

## Renewable catalyst with Cu nanoparticles embedded into cellulose nano-fiber film†

Cite this: *RSC Advances*, 2013, 3, 16279

Received 31st May 2013,  
Accepted 19th July 2013

DOI: 10.1039/c3ra42689k

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**TEMPO-oxidized cellulose nano-fibril film embedded Cu nanoparticles had an excellent catalytic efficiency for nitroaromatic hydrogenation. Thus, this Cu-loaded film is an eco-friendly catalyst with a high performance, and this novel technique is expected to comprise a promising approach toward green and sustainable development.**

Cellulose, the most abundant natural organic polymer, is a main component of wooden plants consisting of  $\beta$ -glucose.<sup>1–4</sup> Because of inter-fibril hydrogen bonds, the cellulose can take a tightly packed sheet structure and it is very difficult to obtain individual cellulose nano-fibers.<sup>5</sup> Some research groups have reported mechanical and/or acidic treatments, and they prepared dispersed fibers with bundles of cellulose nano-fibrils.<sup>6–8</sup> On the other hand, it has been reported that the reaction mediated by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) allows selective oxidation of the C6 primary hydroxyl group of cellulose to a carboxylate group.<sup>9–11</sup> This method can provide a single cellulose nano-fibril with negatively charged carboxylate ions,<sup>9</sup> which are loaded exclusively on the fibril and act to maintain the dispersion of nano-fibrils or to protect nano-fibrils from the reaggregation.

The uptake of metal particles in the TEMPO-oxidized cellulose nano-fiber (TOCNF) network can bring benefits like improvement of properties and supply of unique functions like magnetic, photocatalytic, antibacterial, electro-conductive, deodorizing, and photoluminescent properties.<sup>12</sup> When the wood cellulose is used as a soft matrix to incorporate inorganic particles, composites bring both bio-interfaces by the cellulose fibers and intrinsic functionalities of the particles.<sup>13–15</sup> We focused on the synthesis and the catalytic features of Cu nanoparticle-loaded TOCNF (Cu-TOCNF) film using aqueous suspensions of TOCNF and Cu nanoparticles, which were prepared from Cu ions as a precursor and ascorbic acid as a reducer.

4-Nitrophenol is one of the most hazardous and toxic organic pollutants in waste-water generated from agricultural and industrial sources.<sup>16–18</sup> On the other hand, 4-aminophenol is an important intermediate on the manufacture of antipyretic and analgesic drugs.<sup>19</sup> Therefore, the development of an effective and environmentally friendly catalysts is expected for the reduction of 4-nitrophenol to 4-aminophenol. Cu-TOCNF film is an eco-friendly catalyst, since the metal particles are entrapped in the fiber network of the film. To the best of our knowledge, this is the first report that Cu nanoparticles could be embedded into TOCNF film for catalytic applications, especially, of 4-nitrophenol (see Table S1 in ESI†).

Sliced wood (softwood) was de-waxed by continuous reflux with toluene-ethanol mixture (2 : 1 by volume) in a soxhlet extractor for 8 h. Delignification of the de-waxed wood was performed with sodium chlorite at pH 4–5 (maintained by adding acetic acid) and 75 °C for 1 h, according to Wise's method.<sup>20</sup> This delignification treatment was repeated four times with fresh chemicals. Thus-obtained wood holocellulose was thoroughly washed with water and kept in the wet state.

The wet wood holocellulose fibers (1 g dry weight) were suspended in water (100 mL), which contained TEMPO (0.016 g) and sodium bromide (0.1 g). The TEMPO-mediated oxidation was performed by adding an excess amount of 13 vol% sodium hypochlorite (NaClO) to the slurry of cellulose. The slurry was stirred at room temperature and pH 10. Thus-obtained TEMPO-oxidized wood holocellulose nano-fibers with sodium carboxylate groups (TOCNF-COONa) were washed thoroughly with water, centrifuged and stored in the wet state, which corresponds to 50 wt% TOCNF-COONa.

