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Magnetic Responsive Cellulose Nanocomposites and Their Applications

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1. Introduction

Magnetically responsive cellulose materials are specific subset of smart materials, in which magnetic nanoparticles are embedded in the polymer matrix, which can adaptively change their physical properties due to an external magnetic field. These kind of materials are expected to exhibit interesting magnetic field-dependent mechanical behavior with a wide range of potential applications, such as fibers and fabrics for protective clothing for military use (Raymond et al., 1994), magnetic filters (Pinchuk et al., 1995), sensors (Epstein & Miller, 1996), information storage, static and low frequency magnetic shielding (Dikeakos et al., 2003) and health care or biomedical products (Wang et al., 2004). In general, magnetic cellulose materials can be prepared with different morphologies, such as films, fibers, microspheres, hydrogels and aerogels, and they respond differently to externally applied magnetic field because of the different natures and structures. The main purpose of the present review is to overview on recent advances in the development of magnetic field-responsive cellulose composites with emphasis on the fabrication, properties and possible applications.

2. Magnetic cellulose fibers

Natural cellulose fibers are composed of microfibrils of 10-30nm width and three-dimensionally connected with each other (Mark & Kroschwitz, 1985). The surface of the fiber is rough and consists of pores with diameter of 30-70 nm, with specific surface area of 30-55 $m^2 \cdot g^{-1}$ (Kaewprasit et al., 1998). These nanopores may allow guest molecules to penetrate into their inner spaces. The preparation of magnetically responsive fibers based on cellulose and magnetic nanoparticles has been investigated by several approaches. In the past 2 to 3 decades, magnetically responsive cellulose fibers have been prepared by vigorously agitation of cellulose pulp in a concentrated suspension of iron oxide particles

such as magnetite and maghemite particles, followed by a mild washing step to remove all the unbound-magnetic particles. This preparation process is called lumen-loading (Chia et al., 2009; Rioux et al., 1992). The process proceeds in three stages. Firstly, a short initial stage with an advancing diffusion front penetrating the lumen with negligible deposition of filler particles on the internal surface. Secondly, a quasi-steady state regime (the main stage) in which the number of fillers particles entering the lumen equals the number being deposited on the lumen wall, and for which the concentration of filler particles suspended in the lumen is approximately constant, and finally the rate determining step switches from being the rate at which particles can enter into the lumen, and particle deposition occurs on the remaining empty spots of the lumen. The lumen-loading is a physical approach, and the diffusion kinetics of the method is mainly limited by the transport of filler particles through the pit apertures in the fiber walls (Zakaria et al., 2004 a, 2004b). It often results in a heterogeneous composite with deleterious particle dispersion, aggregation and therefore inferior performance. In contrast, the latter co-deposits both matrices and particles simultaneously from a premixed precursor offer more homogeneous and uniform composites. One common procedure is the integrating of pre-synthesized Fe_3O_4 particles into the lumens of disintegrated cellulose fibers with the aid of certain retention agent (Chia et al., 2006; Zakaria et al., 2005). After impregnation with an agitation and washing step to remove the unwanted particles, the filler particles are introduced exclusively into the lumen of the fibers while leaving the external surfaces free of filler. The filler is protected by the cell wall from dislodgement and the particles do not interfere with interfiber bonding. In addition, the resultant material shows relatively higher saturation magnetization and coercivity. However, the particles are spatially aggregated presumably due to the effect of the magnetic dipole within the short range. This represents a phenomenon commonly encountered in particle nanocomposite. Moreover, this morphology also lowers the mechanical properties, such as tensile strength and results in brittle material as compared to the host matrix (Zakaria et al., 2004; Middleton & Scallan, 1989).

To circumvent these problems, a modified pathway has been performed by using surface coating method. In this process, a colloidal suspension of magnetic nanoparticles is prepared firstly, and then cellulose fibers are dispersed in it and stirred vigorously. After successive washing and sonication, the particles remain bonded to the surface of the fibers. One significant finding is that, a new bonding phase of α-FeOOH is formed at the interface between the Fe_3O_4 particles and cellulose fibers. The formation of such a bridge is crucial to the integrity of heterogonous hybrid materials in processing and practical applications. In the meanwhile, it allows the inherent properties of the fiber, e.g. tensile strength and flexibility, to be retained while enabling the magnetic properties to the matrix. In addition, the surface of the fibers is completely and uniformly encapsulated by the nanoparticles (Small & Johaston, 2009).

Another approach to prepare magnetically responsive cellulose fibers involves synthesis of iron oxide particles within the cellulosic matrix itself by vigorously agitation of cellulose pulp in iron ion solution, and then iron ions are converted to iron oxide particles within cellulosic matrix by the addition of an excess NaOH solution. This preparation method is called in situ

