MFC aerogel-MNPs composite

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Abstract. MFC aerogel was prepared, magnetic nanoparticles (MNPs) were loaded in the aerogel. MNPS were obtained successfully in the matrices. The aerogel MNPS size was defined by TEM. The thermal-stability was tested by TGA. XRD was examined to define the particles of Fe3O4. This aerogel performed superior properties for MNPS loading. MFC aerogel will have potential application in magnetic substrate.

Introduction

Metal particles in the nanometer size range have attracted considerable interest in recent years, as they have many attractive applications in various fields [1-6], since they have unique size-dependent optical, electrical, magnetic, and antimicrobial properties.

Magnetic nanoparticles have been a research topic of great interest in a wide range of applications, including catalysis [7,8], biotechnology/biomedicine[9], and environmental remediation [10,11]. In most of the envisaged applications, the particles perform best when the size of the nanoparticles is below a critical value, typically around 10–20 nm. In this case, each nanoparticle becomes a single magnetic domain and shows superparamagnetic behavior when the temperature is above the blocking temperature [12]. Well dispersed MNPs must be remained. It is basically difficult to disperse metallic nanoparticles in a solvent, as nanoparticles tend to aggregate due to their high surface energy. A simple synthesis strategy with controlled nanoparticles is a significant nanotechnology.

Micro-fibrillated cellulose (MFC) is isolated from natural cellulose fibers by basically mechanical action after enzyme or chemical pretreatment. Its higher aspect ratio, biocompatibility and rich active hydroxyl groups and carboxyl groups made MFC an attractive application of providing a more beneficial template to accommodate nanoparticles, for example, with silver nanoparticles [13,14], with magnetic particles [15], and with drug nanoparticles [16,17].

In this work, a different method to load nanoparticles is provided. MFC is the template. MFC aerogel was prepared, followed by nanopartilces generation on the aerogel. Generally, MFC-based MNPs aerogel showed the best properties for nanoparticles loading than NFC aerogel.

Experimental part.

1 Magnetic nanoparticles (MNPs) loading

MFC aerogel was prepared in our lab and described in elsewhere [18]. In situ loading of magnetic nanoparticles onto the aerogel was carried out through the co-precipitation method. Under ambient temperature (~25°C), mixing 0.05M FeCl2 solution with 0.1M FeCl3 solution using same volume. Mixture solution was dropped and spread on the porous matrix, keeping totally wet for enough long time till the substrates were not absorbing solution.

After a certain time of air drying, a partially dehydrated matrix was obtained. It was then immersed in 60^{o} C aqueous solution of NaOH (0.2M) for 60 min. Meanwhile, the color of the resultant samples turned to yellow or dark brown due to magnetic nanoparticles formation. The composite was rinsed with Milli-Q water three times to remove water-soluble substances and free resultant particles. Each wash time took at least 1h. Finally, the composite was liquid nitrogen frozen and freeze dried.

2 SEM and TEM scanning of MFC aerogels with MNPs

The porous structures of MFC aerogels were examined using FESEM (a field emission scanning electron microscope) at an accelerating voltage of 20 kV (a high resolution JEOL 6400F cold field emission SEM). The MFC aerogels with MNPs were characterized using VPSEM (Variable Pressure Scanning Electron Microscope – Hitachi S3200N with an energy dispersive x-ray spectrometer).

A JEOL 2000FX transmission electron microscope (TEM) operating at 20.0 kV was utilized to define the MNPs in the MFC aerogels.

3 Thermal Gravimetric Analysis (TGA)

In order to determine the thermal decomposition temperature of composite aerogels, thermogravimetric analysis (TGA) was used. It was operated on a Perkin Elmer TGA Q500 with a heating rate of 10°C/min in a nitrogen atmosphere to 500°C. In order to obtain the MNPs amount in aerogel, TGA under oxygen in the range of 500-575ºC was continued. The isothermal time was set 25min at 575ºC.

4 X-ray diffraction (XRD) Test

Iron loaded MFC aerogel with 2 theta at both small angle and wide angle were utilized XRD to identify iron crystallites . PANalytical Empyrean X-Ray Diffractometer was used. Scan range is in 5-40 for small angle, and 10-80 for wide angle.