Fig. 1 illustrates the process for fabricating Cu nanoparticles into cellulose nano-fiber network. An aqueous suspension (1.0 wt%) of TOCNF-COONa was prepared by diluting TOCNF-COONa in the wet state with water and homogenized in a mixer until the suspension becomes opalescent.  $\text{CuCl}_2$  was dissolved in 10 ml of 2 M hydrochloric acid solution and sodium ascorbic acid (of 4-fold moles of Cu(II)) as a reducer from Cu(II) to Cu(0) was further added there, followed by stirring at room temperature for 15 min. The solution was added to an aqueous suspension of TOCNF-COONa

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra42689k

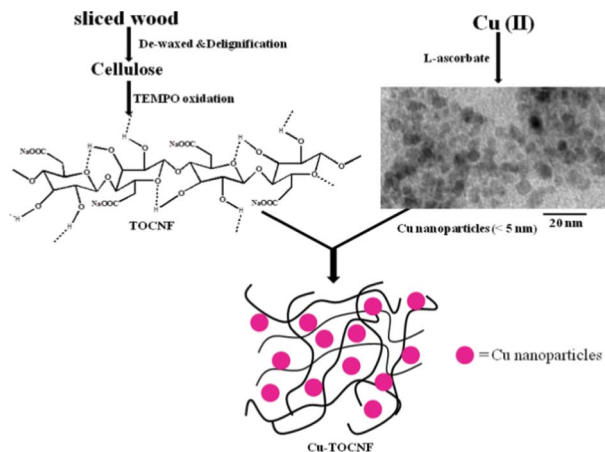


Fig. 1 Schematic representation of preparation of Cu-TOCNF film.

and stirred at room temperature for one hour to obtain a well dispersed nano-fiber suspension. The Cu-TOCNF film was prepared by the filtration of this suspension on the cellulose acetate filter membrane with 47 mm diameter and 0.2  $\mu\text{m}$  pore size. Then the Cu-TOCNF film was separated from the filter membrane. By way of comparison, the Cu-free TOCNF film was also prepared from the suspension without Cu in the presence of ascorbic acid. Additional experimental sections are described in the experimental section of ESI†

Fourier transform infrared (FT-IR) absorption spectra were recorded for qualitative identification of functional groups in the TOCNF and Cu-TOCNF films, as seen in Fig. 2A. The IR absorption band at 1730  $\text{cm}^{-1}$  is attributed to a C=O stretching mode of carboxyl groups with hydrogen bonds.<sup>21</sup> When TOCNF was treated with Cu nanoparticles, the characteristic new band appeared around 1640  $\text{cm}^{-1}$ , which corresponds to a  $\text{COO}^-$  antisymmetric stretching vibration. This indicates the existence of carboxylate combined with Cu ion.<sup>1</sup>

Fig. 2B shows ultraviolet-visible (UV-Vis) absorption spectra of TOCNF and Cu-TOCNF films, which provide a qualitative evidence for Cu nanoparticles dispersed in the Cu-TOCNF film. A distinct absorption band was observed at  $\sim 280$  nm, and an absorption band in this range can be attributed to an absorption of oligomeric copper nano-clusters.<sup>22,23</sup> On the basis of Mie theory, the surface plasmon resonance for copper nano-crystals is

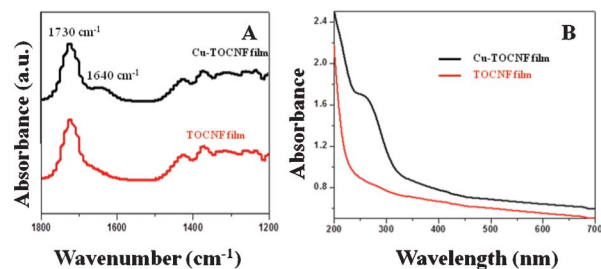


Fig. 2 Characterization of TOCNF and Cu-TOCNF films. A) FT-IR spectra and B) UV-Vis spectra.

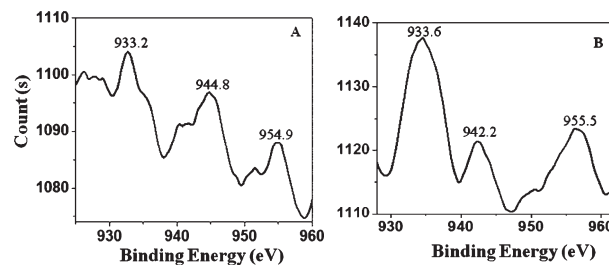


Fig. 3 XPS analyses of Cu-TOCNF films before and after catalytic reaction.

