Strong transparent magnetic nanopaper prepared by immobilization of Fe$_3$O$_4$ nanoparticles in a nanofibrillated cellulose network

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Nanofibrillated cellulose (NFC) is highly regarded as a popular new material due to its impressive mechanical properties, great potential for functionalization, easy accessibility, and environmental sustainability as precursors. The immobilization of nanoparticles in an NFC network is an effective way to fabricate transparent functionalized nanopaper. In this work, a uniform, flexible, magnetic nanopaper is prepared by the immobilization of Fe$_3$O$_4$ nanoparticles in an NFC network in an aqueous medium. The resulting transparent magnetic nanopaper (TMNP) possesses excellent transparency and magnetic properties combined with outstanding mechanical performance and flexibility. The combination of these characteristics makes TMNP an excellent candidate for magneto-optical applications.

Introduction

Transparent magnetic materials play an important role in bioanalytical applications, magneto-optical switches, magneto-optical sensors, modulators, optical circulators, and optical isolators.$^{1-3}$ Preparation of transparent magnetic materials with excellent magnetic, optical, mechanical, and thermal properties has attracted great interest over the last twenty years.$^{4-7}$ A transparent magnetic thin polyvinyl alcohol (PVA) film is prepared by spin coating a solution of magnetite fine particles on glass substrates, and followed by drying at 80 °C and solidifying at 200 °C in a magnetic field.$^4$ Hyon Min Song obtained transparent magnetic composites by covalently bonding liquid crystals to the siloxane backbones and then linking them to dopamine-functionalized Fe$_3$O$_4$ nanocrystals.$^5$ Yibo Dou fabricated transparent magnetic films via layer-by-layer assembly of layered double hydroxide nanoplatelets, PVA and a styrylbiphenyl derivative.$^6$ Co-doping of TiO$_2$ thin films as well as selective oxidation of a metallic glass are also the reported methods to obtain transparent magnetic films.$^7$ The main design approach is to embed magnetic particles into a transparent matrix, such as polymers, silica gels, glass, and ion exchange resins.$^8-13$

Embedding magnetic particles into a transparent matrix is a relatively easy procedure and the resulting composites provide necessary stability and processability for applications. However, the challenge for this method is that magnetic particles are unable to be uniformly dispersed in the organic matrix due to agglomeration.$^{14}$ Only a low concentration of magnetic particles can be dispersed in the matrix, resulting in high transparency but poor magnetic properties. Recently, the stability of high quality magnetic particles has been increased through the use of monomeric stabilizers, or by coating iron oxide nanoparticles with inorganic particles (silica or gold) and organic polymers (like PVA, alginate and chitosan).$^{14,15}$ In situ synthesis of magnetic particles is another way to reduce agglomeration during composite processing because the aggregation of nanoparticles is prevented via the organic matrix and modification.$^{8,16}$ The magnetic and optical properties of magnetic nanocomposites mainly depend on the magnetic particle size and magnetic particle loading. Nanosized particles are favored in the transparent nanocomposite preparation because the particle size is smaller than the wavelength of visible light. Small diameter magnetic particles with a narrow size distribution are important to guarantee transparency and favorable magnetic properties. Additionally, a higher concentration of magnetic particles in the matrix maintains good magnetic properties, but decreases transparency.

