worn surface which exhibit excellent anti-wear property. However, it is worth noting that serpentine, as a natural mineral, has a very complex composition. Besides the main component magnesium silicate hydroxide (MSH, $Mg_6Si_4O_{10}(OH)_8$), it also contains small amounts of metal oxides, such as alumina, calcium oxide, and iron oxide [1,5]. Studies show that some of these compositions exhibit the ability to reduce wear, such as magnetite [8], alumina [9], which have demonstrated the ability to form the lubricating tribofilm to exhibit excellent anti-wear properties. Therefore, it is difficult to explain how the exact compositional ratio affects the anti-wear mechanism of serpentine. The serpentine groups of natural minerals are polymorphous and, in addition, their composition greatly depends on the geographical location [10]. Therefore, it is meaningful to study the tribological properties of MSH since it is the main component of serpentine.

In the previous study, we synthesized different type of MSH nanoparticles by controlling the reaction conditions, and also study the tribological properties of these nanoparticles [11]. Due to the excellent tribological properties of hydrogenated amorphous carbon [12,13], we try to combine it with MSH nanoparticles, which are coated with a layer of hydrogenated amorphous carbon on the surface. The amorphous carbon film can be prepared by using several methods, such as pulsed laser deposition (PLD) [14], chemical vapor deposition (CVD) [15]. In this paper, the preparation of MSH nanoparticles is carried out on a subcritical water condition. Thus, in order to coat the nanoparticles during the synthesis process, the oleic acid was chosen as the raw material for this amorphous carbon film whose formation mechanism mainly depends on the decomposition and polymerization reactions. Related studies of tribological properties need further analysis. In this article, we mainly characterize and analyze the morphology, structure of the resulting nanoparticles and, at the same time, the possible formation mechanism of this amorphous carbon film.

2. Synthetic process and characterization methods

2.1. The preparation of MSH nanoparticles

The MSH nanoparticles are prepared within a subcritical water environment. The raw materials and synthetic parameters are

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Table 1
The raw materials and synthetic parameters.

Raw materials and synthetic parameters	Details	Source
Silica (g)	4.286 (AR), >99.9 wt%	ST-NANO, China
Magnesium oxide (g)	4.286 (AR), >99.9 wt%	ST-NANO, China
Oleic acid (g)	2.673, >79 wt%	Evyap, Malaysia
H_2O (mL)	400 (Deionized water)	Haibiao Tech, China
Pressure (MPa)	1.5	
Reaction time (h)	12	
Temperature (°C)	200	
pH value	13 (Adjust with NaOH solution, 1 mol/L)	Haibiao Tech, China
Stirring speed (r/min)	450 ± 10 (Magnetic stirring)	

listed in Table 1. The purity of silica and magnesium oxide is very high, which belongs to the analytical reagent (AR).

2.2. Characterization

In this study, X-ray diffraction system (XRD, Bruker D8 ADVANCE), scanning electron microscopy (SEM, Hitachi SU8010) and high-resolution transmission electron microscope (HRTEM, FEI Technai G2 F20) are used to characterize the morphology and structure. The coated amorphous carbon are analyzed by using Raman spectroscopy (325 nm, Renishaw inVia), Fourier transform infrared (FTIR, Nicolet 6700) spectrum and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi).

3. Characterization results

The XRD result of MSH nanoparticles shown in Fig. 1 matches with the serpentine mineral (PDF#25-0645). All the diffraction peaks correspond to serpentine crystal planes. No impurities peaks are found according to the XRD pattern. The SEM image shown in Fig. 2 indicates that MSH nanoparticles exhibit a granular shape and a highly fragmented schistose shape in which the size of the granular particles is 30–50 nm and the size of the schistose particles is 60–100 nm. The HRTEM image shown in Fig. 3 clearly shows the existence of a carbonaceous shell with the thickness of 3–5 nm. As it can be seen, besides the amorphous structures, the curved