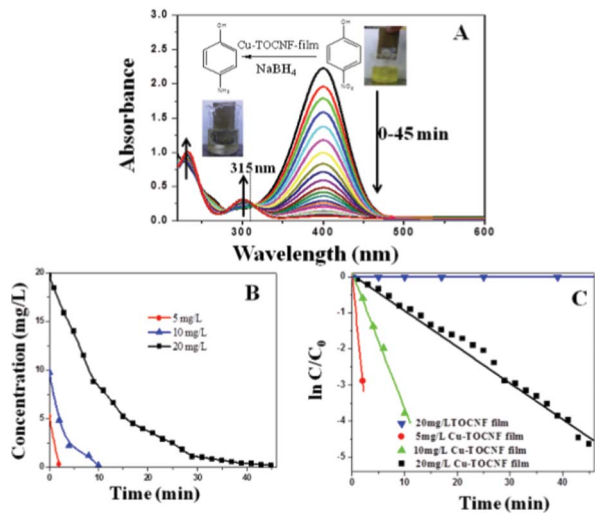
expected to have a strong broadening effect for particles smaller than 10 nm.<sup>24</sup> Transmission electron microscopic result showed Cu nanoparticles with an average size of 5.1 nm (Fig. S1 in ESI†) and, therefore, the surface plasmon resonance band for copper metal ( $\sim 560$  nm) was noticeably absent.

Fig. 3A represents an X-ray photoelectron spectrum (XPS) at Cu 2p binding energy level of a Cu-TOCNF film. The strong peaks around  $\sim 933$  and  $\sim 955$  eV correspond to 2p<sub>3/2</sub> and 2p<sub>1/2</sub> levels of Cu(0) particles.<sup>25</sup> Moreover, Cu(II) is known to exhibit a satellite peak at binding energy between 940–945 eV associated with the existence of a Cu 3d hole state (Cu 3d<sup>9</sup>), while Cu(0) do not show any such satellite peak, since a 3d peak is filled and a 4s peak is occupied.<sup>26</sup> As a satellite peak was observed with 2p peaks of Cu(0) (Fig. 3A), the coexistence of Cu(II) was confirmed in the Cu-TOCNF film. This result is consistent with the observation of a  $\text{COO}^-$  stretching band at 1640  $\text{cm}^{-1}$ .

Catalytic activity of the Cu-TOCNF film was demonstrated for the reduction of 4-nitrophenol to 4-aminophenol in an aqueous medium using  $\text{NaBH}_4$  as a hydrogen generator. An absorption band of 4-nitrophenol in water occurred at 313 nm but, after adding  $\text{NaBH}_4$ , the absorption band shifted to 400 nm (from light yellow to dark yellow) due to the formation of the corresponding nitrophenolate anion<sup>27</sup> (Fig. S2 in ESI†). This spectrum did not change with time without addition of any catalyst.

When the Cu-TOCNF film including a catalyst (Cu(0)) was immersed in the solution of 4-aminophenol including  $\text{NaBH}_4$ , the colour of the solution faded, indicating the reduction of 4-nitrophenol to 4-aminophenol. The formation of 4-aminophenol was successively confirmed by the hypochromism of a UV-Vis absorption band of 4-nitrophenol at 400 nm with time, accompanied by the simultaneous appearance of new bands at 230 and 300 nm (Fig. 4A). A blank experiment using the TOCNF film without Cu(0) showed that it has no catalytic activity for this reaction. The UV-Vis spectra also showed an isosbestic point (315 nm), indicating that the catalytic reduction of 4-nitrophenol produces only 4-aminophenol without the formation of by-product.<sup>28</sup> The complete conversion of 4-nitrophenol can be also confirmed by the clear bleaching of the solution from dark yellow.