co-precipitation method. This method offers better control of both the magnetic properties and the variety of magnetic particles that are incorporated into the final product than the lumen-loaded method (Marchessault et al., 1992a, 1992b). This method is widely used for the preparation of magnetic cellulose materials. Recently, a modification of the in situ co-precipitation method has been carried out. In this method, bacterial cellulose pellicles are firstly dipped in a solution of $FeCl_2 \bullet 4H_2O$, followed by dipping in a fresh solution of NaOH. The suspension is then heated in a water bath at 65 °C, followed by adding H_2O_2 solutions. Finally, samples are washed with distilled water. By using this method, the individual reaction is exclusively occurred step by step inside the bacterial cellulose. However, this stepwise dipping process still has some drawbacks. The obtained samples show the non-uniform dispersion of the precipitated nanoparticles across the cross-sectional area of bacterial cellulose. Formation of the darker skin at the surface results from the predominant forming of ferrites at the surface of the processed bacterial cellulose. Moreover, the dipping process is done under ambient condition. As a result, the presence of oxygen gas in the atmospheric air promotes the formation of maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). In order to make homogeneous dispersion and control the crystalline phase of magnetic nanoparticles in cellulose matrix, ammonia gas-enhancing in co-precipitation method operated in a closed system without oxygen has been used (Katepetch & Rujiravanit, 2011). The use of ammonia gas, instead of conventional aqueous basic solutions, can prevent the magnetic particles from accumulation at the surface of cellulose fibers, resulting in the homogeneous dispersion of the magnetic nanoparticles throughout the cellulose matrix. Accordingly, the as-prepared magnetic nanoparticles-incorporated cellulose sheet exhibits the uniform magnetic properties throughout the cellulose matrix. Moreover, the homogeneous dispersion of the magnetic nanoparticles throughout the cellulose matrix can enhance the percent incorporation of magnetic nanoparticles into cellulose samples, leading to high and uniform magnetic properties throughout the matrix of cellulose. Regarding to the use of cellulose pellicle and ammonia gas-enhancing in situ co-precipitation method, magnetic particles in the crystal form of magnetite (Fe_3O_4) are obtained and the diameter of the as-synthesized magnetic particles are ranged in nanoscale. The average particle size of the magnetic nanoparticles is in the range of 20–39 nm. The particle size and particle size distribution of magnetic nanoparticles are controllable by adjusting the concentration of aqueous iron ion solution. The saturation magnetization of the magnetic nanoparticle-incorporated cellulose sheet ranges from 1.92 to 26.20 emu$\bullet$g^{-1} with very low remnant magnetization (0.15–2.67 emu$\bullet$g^{-1}) and coercive field (40–65 G) at room temperature. Moreover, the responsiveness to an externally applied magnetic field of the magnetic nanoparticle-incorporated bacterial cellulose sheet is exhibited by its deflection in the direction of increasing magnetic field.

Magnetic cellulose fibers can also be obtained by adding ferro-magnetic powders into the cellulose solution, and then spun into fibers. This technique is one of the most effective methods of imparting new features to fibers as it guarantees stability of their properties, due to the fact that the stabile magnetic modifier is firmly integrated in the polymer matrix, and its percentage content does not change while using the fibers. N-methylmorpholine-N-oxide hydrate (NMMO) is a direct solvent for cellulose, a ferromagnetic compound can be added into the solution, and magnetic cellulose fibers can be spun directly from the mixed solution

(Rubacha et al., 2007). The obtained composite fibers can be used to build textile magnetic coils with a textile core. The magnetic properties of the composite fibers depend on the kind of implemented magnetic filler and the percentage content by volume in the fiber matter, and the composite fibers have an increase in the efficiency of shielding the magnetic field. However, mechanical mixing magnetic fills into dissolved cellulose solution often results in an inhomogeneous dispersion of particles in the cellulose matrix, thus considerable attention has been paid to the in situ chemical synthesis of metal nanoparticles in polymer matrices. In our previous works, 7wt% NaOH/12wt% urea aqueous solvent at low temperature is used for cellulose dissolving, and regenerated cellulose fibers can be spun from this solution (Chen et al., 2006; Mao et al., 2008). The cellulose fiber at swollen state exhibits an interpenetrating macroporous structure with a mean pore diameter of about 150 nm. This unique structure makes the porous structured cellulose fibers can be used as reacting sites for the in situ synthesis of inorganic nanoparticles. Magnetic Fe_2O_3 nanoparticles can be synthesized in situ in the cellulose fibers for the preparation of magnetic cellulose fibers (Liu et al., 2008a, 2008b), as it is shown in Fig. 1. The synthesized Fe_2O_3 nanoparticles with a mean diameter of 18 nm are uniformly dispersed in the cellulose matrix. There has strong interaction between Fe_2O_3 nanoparticles and cellulose matrix, the composite fibers are kept in water for a long time, and the Fe_2O_3 nanoparticles can hardly move out from the composite fibers. The composite fibers exhibit improved mechanical strength and a strong capability to absorb UV rays, superparamagnetic properties, as well as a relatively high dielectric constant; it indicated that the composite fibers can be used as protective materials for low frequency magnetic shielding.
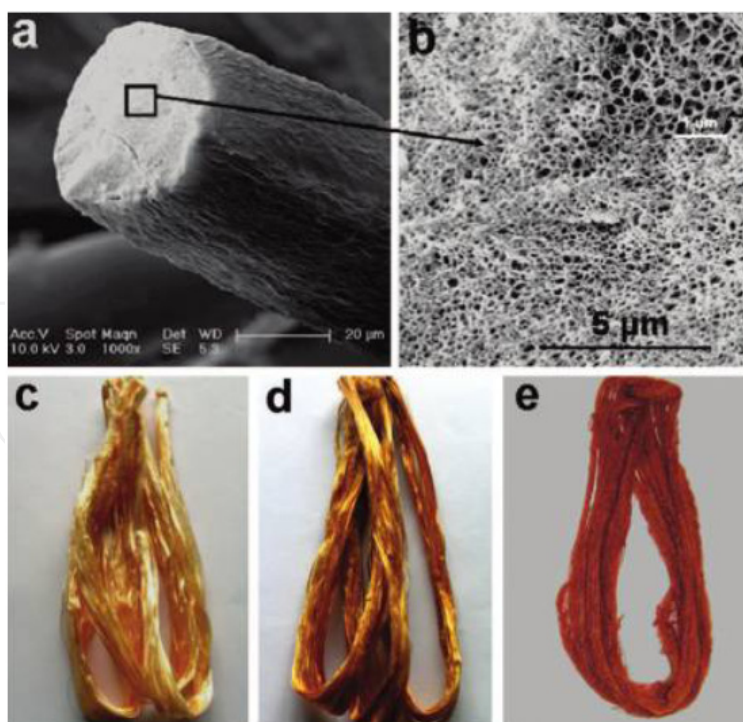

Figure 1. SEM images of surface (a) and cross section (b) for a single swollen RC (regenerated cellulose) fiber (insert is its enlarged image and the scale bar is 1 μm), as well as photographs of the composite fibers F001($FeCl_3$, 0.01M) (c), F01 ($FeCl_3$, 0.1M) (d), and F05($FeCl_3$, 0.5M) (e), respectively.