The mechanical properties of magnetic nanocomposites also need to be taken into account for applications. The mechanical properties are mainly determined by the matrix material. Nanocellulose prepared from plant, bacteria, or selected marine creatures is being praised for its high aspect ratio, high specific
surface area, impressive mechanical properties, and low weight.\textsuperscript{17–24} 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) oxidized nanocellulose is stable in water without aggregation due to the introduction of charged groups (–COO\textsuperscript{−}) on the fiber surface.\textsuperscript{25} The charged groups and hydroxyl groups decorating the nanocellulose surface are sites for chemical functionalization and adsorption of polymers and particles through electrostatic forces and hydrogen bonding.\textsuperscript{26–28} R. T. Olsson prepared magnetic aerogels using freeze-dried bacterial cellulose nanofibril aerogels as templates to adsorb metal ions for CoFe\textsubscript{2}O\textsubscript{4} \textit{in situ} synthesis.\textsuperscript{29} Another emerging application of nanocellulose is making transparent paper for electronic device substrates.\textsuperscript{30} The biocompatibility of nanocellulose makes it suitable for life science applications including use with human fibroblasts.\textsuperscript{31} Nanocellulose forms a three-dimensional (3D) network in the paper, which is good for the immobilization of particles. Based on these concepts, we fabricated highly transparent free-standing magnetic nanopaper with excellent mechanical and magnetic properties. Nanofibrillated cellulose (NFC) was first used as a stabilizer for Fe\textsubscript{3}O\textsubscript{4} NPs to make uniformly dispersed, stable Fe\textsubscript{3}O\textsubscript{4} NPs in aqueous medium. The transparency, tensile strength and magnetic properties of the transparent magnetic nanopaper (TMNP) are some of the highest reported values among recently prepared TMNPs. The excellent properties and green and biocompatible nature of our TMNP have great potential in applications including magneto-optical applications, electromagnetic shielding, and \textit{in vitro} magnetic separation in the life sciences.\textsuperscript{11,32–34}

Experimental

Magnetic nanoparticles and NFC preparation

Fe\textsubscript{3}O\textsubscript{4} nanoparticles (NPs) were obtained from Nanjing Emperor Nano Material Co., Ltd., China. The particles are spheres with an average particle size of 20 nm, and a specific surface area of greater than 60 m\textsuperscript{2} g\textsuperscript{−1}.

NFC was prepared according to an existing method.\textsuperscript{34} Briefly, TEMPO (78 mg), sodium bromide (NaBr, 514 mg) and 5 g Kraft bleached softwood pulp were mixed together. TEMPO oxidation of cellulose was triggered by adding sodium hypochlorite (NaClO) at room temperature under gentle agitation. During the oxidation process, the pH was maintained at 10.5. After TEMPO treatment, the fibers were thoroughly washed with distilled water and disintegrated by one pass through a Microfluidizer M-110EH (Microfluidics Ind., USA) to obtain a NFC suspension.

Transparent magnetic nanopaper preparation

First, NFC and Fe\textsubscript{3}O\textsubscript{4} NPs were uniformly dispersed and mixed together with weight ratios of 95 : 5, 90 : 10 and 80 : 20 for transparent magnetic paper samples containing different Fe\textsubscript{3}O\textsubscript{4} loadings. The resulting dispersion was poured into a Buchner funnel for filtration. Finally, a gel cake formed on top of the filter membrane, and the cake was dried under pressure. After drying, magnetic nanopaper samples with a diameter of 90 mm were obtained. The paper thickness and diameter were easily tailored by controlling the mixture volume and filter size in the paper forming process. The transmittance of TMNP was analyzed with a Lambda 35 UV-Vis Spectrometer (PerkinElmer, USA). The tensile strength of the TMNP was characterized with a Tinius Olsen H25KT universal material strength testing machine. Each specimen was cut into a strip of 5 mm × 50 mm.