The absorbance of a band at 400 nm varies with a concentration of 4-nitrophenol according to a Lambert-Beer law. Then, the decrease of the concentration of 4-nitrophenol with time was plotted for different initial 4-nitrophenol concentrations (5, 10, 20  $\text{mg L}^{-1}$ ) in Fig. 4B. An initial concentration of 4-nitrophenol markedly affected the reaction time necessary to conversion. The



**Fig. 4** Catalytic activity of Cu-TOCNF-film. (A) Change of absorption spectra with time, (B) plot of concentration versus time for 4-nitrophenol reduction and (C) kinetics plots of 4-nitrophenol reduction.

rapid conversion occurred for the initial concentration of  $5 \text{ mg L}^{-1}$ , where 4-nitrophenol was completely converted to 4-aminophenol within 2 min. Whereas, the conversion slowed for the initial concentration of 10 and  $20 \text{ mg L}^{-1}$  and took 10 and 45 min, respectively. At the low concentration of 4-nitrophenol, the number ratio of nitrophenolate anion to available catalytically active site may be enough low. Multiple runs (1–10) for the reduction of 4-nitrophenol on the same Cu-TOCNF film were performed for a solution at an initial 4-nitrophenol concentration of  $20 \text{ mg L}^{-1}$  (Fig. S3 in ESI†). The catalytic activity of the Cu-TOCNF film operated similarly even after ten cycles, implying that the designed film was highly stable in aqueous medium, sufficiently tough during use, and easy for recovering towards the next run. An XPS spectrum of Cu-TOCNF film after the catalytic performance test showed that the Cu particles remained on the film even after 10 runs (Fig. 3B).

It is apparent that the catalytic reduction of 4-nitrophenol to 4-aminophenol proceeded with the first-order kinetic behaviour, since plots of  $\ln(C/C_0)$  against time provided a linear relation (Fig. 4C), where  $C_0$  and  $C$  are the initial concentration and the concentration at each time of 4-nitrophenol, respectively. These results indicate that the catalytic reduction follows the pseudo-first-order behaviour. The rate constant for the Cu-TOCNF film was calculated from the slope in Fig. 4C and listed in Table S2 in ESI.† The rate constant decreased with increasing the initial concentration of 4-nitrophenol but it was almost constant for multiple runs, indicating that the Cu-TOCNF film served as a very effective catalyst for 4-nitrophenol conversion.

It has been observed that the reduction of 4-nitrophenol by  $\text{NaBH}_4$  doesn't occur to an appreciable extent in the absence of the Cu-TOCNF film (Fig. 4C). The catalytic process can then be explained by an electrochemical mechanism, where the Cu-TOCNF film serves as an electron relay for an oxidant and a reductant, and the electron transfer occurs *via* the embedded

metal nanoparticles. 4-Nitrophenol is electrophilic, while  $\text{BH}_4^-$  ions are nucleophilic in nature with respect to Cu nanoparticles. In general, a nucleophile can donate electrons to metal particles. In contrast, an electrophile captures electrons from metal particles. It is assumed that  $\text{BH}_4^-$  ions and 4-nitrophenol were simultaneously adsorbed on the surface of Cu nanoparticles, when they coexist. Therefore, the electron transfer from  $\text{BH}_4^-$  ions to 4-nitrophenol *via* Cu-nanoparticles is imaginable (Fig. S4 in ESI†).

## Conclusions

A catalytic system was designed with nano-composites of Cu nanoparticles and cellulose nano-fiber. The uptake of active Cu nanoparticles into a TOCNF film was successfully achieved. The Cu-loaded TOCNF film showed high catalytic activity towards the reduction of 4-nitrophenol, meanwhile the Cu-free TOCNF film had almost no catalytic activity. The film was easily recycled, and its catalytic activity did not decrease significantly up to at least 10 cycles of the reaction. It was suggested that the Cu nanoparticles embedded in the TOCNF film efficiently promoted the catalytic reaction. Thus, this novel concept demonstrates the potential to prepare an eco-friendly film-type catalytic system with a good selectivity.

## Acknowledgements

RB gratefully acknowledges National Taiwan University of Science and Technology, Taiwan, for the financial support by Postdoctoral Fellowship. We thank Prof. M. Ujihara of National Taiwan University of Science and Technology, Taiwan, for his valuable discussion.

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