3. Magnetic cellulose films

Cellulose products are used traditionally in paper, packagings and artificial fibers, but technologies such as magnetic nanopapers open up opportunities for entirely new product areas. By using the lumen-loading technology, commercially available magnetic pigments can be introduced into the lumens of softwood fibers from which magnetic paper may be prepared. Lumen-loaded fibers act as magnetic dipoles allowing manipulation of fiber orientation in papermaking (Marchessault et al., 1992b). Another classic mixing of magnetic nanoparticles in the cellulose solution often results in the aggregation of magnetic nanoparticles in the composite films, because of the interparticle dipolar forces worsens their dispersion, which often decreases the properties of the composites and the single function of the magnetic nanomaterials. Precipitation of nano-sized ferrite (Fe_3O_4 and $CoFe_2O_4$) particles with the presence of cellulose fibers has also been used to produce films with good magnetic properties (Chia et al., 2008). The magnetic properties of the films increased with the loading of the magnetic particles. The coercivity of the magnetic films prepared with $CoFe_2O_4$ is higher than that with Fe_3O_4, and the thermal stability of the magnetic film depends on the degree of crystallinity of the precipitated particles. The magnetic particles deposited on the surface of the fibers have detrimental effects on the film strength. However, it is difficult to control the dispersion or particles size of the loaded magnetic particles for the above mentioned methods.

An interesting advance in the development of nanofibril cellulose (NFC) template materials may further enable nanocomposites to have tunable properties and open up many new multifunctional utilities. In-situ precipitation of the magnetic nanoparticles onto the individual cellulose nanofibrils has been used for the preparation of magnetic cellulose films (Galland, 2012). In this process, aqueous nanofibril suspension is used for magnetic functionalization. This method is based on aqueous co-precipitation of cobalt and iron species by forced hydrolysis to form cobalt-ferrite ($CoFe_2O_4$) magnetic nanoparticles. The stable suspension of NFC is favorable for the black suspension of magnetic NFC, and it is then used for membrane formation by a suitable vacuum filtration procedure. In the magnetically functionalized cellulose nanofibril networks, the processing conditions have a major effect on size distribution of magnetic nanoparticles, with the interesting observation that presence of NFC during precipitation results in smaller particle formation. In turn, this directly has an influence on magnetic properties of the material, with e.g. reduced coercivity for materials with smaller nanoparticles. The introduction of nanoparticles results in increased porosity and reduced interaction between fibers, which acts negatively on stiffness and strength of the magnetic nanopaper membranes. But ductility is preserved leading to remarkable tough nanocomposite materials.

Another alternative method is the in situ co-precipitation method by using the porous structured cellulose films as reacting sites. The cellulose hydrogel films prepared from LiOH/urea and NaOH/urea aqueous solution have unique fibrous network structure. The fibrous network structure, apart from providing high mechanical strength, offers macro/mesoporous spaces which can be used as reaction chambers for precipitation of

nanoparticles with the fibers providing a support structure to hold the particles. (Liu et al., 2006, 2011a, 2012a). In this method, cellulose films are immersed into $FeCl_2$ or $FeCl_3$ solution firstly and metal ions can be readily impregnated into the cellulose films through the pores. The incorporated Fe^{2+} ions can be bound to cellulose macromolecules via electrostatic interaction, because the electron-rich oxygen atoms of polar hydroxyl of cellulose are expected to interact with electropositive transition metal cations. When the films are treated with aqueous NaOH solution, Fe_2O_3 nanoparticles can be synthesized in the cellulose scaffolds in situ. The obtained Fe_2O_3 nanoparticles in the composite films prepared from $FeCl_2$ or $FeCl_3$ solution are γ-Fe_2O_3. The Fe_2O_3 nanoparticles are plate-like, and distribute randomly in the cellulose matrix before drying. It is different from those reported works about in situ synthesis of inorganic nanoparticles in a polymer matrix. In order to clarify the mechanism for the formation of the plate-like inorganic nanoparticles, Fe_3O_4, CdS, $Co(OH)_2$ nanoparticles have been synthesized from different precursors through the same pathway (Liu et al., 2011b, 2011c; Zhou et al., 2009). It indicates that the prepared nanoparticles are irregular particles and are homogeneously dispersed in the cellulose matrix. The possible mechanism for the formation of plate-like magnetic nanoparticles is ascribed to the non-negligible magnetic dipole-dipole interactions between the magnetic nanoparticles, transforming from $Fe(OH)_3$ or $Fe(OH)_2$ to Fe_2O_3. The cellulose films that immersed into $FeCl_2$ or $FeCl_3$ solution and Fe^{2+}-cellulose or Fe^{3+}-cellulose are formed, when treated with NaOH. $Fe(OH)_3$ or $Fe(OH)_2$ are obtained in the cellulose matrix firstly. After drying, they transform into Fe_2O_3 nanoparticles. During this process, there is an anisotropic growth happens to the nanoparticles. While for the preparation of Fe_3O_4/cellulose films, Fe_3O_4 nanoparticles are directly formed in the cellulose matrix when treated with NaOH solution, therefore, the morphology of the magnetic nanoparticles is irregular particles, which agrees well with the reported works about the preparation of inorganic nanoparticles in polymer matrix from one-step method. The concentration of $FeCl_2$ or $FeCl_3$ solution has little influence on the crystal structure and morphology of the Fe_2O_3 nanoparticles, but had an obvious influence on the content of the Fe_2O_3 nanoparticles in cellulose films. The Fe_2O_3 nanoparticles in composite films that dried at ambient conditions distribute in a regular way, and the composite films have an obvious magnetic anisotropy property, while for the freeze-dried composite films, the Fe_2O_3 nanoparticles distribute randomly, and the resulting composite films displayed superparamagnetic properties without magnetic anisotropy. This interesting phenomenon may be ascribed to the shrinkage of the composite films during drying process and the magnetic dipolar-dipolar interactions between the magnetic nanoparticles. The size of the Fe_2O_3 nanoparticles is far smaller than that of the macropores of the wet cellulose film. Magnetic nanoparticles can rotate freely, and randomly align within the pores at wet state. When it is fixed and dried in air, the composite films only shrink in the longitudinal direction from 300 μm in wet state to about 30 μm in dry state. Furthermore, there is non-negligible magnetic dipole-dipole interaction between the magnetic nanoparticles, leading to the regulative distribution of the nanoparticles. In order to clarify the regular distribution behavior of the Fe_2O_3 nanoparticles in the cellulose matrix, an exo-magnetic field (static and dynamic magnetic field) is applied during the drying process of the composite films at ambient conditions. The regular distribution of Fe_2O_3