Results and discussion

The optical transmittance, magnetic properties, and mechanical properties of optical composites are particle size dependent; a smaller particle size will improve light transmittance and magnetic and mechanical performance. Smaller particles, however, possess a higher specific surface area and as a result are more prone to agglomeration.\textsuperscript{35} Thus, a uniform dispersion of magnetic particles with a smaller size in an NFC suspension is critical for tuning the desired properties of functionalized nanopaper. Scheme 1 illustrates the TMNP structure. In this work, Fe\textsubscript{3}O\textsubscript{4} NPs are immobilized in an NFC fiber network through interactions between carboxyl groups/hydroxyl groups of NFC and surface hydroxyl groups of Fe\textsubscript{3}O\textsubscript{4} NPs.\textsuperscript{36–37} The Fe\textsubscript{3}O\textsubscript{4} NPs used are spherical with an average particle size of 20 nm. The prepared NFC is about 10 nm in diameter and hundreds of nanometers long, as measured using a transmission electron microscope (TEM) (Fig. 1 a). After TEMPO oxidation, large amounts of charged carboxyl groups (–COO\textsuperscript{−}) are introduced onto the surface of the NFC fibers. The surface carboxyl groups generate repulsive forces between NFC fibers, making them stable in water without aggregation. The TMNP is made by first adsorbing the Fe\textsubscript{3}O\textsubscript{4} NPs onto the NFC fibers in solution and then filtering out the solvent. The Fe\textsubscript{3}O\textsubscript{4} NPs are easily adsorbed onto NFC, and the repulsive forces generated by surface carboxyl groups between NFC fibers provide stability in water. During filtration, NFC deposits on the filter paper and forms a 3D gel network, with the magnetic particles wrapped by NFC. A final drying step fixes the magnetic particles within the fiber network. The surface carboxyl groups and hydroxyl groups in the formed fiber network make NFC an excellent matrix for immobilization of not only Fe\textsubscript{3}O\textsubscript{4} NPs but also other nanoparticles as well. This method will allow for the functionalization of nanopaper with a wide range of nanomaterials. Here, the NFC also acts as a dispersant and a stabilizer for Fe\textsubscript{3}O\textsubscript{4} NPs in water. We prepared 0.2 wt% Fe\textsubscript{3}O\textsubscript{4} NP water solutions with 10 wt% NFC (relative to the Fe\textsubscript{3}O\textsubscript{4} NP weight) to investigate the stability of the solution. The Fe\textsubscript{3}O\textsubscript{4} NP/NFC solution was stable after 20 days, whereas Fe\textsubscript{3}O\textsubscript{4} NP solutions without NFC settled out and the solution became clear as observed in Fig. 1(b). The obtained TMNP is 26 µm thick with Fe\textsubscript{3}O\textsubscript{4} NPs uniformly dispersed. Fig. 1(c) shows the cross-section of TMNP and Fig. 1(d) is the element map of Fe in the TMNP cross-section. Fe uniformly dispersed throughout the cross-section indicates the uniform dispersion of Fe\textsubscript{3}O\textsubscript{4} NPs in the whole paper.

The fabricated TMNP is transparent in visible light with excellent flexibility. In Fig. 2(a) the words “cellulose paper” are clearly visible under the bent paper. This is attributed to the excellent transmittance of nanopaper. Reducing the diameter of paper fibers will decrease optical scattering, improving the transparency of paper.\textsuperscript{34} Pure nanopaper composed of fibers
with a diameter on the order of 10 nm possesses a high transmittance of 93% at a wavelength of larger than 550 nm. Nanopaper also possesses a 3D fiber network structure with high flexibility. The Fe$_3$O$_4$ NPs are uniformly fixed in the network through chemical bonding and mechanical wrapping. The transparency of the magnetic nanopaper can be tailored by Fe$_3$O$_4$ NP loading. Nanopaper with a lower Fe$_3$O$_4$ NP loading exhibits higher transparency. As the weight ratio of Fe$_3$O$_4$ NPs is increased from 0 to 10%, the letters beneath the paper are more obscured, as shown in Fig. 2(b). At the same time, the color changes from light yellow to dark brown, due to the dark color of Fe$_3$O$_4$ NPs. Fig. 2(c) shows the transmittance curves of three TMNP samples. As the Fe$_3$O$_4$ NP loading increases, the transmittance decreases in the 350–1100 nm wavelength region. This is mainly due to the optical absorption of Fe$_3$O$_4$ NPs. The highest transmittance is 86%, which is good enough to be applied in transparent magnetic devices.