Results and discussions

1 MNPs Formation and Morphology

The MFC aerogel microstructures were shown below in Figure.1(left). In Fig.1, we can see that MFC aerogel has open structure and has more pores. These pores will be helpful for nanoparticles loading and filling.

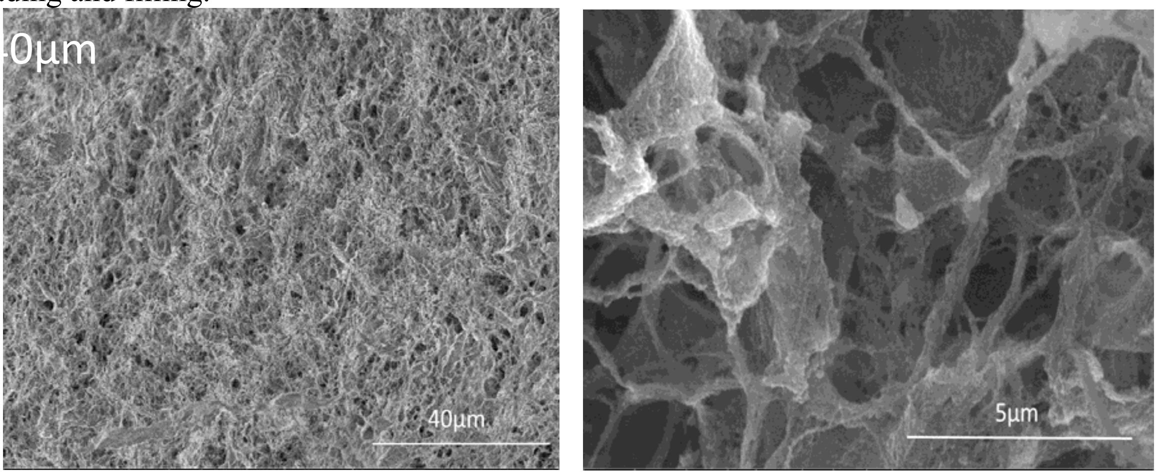

Figure.1 MFC aerogel (left) and MFC aerogel with MNPs (right) SEM images

After MNPs loading, the aerogels structure and nanoparticle distribution were shown in Figure 1(right). In Fig.1, MFC aerogel has many small particles attached on fibrils.

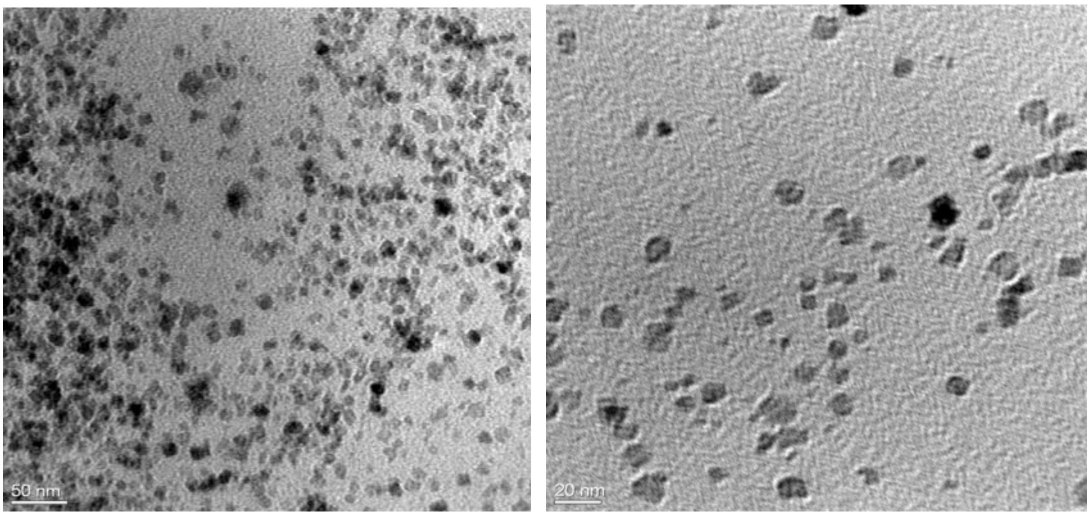

Figure.2 TEM images of MFC aerogel MNPs distribution

In order further to know MNPs size and distribution for MFC aerogel, TEM was conducted (see Figure.2). The particles are very small with diameter less than 20nm, most particles in the range of 10nm. This is because the aerogel has huge hydroxyl groups and some carboxyl groups which are the anchors to be nucleus of particle growth. Nanofibrils placed an important role to physically stop the Fe2+/Fe3+ free move, then mono-dispersed small particles were formed.