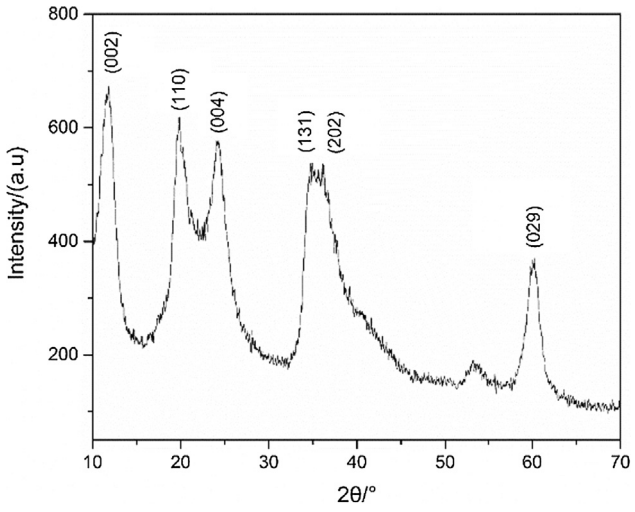

Fig. 1. The XRD patterns of MSH nanoparticles.

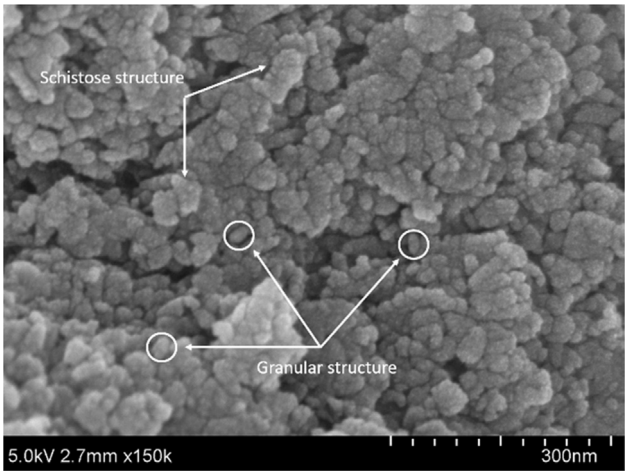

Fig. 2. The SEM image of MSH nanoparticles.

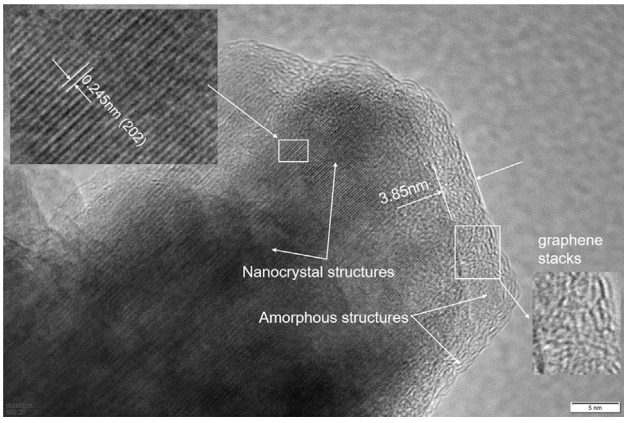

Fig. 3. The TEM image of MSH nanoparticles.

graphene stacks can be clearly observed, so this shell structure can be defined as a mixture of amorphous and turbostratic carbon. It is possible that a weak peak attributed to (002) carbon planes, similar with those observed in carbon blacks around 2θ 23–25° to exist [16], yet to be masked by more intense (110) and (004) convoluted MSH diffraction peaks.

The carbonaceous shell is characterized by Raman spectroscopy, FTIR spectrum, and XPS, respectively. Raman spectroscopy is a powerful and sensitive characterization method for carbon materials, such as diamond, graphite, amorphous carbon. For all carbon materials, the visible excitation Raman spectra show D and G peaks appear around 1360 and 1560 cm^{-1} which are owing to the sp^2 site in a ring configuration and the sp^2 site in both chain and ring configuration, respectively [17–19]. Since low energy visible light could not excite the higher energy σ state and can only excite the lower energy π state, so the visible Raman spectra reflect the sp^2 bond vibration [20]. However, the ultraviolet with higher energy could excite both σ state and π state. Thus, besides the G and D Peak, one more peak often named T peak site appears around 1060 cm^{-1} for H-free carbons and 980 cm^{-1} for hydrogenated carbons which is due to the sp^3 site [17]. It should be noted that the sp^3 bonded C atoms include C—C and C—H bonds in the hydrogenated amorphous carbon. The T peak is only owing to the C—C sp^3 bonds [21].

In this study, UV Raman spectra are used to analyze this carbon shell. The nanoparticles samples are excited by ultraviolet light source (325 nm). It is obvious that the Fig. 4 shows the two well-