An entire TMNP sample with a Fe$_3$O$_4$ NP loading of 10% is easily lifted with a household magnet, as shown in Fig. 3(a). In addition, the TMNP is writable; conductive ink can be used to write on it through a ballpoint pen as shown in Fig. 3(b). The TMNP with a written circuit is an excellent magnetic switch as...
is zero. The magnetic (Oe), (a) parameter of magnetic paper, the paper moved to contact with Sn wire and lighted the LED, showing the magnetic switch, there is a gap between conductive magnetic paper.\(^{41}\) The TMNP measured at room temperature.\(^{15}\)

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The best fit to eqn (1) is obtained by a nonlinear fitting of and using the Polymath software. The \(a\) for the as-received \(\text{Fe}_3\text{O}_4\) NPs and magnetic paper with a \(\text{Fe}_3\text{O}_4\) nanoparticle loading of 5, 10, and 20 wt% is 3.24 × 10\(^{-3}\), 3.63 × 10\(^{-3}\), 3.46 × 10\(^{-3}\), and 3.32 × 10\(^{-3}\) T\(^{-1}\), respectively. According to eqn (2), the magnetic moment \(\mu\) can be calculated from \(a\). The \(\mu\) of the as-received \(\text{Fe}_3\text{O}_4\) NPs and TMNP with \(\text{Fe}_3\text{O}_4\) NP loadings of 5, 10, and 20 wt%, is 1.41, 1.56, 1.49, and 1.43 \(\mu_B\), respectively. The calculated \(\mu\) does not change much between the four samples, indicating that NFC has little effect on the magnetic moment of the \(\text{Fe}_3\text{O}_4\) NPs.

Another noticeable property of the transparent magnetic paper is the outstanding mechanical strength. The mechanical strength of cellulose paper is mainly affected by fiber orientation, fiber strength and the bonding strength between fibers. Nanocellulose paper possesses an extraordinarily high modulus of 10 GPa, due to the abundant hydroxyl groups on the surface.\(^{16}\) The tensile strength of pure nanopaper is 213.5 MPa. When \(\text{Fe}_3\text{O}_4\) NPs are added into nanopaper, they reduce the hydrogen bonding between fibers and decrease both the tensile strength and elastic modulus. Increasing the \(\text{Fe}_3\text{O}_4\) NP loading further reduces the strength and elastic modulus. The relationship between the \(\text{Fe}_3\text{O}_4\) NP and their mechanical properties is presented in Fig. 4(a). However, the TMNP still possesses a high strength and elastic modulus. TMNP with \(\text{Fe}_3\text{O}_4\) NP loadings of 5, 10, and 20 wt% possesses tensile strengths of 171.3, 137.8, and 120.4 MPa, respectively. This is the highest strength reported for transparent magnetic films and magnetic paper.\(^{1,16}\) The elastic modulus of TMNP with a \(\text{Fe}_3\text{O}_4\) NP loading of 0, 5, 10, and 20 wt% is 10.7, 8.3, 7.7 and 7.1 GPa, respectively. The high strength broadens the application of TMNP. Fig. 4(b) shows the cross-section of TMNP after breaking. The TMNP exhibits a layered structure similar to pure nanopaper. After failure, the NFC fibers at the failure site are aligned parallel to the pulling direction.
Conclusion

In summary, highly transparent magnetic nanopaper was fabricated by immobilization of magnetic particles in a nanocellulose fiber network. The optical, magnetic, and mechanical properties depend on the concentration of magnetic particles in the paper. The obtained magnetic paper is transparent in visible light with a high transmittance of 86% and possesses an excellent tensile strength of 171.3 MPa. Combining these outstanding properties with low cost, green, cellulose fibers and a relatively simple manufacturing procedure makes this material an excellent candidate for magneto-optical applications.37

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Notes and references