2 Thermogravimetry test

In view of the importance of thermal stability of MNPs loaded MFC aerogels, thermal decomposition of composites loaded MNPs was examined by thermogravimetry (TGA) in a nitrogen atmosphere under 500ºC, as shown in Figure.3. Under nitrogen, the most weight loss of the MFC MNPs aerogel took place at 260°C, and of pure MFC aerogel around 310º C. In order to obtain the MNPs amount in aerogel, TGA under oxygen in the range of 500-575ºC was continued. The MNPs amount in MFC aerogel remained in 15.3%, in Fig.3.

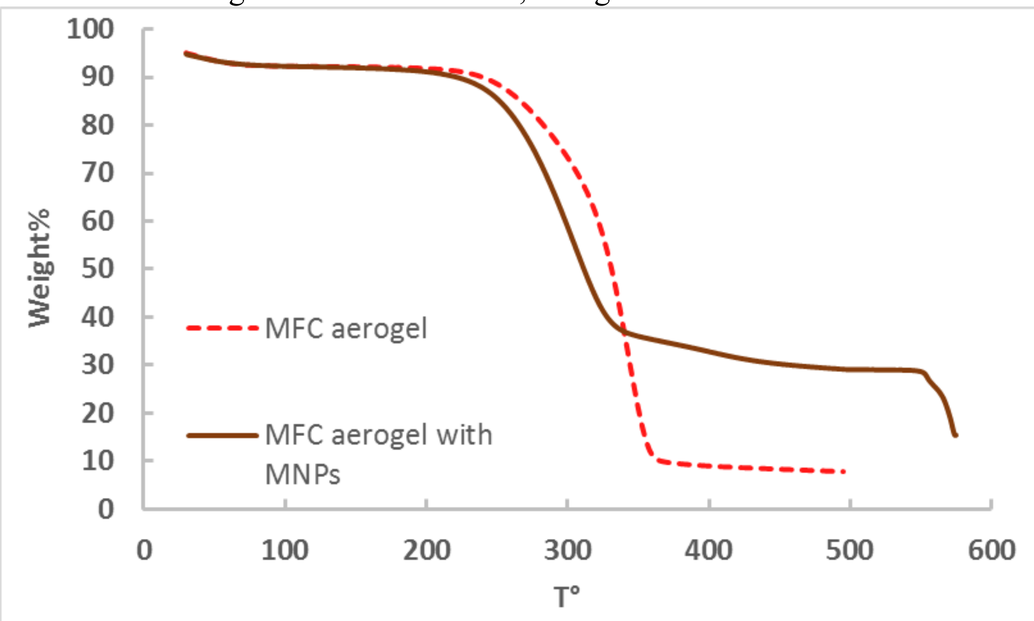

Figure.3 MFC aerogel and MFC-MNPs aerogel TGA

3 X-ray diffraction (XRD)

Iron loaded MFC aerogel with 2 theta at both small angle and wide angle were utilized XRD to identify iron crystallites. The XRD pattern at small angle was drawn in Figure 4. For Fe3O4 crystine identification, 35º is the symbol for it in the XRD curve. The pattern of MNPs MFC aerogels displays a most intense at 2θ = 35.28◦.The line corresponds that of pure Fe3O4, confirming the presence of Fe3O4.

Using wide angle scanning method, the XRD pattern showed similar result to that at small angle, n in Figure 5. The peak of 35º corresponds pure Fe3O4 crystalline, confirming the presence of Fe3O4. The observed broadness and lower intensity of that curve indicate the lower degree of crystallinity of imbedded Fe3O4 particles in cellulose.