nanoparticles in cellulose matrix has been destroyed in the exo-magnetic field, and the dynamic exo-magnetic field has a more obvious effect on the distribution of Fe_2O_3 nanoparticles than that of static exo-magnetic field. The composite films prepared from static-magnetic field have weak ferromagnetic properties, while the composite films prepared from dynamic exo-magnetic field display superparamagnetic properties without magnetic anisotropy, which indicates that magnetic filed has an influence on the distribution of the Fe_2O_3 nanoparticles in cellulose matrix. The effects of different forces on the distribution of the magnetic nanoparticles in cellulose matrix are characterized by using TEM, as it is shown in Fig. 2. Moreover, the influence of uniaxial drawing on the distribution of Fe_2O_3 nanoparticles has been investigated. Interestingly, there is no rearrangement of the Fe_2O_3 nanoparticles in cellulose matrix happened after being drawing, and the distribution of Fe_2O_3 nanoparticles are destroyed, as it is shown in Fig. 3. With an increase of the draw ratio, the irregularity of the Fe_2O_3 nanoparticles in cellulose matrix is increased, and the magnetic anisotropy of the resulting composite films is decreased. The porous structure of the regenerated cellulose filmsare destroyed by uniaxial drawing, therefore, the rotation of the Fe_2O_3 nanoparticles in the pores of cellulose films is hindered, leading to the irregular distribution of the Fe_2O_3 nanoparticles in cellulose matrix. These results support that a transformation process took place in the synthesized Fe_2O_3 from $Fe(OH)_3$ or $Fe(OH)_2$. The magnetic dipole-dipole interaction between the Fe_2O_3 nanoparticles is the important factor of the regular distribution of the Fe_2O_3 nanoparticles in cellulose matrix.

Bacterial cellulose also can be used for the preparation of magnetic cellulose films. Bacterial cellulose is synthesized in the form of fibrous structure which constitutes a three-dimensional non-woven network of nanofibers with diameters less than 100 nm, and it is much smaller than the diameter of typical plant cellulose bundles (ca. 100nm). Bacterial cellulose fiber has the same chemical structure as plant cellulose, but has higher specific surface area than the cellulose nanofibers, indicating that bacterial cellulose has much more surface hydroxyl and ether groups than plant cellulose. These hydroxyl groups make up of active sites for metal ion adsorption (Li et al., 2009). Moreover, the porous structure of nanofibrous bacterial cellulose provides large amount of sub-micron pores. The precipitated metal nanoparticles are stabilized by the sub-micron pores of the bacterial cellulose, leading to good dispersion of the as-synthesized nanoparticles (Zhang et al., 2011), the detail preparation process is shown in Fig. 4. Magnetic ferrite nanoparticles loaded bacterial cellulose (BC) membranes have been synthesized earlier. The size of the ferrite particles varies from ~2 to 20 nm with the particles existing both individually and as aggregates in the matrix. These magnetic BC membranes are superparamagnetic at room temperature with no coercivity or remanence (Raymond et al., 1994, 1995; Sourty et al., 1998; Small & Johnston, 2009).

