Synthesis of nano-fibrillated cellulose/magnetite/titanium dioxide (NFC@Fe$_3$O$_4$@TNP) nanocomposites and their application in the photocatalytic hydrogen generation

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ABSTRACT

Nano-fibrillated cellulose (NFC), an abundant renewable bio-macromolecule, has received much attention in the research community. The study detailed herein is related to the preparation of photocatalytic nanocomposites consisting of nano-fibrillated cellulose/magnetite/titanium dioxide nanoparticles (NFC@Fe$_3$O$_4$@TNP). The aim of this study is to improve the photocatalytic efficiency of NFC-TNP composites and to improve their recyclability during the photocatalytic hydrogen generation. The NFC@Fe$_3$O$_4$@TNP nanocomposites were characterized by TEM, EDX, SAED, XRD, XPS, FTIR, Raman spectra and VSM techniques. The results showed that Fe$_3$O$_4$ NP and TNP were well-distributed on the surface of NFC. The photocatalytic efficiency study showed that NFC@Fe$_3$O$_4$@TNP nanocomposites represented a higher photocatalytic hydrogen generation rate in comparison with that of NFC-TNP sample. In addition, the NFC@Fe$_3$O$_4$@TNP nanocomposites can be readily recovered from the system using a magnet due to their stable superparamagnetic properties, and they had only a marginal loss of TNP and photocatalytic efficiency after fifteen cycles.

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1. Introduction

Nanocellulose, which is a generic term of rod-like or ribbon-like cellulose with a nano-scale dimension, mainly contains nano-fibrillated cellulose (NFC) [1,2], cellulose nano-crystals (CNC) [3] and bacterial cellulose (BC) [4]. NFC, typically produced from cellulosic fibers by mechanical disintegration [5], has generated a great deal of interest as a bio-based nano-sized material due to its sustainable nature, biocompatibility, biodegradability, high specific strength and surface area, among others [6,7].

Among the various applications of NFC, its potential as a support/carrier for catalysts nanoparticles has attracted increased interest in recent years [8]. For instance, Koga et al. applied crystalline cellulose single nanofibers (CSNFs) as a support for gold nanoparticles (Au NP) to obtain CSNFs@AuNP composites, which exhibited an excellent catalytic efficiency (840 times of conventional polymer-supported Au NP) during the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) [9]. Additionally, a versatile support/carrier of titanium dioxide nanoparticles (TNP) to prepare NFC-TNP nanocomposites for photocatalytic hydrogen generation was investigated, and the as-prepared nanocomposites showed 2–5 times higher efficiency in comparison with the control TNP [10].

However, two main challenges need to be addressed: first, the cellulose structure of NFC-TNP nanocomposites can be photodegraded by TNP during photocatalytic hydrogen generation, thus some of the loaded TNP may be lost during the recycling process. Puls et al. [11] and Iguchi et al. [12] also found that TiO$_2$ can cause the surface pitting/damage of cellulose acetate/cellulose pulp fibers under UV light conditions. Secondly, the photocatalytic efficiency of TiO$_2$ is limited due to the fast recombination rate of photo-generated electron-hole pairs [13,14].

Magnetite (Fe$_3$O$_4$) has been shown to cause no photo-degradation on the cellulose structure during UV irradiation

[15,16]. Additionally, Fe_3O_4 NP were used in numerous applications, such as drug delivery [17], magnetically assisted separation [18] etc., due to their low toxicity, biocompatibility, and superparamagnetic properties [19,20]. Incorporating Fe_3O_4 NP with photocatalysts can be a practical approach to recycle the photocatalysts with an external magnet [20]. Furthermore, the performance of the photocatalysts, such as ZnO [21] and TiO_2 [22], doped with Fe_3O_4, was found to have a higher efficiency than the pristine one. The proposed mechanism was that for Fe_3O_4-based photocatalysts, large amounts of effective electron-trapping sites can be induced by the presence of iron, which would minimize the fast recombination of photo-induced electron-hole pairs, thus improving the photocatalytic efficiency of the Fe_3O_4-based photocatalysts [23–25].

He et al. successfully prepared an innovative Fe_3O_4@TiO_2 biomaterial for the treatment of malignant tumors. It was found that the photocatalytic activity of TNP was effectively improved due to the inhibition of the fast recombination of photogenerated electron-hole pairs by Fe_3O_4, and that the recyclability of Fe_3O_4@TiO_2 biomaterial was enhanced via an extra magnetic field, compared with the control TiO_2 [26].

In this study, NFC was used as the support/carrier of both Fe_3O_4 NP and TNP to improve the photocatalytic efficiency and recyclability of TNP, and to prepare NFC@Fe_3O_4@TNP nanocomposites for photocatalytic hydrogen generation. TEM, EDX, SAED, XRD, XPS, FTIR, Raman spectra and VSM techniques were carried out to characterize the nanocomposites. Moreover, the photocatalytic efficiency and recyclability of the nanocomposites were also studied.