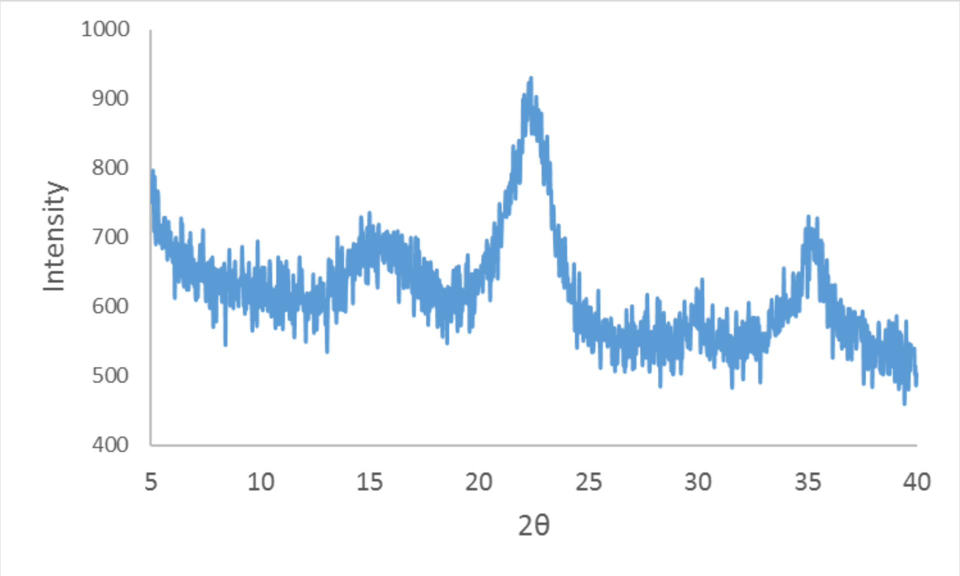

Fig.4 XRD pattern of MFC-MNPs aerogel at small angle

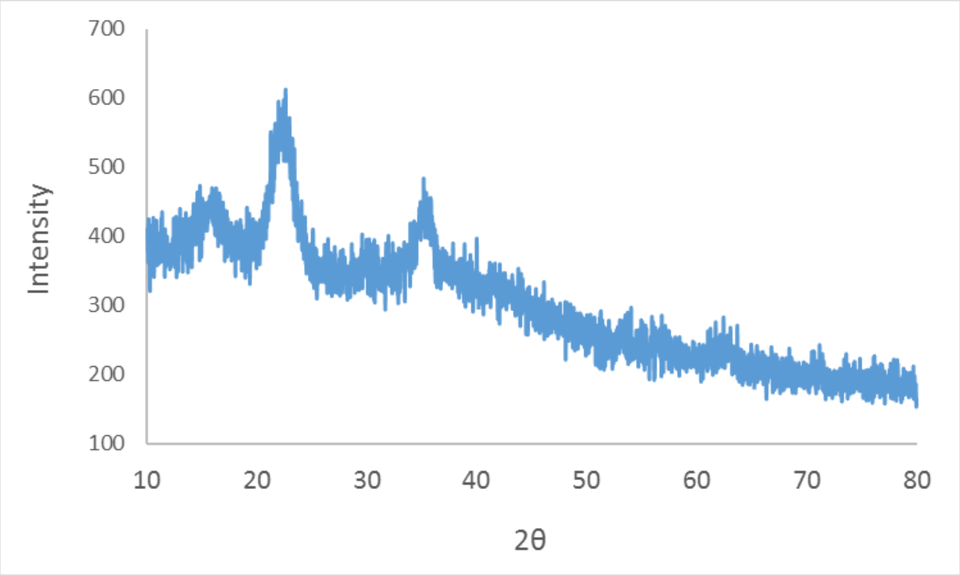

Fig.5 XRD pattern of MFC-MNPs aerogel at wide angle

Conclusion

In this work, MFC aerogel facilely used as substrate for preparation and stabilization of nanoparticles of MNPs. MNPs are well dispersed on the MFC aerogel. We therefore propose that during on site loading, the metal ions are anchoring on the negative charged groups of aerogel, to first perform chemical reactions as the core, and then grow into particles. The procedure will provide a technically more feasible strategy. We actually practiced in AgNPs loading successfully as well. They proved that MFC aerogel is a novel substrate for MNPs loading.

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