The precipitation reaction method of loading magnetic particles in the BC matrix does not allow complete control of particles formation-nucleation, growth, aggregation, and density, if surfactant molecules which cap the metal particles are not used. As a result, the synthesized particles may have a broad distribution of sizes and different interparticle
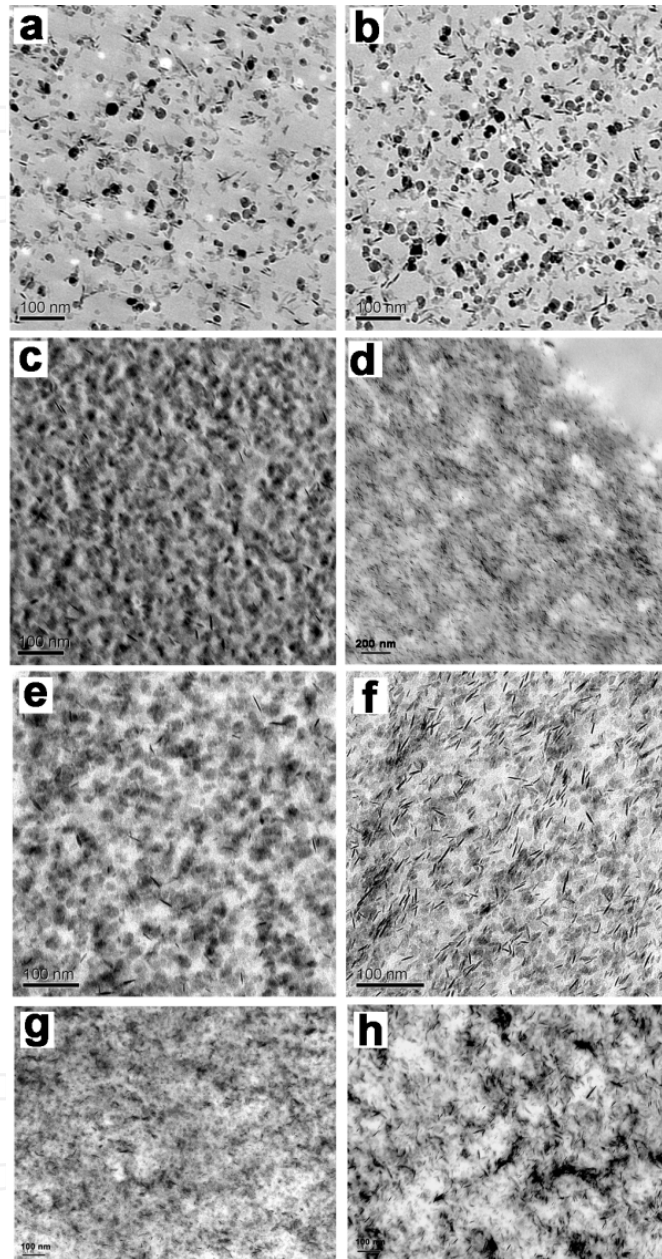
Figure 2. TEM images of the composite film prepared by freeze-dried (a, b) and being dried at ambient conditions (c, d); (a, c), the slice was parallel to the film plane; (b, d), the slice was perpendicular to the film plane, and the composite film fixed on a PMMA plate with a static magnetic field and air-dried. (e), the slice was parallel to the film plane; (f), the slice was perpendicular to the film plane, and the composite film dried on a rotating magnetic field at room temperature. (g), the slice was parallel to the film plane; (h), the slice was perpendicular to the film plane.
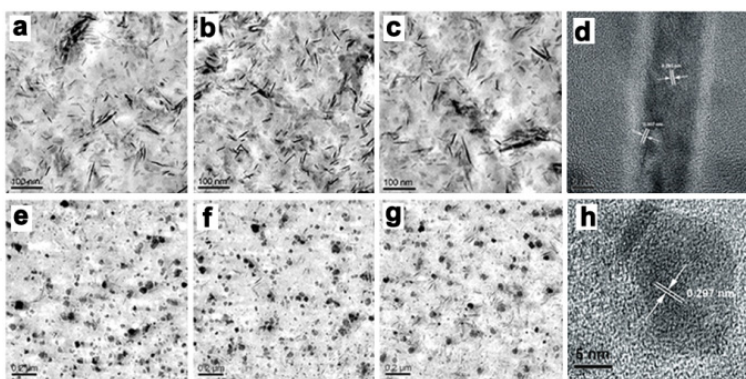
Figure 3. TEM images of the composite films with draw ratios different from 1.04 to 1.22: a, b, c are the slices that perpendicular to the surface of the films, e, f, g are the slices that parallel to the surface of the films, d and e were HRTEM images of c and g, respectively.
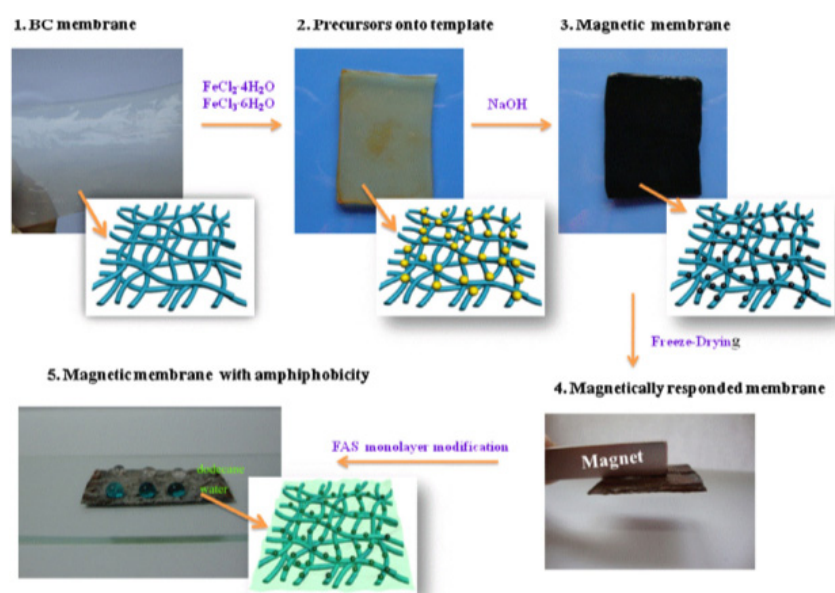

Figure 4. Schematic illustration for the flexible magnetic nanohybrid membrane from bacterial cellulose nanofibers.

distances. Recently, metallic magnetic particles have also been loaded into BC by precipitating from the respective salt solutions using $NaBH_4$, KH_2PO_2, and NaH_2PO_2 as reducing agents. The reaction conditions, type of reducing agent and the reduction medium are found to influence the chemical composition, crystallinity, and size of the metal particles. The saturation magnetization of Ni impregnated cellulose at room temperature is found to be very small compared with that of bulk due to P and B contamination in Ni as well as lack of crystallinity, amorphous structure. The amorphous Ni transforms into crystalline Ni on heat treatment. In the case of Co, NaH_2PO_2 reduction is found to result in the formation of ordered crystals with size of 5-6 nm and aggregates with micron size. The Co loaded cellulose is found to be ferromagnetic at room temperature with obvious coercivity (Pirkkalainen et al., 2007, 2008). The room temperature reduction in an aqueous environment is also an effective method for the controlling synthesis of magnetic nanoparticle with small particle size (Vitta et al., 2010). The formation of crystalline Ni

nanoparticles with controlled particle size inside the bacterial cellulose along with $Ni(OH)_2$ has been performed. The nanocrystals have an equiaxed shape and are found both as individual particles as well as small aggregates depending on the porous network structure of cellulose matrix. The bacterial cellulose does not undergo any change and retains its crystal structure even after chemical reduction reaction. The Ni loaded bacterial cellulose is found to be ferromagnetic at room temperature with a saturation magnetization of 2.81 $emu \bullet g^{-1}$ which increases by an order of magnitude to 21.8 $emu \bullet g^{-1}$ at 1.8 K. The coercive field also increases by two orders of magnitude from 28 G at 300 K to 2900 G at 1.8 K. The zero field cooled magnetization however exhibits a superparamagnetic behavior with a peak at 20 K, the blocking temperature and this behavior is observed even in ac magnetization. The magnetization decreases with the increase of temperature up to 400 K, when extrapolated to high temperature using a power law indicates a Curie transition at 500 K, which is much lower than the Curie temperature of bulk Ni. The fraction of isolated superparamagnetic nanoparticles present in the composite is estimated from the saturation magnetization and is found to be ~88%. These results clearly highlight the presence of two separate magnetic phases, superparamagnetic, and ferromagnetic, and the role of various magnetic interactions in the collective magnetic behavior of Ni nanoparticles in the composite structure. Freeze-dried bacterial cellulose nanofibers can form porous structured scaffolds, which can also be used as a template for in-situ chemical reactions to form Co nanoparticles for the generation of a tunable multifunctional nanocomposite film. In this process, an extremely porous so-called aerogel which consists of only 2% cellulose fibrils and 98% pores is obtained, and then dip the porous cellulose aerogel into a saline solution and create the magnetic particles. The magnetic particles are 40 nm large and consist of cobalt ferrite. The particles bind very strongly with the cellulose. During the production process, it is possible to control the amount of magnetic particles that are formed. The porous nanopaper can also be compressed to different levels of porosity, due to obtain the required strength and the flexibility.