2. Experimental section

2.1. Materials

Nano-fibrillated cellulose (NFC) (~3.0 wt%) was obtained from Cellulose Lab Co., Ltd. (CAS Number: 9004-34-6). TiO_2 nanoparticles (TNP) powder (mostly anatase, contains a trace amount of rutile) were bought from Shanghai Jianghu Titanium Dioxide Chemical Products Co., Ltd. (China). Hydrochloric acid (HCl, 37%, w/w) and methanol came from Sigma-Aldrich Reagent Co., Ltd. Ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), citric acid anhydrous, and sodium hydroxide (NaOH, 50% Soln, w/w) were from Fisher Scientific. All other chemicals were of analytical grade and used without further purification.

2.2. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared using chemical co-precipitation of aqueous ferrous and ferric ions as described in the literature [27]. As an example, for the preparation of #1 NFC@Fe_3O_4 sample, a diluted HCl solution (20 mL, 2 mol/L) was added to 500 g distilled water, then citric acid (1 mg) was added to the above solution, followed by the additions of 0.44 mol $Fe(NO_3)_3 \cdot 9H_2O$ and 0.22 mol $FeSO_4 \cdot 7H_2O$ solid samples successively with nitrogen bubbling and magnetic stirring (500 rpm). The function of citric acid was to minimize the as-prepared Fe_3O_4 nanoparticles from being oxidized by the dissolving oxygen in water [28]. A diluted NaOH solution (360 mL, 2 mol/L) was added dropwise into the above system, followed by bubbling with nitrogen and magnetic stirring (500 rpm) for 120 min at room temperature to generate Fe_3O_4 nanoparticles. The solid was isolated in the magnetic field and washed three times using distilled water, and the obtained sample was stored for further experiment.

2.3. Preparation of NFC@Fe_3O_4 nanocomposites

NFC hydrogel (35 g, ~3 wt%, equivalent to 1 g dried NFC) was diluted to 0.2 wt% with distilled water and stirred for 5 min at 1000 rpm. The diluted NFC suspension was further treated with a sonicator (QSON-ICA) for 3 min to disperse the individual nanocellulose, followed by heating at 65 °C and bubbling with nitrogen for 10 min under magnetic stirring (500 rpm) to remove the dissolved oxygen from NFC suspension. The following procedures for preparation of NFC@Fe_3O_4 nanocomposites were similar to those shown in **Part** 2.2. The amounts of citric acid anhydrous, $Fe(NO_3)_3 \cdot 9H_2O$, $FeSO_4 \cdot 7H_2O$ are listed in Table 1. The NFC@Fe_3O_4 nanocomposites were obtained via a magnetic field and washed three times with distilled water. The amounts of loaded Fe_3O_4 on the NFC were calculated from Equation (1):

$$M_{Fe_3O_4@NFC} = \frac{M_1 - M_0}{M_0} \tag{1}$$

Where M_0 is the dried mass (g) of blank NFC sample before adsorption of Fe_3O_4 NP; M_1 is the dried mass (g) of NFC@Fe_3O_4 nanocomposites after separation. The amounts (mole) of loaded Fe_3O_4 on the surface of NFC were also shown in Table 1. It is noted that not all formed magnetite was loaded onto the NFC, due to the loss in the preparation process, especially at high dosages.

2.4. Preparation of NFC@Fe_3O_4@TNP nanocomposites

TNP suspension was obtained by dispersing 0.2 g of TNP powder in 100 g distilled water, followed by ultrasonic treatment (60% output) for 10 min to disperse the TNP in the aqueous suspension uniformly. The NFC@Fe_3O_4 nanocomposites were dispersed into 500 mL distilled water by ultrasonic treatment (60% output) for 15 min and stirring for 5 min at 1000 rpm. Then the TNP suspension was added dropwise into NFC@Fe_3O_4 nanocomposites suspension under magnetic stirring at 500 rpm to form well-dispersed NFC/Fe_3O_4/TNP/water system, followed by ultrasonic treatment (60% output, 5 min). Further magnetic stirring (500 rpm) for 24 h at ambient temperature was applied to the suspension to ensure good adsorption of TNP on the surface of NFC@Fe_3O_4 nanocomposites. The resultant NFC@Fe_3O_4@TNP nanocomposites were obtained in the magnetic field and washed three times with distilled water to remove free TNP. The amount of loaded TNP on the NFC was calculated by Eq. (2):

$$M_{TNPs@NFC} = \frac{M_2 - M_1}{M_0} \tag{2}$$

Where M_0 is dried mass (g) of blank NFC sample before adsorption of TNP; M_1 is dried mass (g) of NFC@Fe_3O_4 nanocomposites; and M_2 is dried mass (g) of NFC@Fe_3O_4@TNP nanocomposites after separation.

According to Eq. (2) above, the amounts of loaded TNP for NFC@Fe_3O_4@TNP nanocomposites were shown in Table 2.

2.5. Characterization

For the transmission electron microscopy (TEM) analyses, the NFC, TNP powder, NFC@Fe_3O_4 nanocomposites and NFC@Fe_3O_4@TNP nanocomposites were individually dispersed into a diluted water suspension before being transferred to a carbon-coated copper grid (about 10 μL by using micropipette) and afterward air-dried at room temperature overnight. The TEM observation was then conducted on a JEOL 2010 transmission electron microscope with 200 kV acceleration voltages. Elemental analyses of energy dispersive X-ray (EDX) and mapping, as well as selected area electron diffraction (SAED) pattern, in combination with TEM were also conducted. The X-ray counts were obtained by integrat-