4. Magnetic cellulose microspheres

The use of superparamagnetic microspheres (SM) has been widely reported in various applications, such as biomedical research and technology (Šafařík & Šafaříková, 1999) and environmental protection (Yang et al., 2008; Atia et al., 2009), due to their remote responses to external magnetic fields. Ideal magnetic polymer microspheres must have high specific saturation magnetization, small size, narrow particle size distribution, biocompatibility, biodegradable, good chemical stability, rich functional groups on surface and simple process in preparation, cheap as shell. Cellulose, with high biocompatibility, good hydrophilic properties, and biodegradable natures, is a good candidate for magnetic nanocomposite.

Encapsulation of magnetic particles with cellulose polymers is the simple and classical method to prepare magnetic cellulose particles (Luo & Zhang, 2009). In our previous works, maghemite (γ-Fe_2O_3) nanoparticles are prepared. Subsequently, by blending it with cellulose solution and then millimeter-scale magnetic cellulose beads can be prepared via an optimal

dropping technology. In this method, other fillers, such as activated carbon (AC) can be added into the mixed solution for the preparation of composite cellulose beads with improved properties. The cellulose beads containing Fe_2O_3 nanoparticles exhibit sensitive magnetic response, and their recovery can be facilitated by applying a magnetic field. Dyes are adsorbed effectively by the AC/magnetic cellulose beads. The Fe_2O_3 nanoparticles and AC in the AC/magnetic cellulose beads can play important roles in both the formation of spherical shape beads and the improvement of the adsorption capacity. Furthermore, the sorbent can be regenerated and used repeatedly. The magnetic properties of the beads allow the separation from the effluent by applying a magnetic field, leading to the development of a clean and safe process for water pollution remediation.

As for the magnetic cellulose microspheres (MCMS), most of the attentions are focused on the absorption performance. The absorption capacity of MCMS is important for the applications point of view. According to Langmuir theory, the smaller the MCMS, the larger the surface area, thereby the stronger the absorption capacity. However, the crystalline structure of cellulose, due to the hydrogen bonds between and within its chains and the high molecular weight, make the treatment of cellulose very difficult. On one hand cellulose exhibits zero solubility in water and common organic solvents, except for some solutions (Fischer et al., 2003; Ass et al., 2006; Yoshida et al., 2005). On the other hand an ionic solution of cellulose shows considerable viscosity, which causes great difficulty in the dispersal of material into small drops. Under conditions without protection from chemical cross-linking or contact, magnetic fluids dispersed in cellulose solution are impacted in their stability as liquid drops and will easily collapse or coalesce, if dispersing strength solutions are used. As a consequence, the average size distribution of MCMS is most often reported from dozens to hundreds of micrometers (Wolf, 1997; Guo & Chen, 2005). If a critical condition could be found in which the drops could maintain both the smallest diameter and stability, MCMS can be fabricated with the maximum absorption capability. A theory of "the smallest critical size"(SCS) is proposed and tested for the first time as a guideline for forming the desired MCMS (Tang et al., 2010). It indicates that the diameter of the SCS of MCMS is 5.82 µm, while the IgG absorption capability of the MCMS with SCS is 186.8 mg/mL. An innovative approach developed by us has shown that a more controlled nanostructured morphology and geometrical shape of the magnetic cellulose microspheres can be obtained (Luo et al., 2009a), and the incorporated magnetic nanoparticles has an obvious influence on the microstructure of the obtained magnetic microspheres, as it is shown in Fig. 5. In this study, cellulose drops in a precooled aqueous solution of sodium hydroxide and urea are utilized to form regenerated cellulose microspheres (RCS) using sol-gel process. These porous beads are then used as microreactors, which permits in situ co-precipitation of Fe_3O_4 nanoparticles into the cellulose pores of RCS in a solution mixture of $FeCl_3$ and $FeCl_2$ to finally form magnetic regenerated cellulose microspheres (MRCS). This process is able to create MRCS about 6 um in diameter with embedded nanoparticles with particle size of 20 nm. Transmission electron microscopy (TEM) clearly shows that embedded Fe_3O_4 nanoparticles are dispersed uniformly inside MRCS matrix. These ideal nanostructures ensure that the micron-sized cellulose beads maintain the superparamagnetic property. Such beads can be magnetized and attracted to that field in the presence of an external
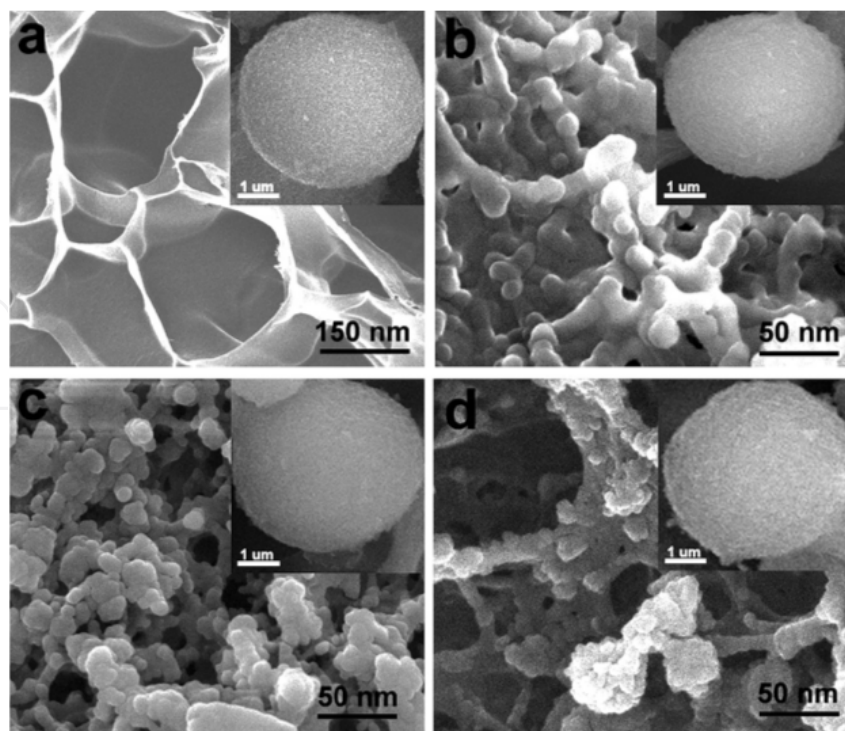
Figure 5. SEM images of the surface of the regenerated cellulose microspheres (RCS) (a), M10 (mixtured solutions of FeCl$_3$/FeCl$_2$ with concentration of 10mmol/5.2mmol) (b), M20(mixtured solutions of FeCl$_3$/FeCl$_2$ with concentration of 20mmol/10.6mmol) (c) and M30(mixtured solutions of FeCl$_3$/FeCl$_2$ with concentration of 30mmol/15.9mmol) (d). The insert illustrates the morphology of RCS and magnetic regenerated cellulose microspheres (MRCS).

magnetic field; however, they will not retain any magnetization when the external field is removed and can flow with the carrier medium like non-magnetic beads. As an embodiment, it demonstrates the magnetic-induced transference for targeting protein delivery and release using these nanocomposite beads.

In recent research aiming at a biomedical application, magnetic carriers based on proteins immobilized onto magnetic cellulose microspheres (MCMS) have also been widely used. The biospecific connection using a specific binding between a protein and the biomatrices displays an excellent repertoire of advantages, including convenient and simple preparation, elimination of toxic compounds, and highly efficient antibody utilization (Luo & Zhang, 2010; Hornes & Korsnes, 1990). The resulting extraction of a pure target molecule by this technique is both convenient and efficient. A novel method has developed for immobilizing antibodies onto MCMS using a cellulose binding domain–protein A (CBD–ProA) linkage, which allows for a one-step isolation of mRNA from eukaryotic cells and tissues (Gao et al., 2009). The produced CBD–SA fusion proteins display binding activities for both cellulose and biotin, and are endowed with superior attributes in the linkage between the MCMS and biotinylated oligo(dT). Using SA–CBD–MCMS for this application allows efficient and rapid isolation of mRNA from eukaryotic cells and tissues and represents an improvement over conventional, available techniques. The stability of the particles, especially the bound CBD to MCMS has been evaluated (Cao et al., 2007).

5. Magnetic cellulose hydrogels and aerogels

Magnetic responsive gels have become an interesting subject of study for several research groups. Cellulose hydrogels can be made stimuli-responsive which makes their study more interesting. Preparation of magnetic cellulose gels is similar to that of other filler-loaded networks. One way is to prepare and characterize magnetic particles separately and then to mix them with polymers, and the cross-linking takes place after mixing the polymer solution and the magnetic sol (Haas et al., 1993), one can precipitate well-dispersed colloidalsized particles in the polymeric material. The in situ precipitation can be made before, during, and after the cross-linking reaction (Mark, 1985). As these gels respond to magnetic stimuli, it can be readily applied in the areas of biotechnology/biomedicine, health care, catalysis, magnetic resonance imaging, and so on. Chatterjee and coworkers have developed a two-step synthesis of magnetic gel (Chatterjee et al., 2004). In the first step, hydroxypropyl cellulose particles are formed with surfactant-modified maghemite by the emulsion method. In the second step, these particles are cross-linked by a commercial cross-linking agent Zirmel M to give a network structure. By this mechanism of network formation, it is possible to introduce a homogeneous distribution of maghemite into the polymer matrix. These magnetic gels have a network of nanoparticles of hydroxypropyl cellulose (30–100 nm) and a homogeneous distribution of nanosized maghemite (~7 nm). The magnetic gel has magnetic moment in an applied field, due to the size distribution in maghemite, single blocking temperature can not be obtained at temperatures below room temperature. Superparamagnetic behavior is observed for the gel. The magnetic gel does not show any unique behavior in terms of the magnetic property though there is a possibility for obtaining different magnetic properties due to the restricted motion (Chatterjee et al., 2003). In order to improve the magnetic properties of the magnetic gels, a modified method has been performed. In this process, HPC is mixed with hexadecyl trimethyl ammonium bromide (CTAB) modified γ-Fe$_2$O$_3$ powder in sodium hydroxide solution (pH=12). The solution is then sonicated for 30s. When the solution become homogeneous, solid crushed pellets of NaOH are added to this solution and mixed thoroughly. A reddish brown gel is formed at pH 13 and can separate from the solution. With the decrease in pH (at pH 9), the gel break down and form a homogeneous dispersion of the HPC–γ-Fe$_2$O$_3$ complex. This brown dispersion again transformed into a gel with an increase in the pH to 13. The HPC can be loaded as much as 100% of its weight of iron oxide to form a complex structure. Therefore, a large value of magnetic moment is obtained from these gels. By this process of gelation with a magnetic material along with the cellulose polymer, heavy metals/metal oxides can be captured and separated with the help of an external magnet.

Cellulose aerogels, consisting of three-dimensional networks, are typically obtained by removing the liquid in cellulose gels under freeze drying or supercritical conditions (Li et al., 2011; Liebner et al., 2010; Kettunen et al., 2011). The unique properties like high internal surface, high porosity, low density, and with the additional advantages and characteristics of the renewable biopolymer cellulose makes the cellulose aerogel an interesting candidate for various applications. The combination of cellulose nanofibers and magnetic nanoparticles allows for the preparation of ultra-flexible porous magnetic aerogels. Strong cellulose nanofibrils derived from bacteria or wood can form ductile or tough networks that

are suitable as functional materials. A bacterial cellulose hydrogel with a large measured surface area is first freeze-dried into a porous cellulose nanofibril aerogel. The dried aerogel template is then immersed in an aqueous $FeSO_4/CoCl_2$ solution at room temperature before heating the system to 90 °C to thermally precipitate the non-magnetic metal hydroxides/oxides on the template. Heating changes the color from transparent to translucent orange. The precipitated precursors are converted into ferrite crystal nanoparticles on immersion in $NaOH/KNO_3$ solution at 90 °C, resulting in highly flexible magnetic aerogels that can sustain large deformations, as it is shown in Fig. 6. Micrographs of freeze-dried samples show that the nanoparticles are located on the bacterial cellulose nanofibril surfaces. Unlike solvent-swollen gels and ferrogels, the magnetic aerogel is dry, lightweight, porous (98%), flexible, and can be actuated by a small household magnet. Moreover, it can absorb water and release it upon compression. Owing to the flexibility, high porosity and surface area, these aerogels are expected to be useful in microfluidics devices and as electronic actuators (Olsson et al., 2010).

In our previous works, regenerated cellulose films that prepared from LiOH/urea or NaOH/urea aqueous solution also can be used as templates for the preparation of magnetic cellulose aerogels (Liu et al., 2012b). In this process, cellulose hydrogel films are immersed in freshly prepared aqueous solutions of $FeCl_3$ and $CoCl_2$ with a molar ratio of
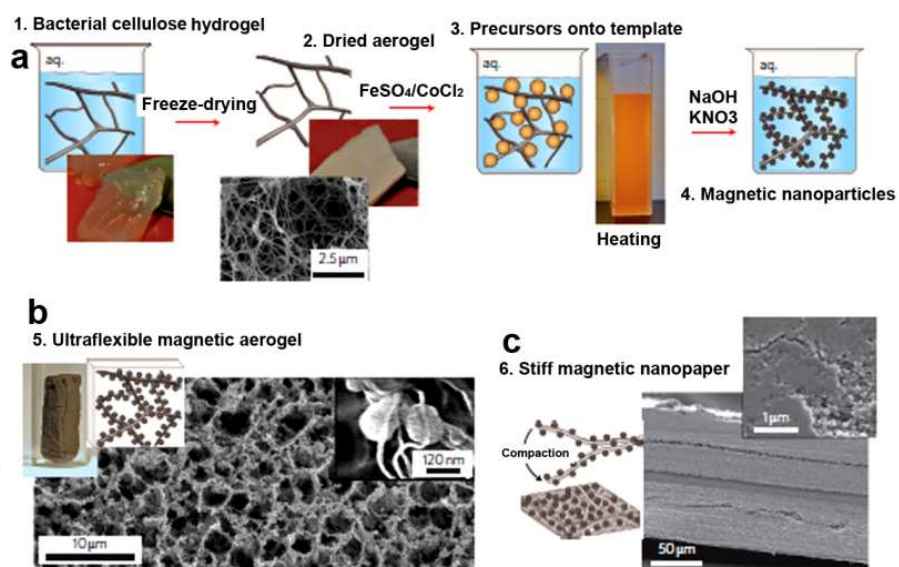

Figure 6. Synthesis of elastic aerogel magnets and stiff magnetic nanopaper. a, Schematic showing the synthetic steps. 1, Bacterial cellulose hydrogel (1 vol%) is produced by Acetobacter xylinum FF-88. 2, Photograph, scanning electron microscopy (SEM) image and schematic of a cellulose aerogel after freeze-drying. 3, Immersion of the dry aerogel in aqueous $FeSO_4/CoCl_2$ solution for 15 min followed by heating to 90 °C for 3 h transforms soluble Fe/Co hydroxides into insoluble complexes. 4, Cellulose networks subjected to $NaOH/KNO_3$ solutions at 90 °C immediately change in colour from red to orange to black as nanoparticles precipitate on the cellulose nanofibrils. b, Representative SEM image of a 98% porous magnetic aerogel containing cobalt ferrite nanoparticles after freeze-drying. Right inset: nanoparticles surrounding the nanofibrils. Left insets: photograph and schematic of the aerogel. c, SEM image of a stiff magnetic nanopaper obtained after drying and compression. Inset: higher magnification image.

[Fe]/[Co] = 2 for 24 h, it allows a homogeneous distribution of the precursor solution obtained inside the cellulose networks. The hydrogel films contain precursor solution is subsequently treated with NaOH solution (2 mol•L^{-1}). The color of the samples changes from red/orange to black immediately, and inorganic nanoparticles can be formed in the cellulose matrix. The composite cellulose films are washed with water to remove counter-ions, and then freeze-dried, and magnetic composite aerogels are obtained. The magnetic aerogels are light-weight, flexible. The porosities of the composite aerogels are ranged from 78 to 52%. The internal specific surface areas and densities of the aerogels are around 300–320 m^2•g^{-1} and 0.25–0.39 g•cm^{-3}, respectively. The content of the incorporated CoFe$_2$O$_4$ nanoparticles increases with the increase of the CoFe$_2$O$_4$ precursor concentration, but the particle size change hardly. The incorporated CoFe$_2$O$_4$ nanoparticles changed the microstructure of the cellulose aerogels obviously, making them different to those of the composite aerogels. The hybrid aerogels show superparamagnetic behaviors, improved mechanical properties with respect to the corresponding inorganic aerogel. Because the concepts of the process are simple and cellulose is sustainable and readily available in large quantities from plants (wood). Thus the suggested route is suitable for industrial-scale production and may be used with many types of nanoparticles, which will open up the new application fields of cellulose based functional materials.

6. Conclusion

The magnetic cellulose composites hold great promise in offering both multiple functionalities and economic functions. Cellulose is not only abundant, renewable, biodegradable, but also the production process is simple. Thus it is very likely to become an economically viable technology, in addition to having profound benefits to sustainable technology and also to our environment. With the versatile properties and a large variety of potential applications revealed in early developments, these new materials have the potential to impact many advanced multifunctional areas such as electromagnetically driven printing, "smart" magnetic biochips, novel localized drug delivery and other applications yet to be envisioned. Furthermore, this research area is expected to grow rapidly, and dramatic improvements in materials' functions will be achieved in the years to come, especially in furthering advanced applications as well as the pursuit of environmental friendly green technologies worldwide.

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