

Direct Synthesis of Gold Nanocatalysts on TEMPO-oxidized Pulp Paper Containing Aldehyde Groups

Akihiro Azetsu,^a Hirotaka Koga,^b Lu-Yang Yuan,^a and Takuya Kitaoka^{a,c,*}

In situ synthesis of gold nanoparticles on paper sheets was achieved without any external reducing reagents and heat treatments. Surface-activated pulp fibers with carboxyl and aldehyde contents of 1.18 and 0.349 mmol g⁻¹, respectively, which were obtained from softwood kraft pulp using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), were fabricated into paper sheets with polyamideamine epichlorohydrin (PAE) resin with a papermaking technique. The TEMPO-oxidized pulp papers were flexible, lightweight, and easy to handle in a wet state due to the PAE-mediated reinforcement. Simple immersion of the white TEMPO-oxidized paper in an aqueous solution of tetrachloroauric acid at room temperature brought about distinct color change from white to red-purple, strongly suggesting the formation of gold nanoparticles. Post-oxidized aldehyde-free paper provided no color variation, and thus the aldehyde groups on pulp fibers made a significant contribution to the *in situ* synthesis of gold nanoparticles. The organic–inorganic paper materials of TEMPO-oxidized pulp and gold nanoparticles demonstrated the catalytic activity for the reduction of 4-nitrophenol to 4-aminophenol in an aqueous system.

Keywords: Aldehyde; Catalysis; Gold nanoparticle; Organic–inorganic material; TEMPO oxidation

Contact information: a: Department of Agro-environmental Sciences, Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan; b: The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan; c: Biotron Application Center, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan; *Corresponding author: tkitaoka@agr.kyushu-u.ac.jp

INTRODUCTION

Catalysts play significant roles in efficient chemical reactions of various industrial manufacturing processes including biomass conversion (Guo *et al.* 2011; Zhang *et al.* 2012); especially, intensive research and development of metal nanoparticles (NPs) have recently been conducted for the use of the nanomaterials as new catalysts with large surface area to volume ratios and high catalytic activities (White *et al.* 2006; Bratlie *et al.* 2007; Wen *et al.* 2008). In most cases, the electron-mediated properties of NPs are much different from those of the corresponding bulk metals, leading to great enhancement of catalytic activities (Ishida and Haruta 2007; Park *et al.* 2008). Gold nanoparticles (AuNPs), which are one of the most innovative and promising nanocatalysts, allow unique catalysis such as low-temperature CO oxidation, gaseous propylene epoxidation, and liquid-phase reduction, despite bulk Au metal being regarded as stable and inactive (Haruta 2003). However, metal nanocatalysts are frequently difficult to use in their original nanostructured forms since they easily aggregate to minimize their large specific surface areas. The inevitable aggregation of nanocatalysts eventually yields bulk-like materials with remarkable reduction of catalytic activities. Therefore, enormous efforts

have been devoted to establishing an efficient, practical immobilization method that enables highly active metal nanocatalysts to be fixed onto easily handled support materials, such as porous membranes and nanostructured materials, without sacrificing their excellent functionality (Braunstein *et al.* 2000; Xu *et al.* 2005; Dotzauer *et al.* 2006; Xu and Bhattacharyya 2007; Wang *et al.* 2008). Another effective approach to inhibit such aggregation is to immobilize metal NPs on synthetic polymers, and the polymer–NPs nanocomposites are attracting attention for practical applications due to their tunable properties (Ding and Gin 2000; Biffis *et al.* 2007; Wang *et al.* 2007; Liu *et al.* 2011). However, the embedding of active metal NPs inside the polymer layers frequently causes a drastic decrease in catalytic efficiency, and thus further improvement of catalyst supports is strongly required.

Recently, Saito *et al.* (2006) reported that 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) catalyzes the selective oxidation of the C6 primary hydroxyl group of cellulose to a carboxylate *via* the intermediate formation of an aldehyde group, and such oxidation occurs only on the surface of each crystalline cellulose nanofibril under mild aqueous conditions (Fig. 1). This TEMPO-mediated oxidation can provide individually dispersed crystalline cellulose nanofibers with a high carboxylate density. The carboxyl groups accumulate exclusively on their surfaces and act as anchor sites for metal NPs' synthesis. In previous studies, the synthesis of AuNPs and Au–Pd bimetallic NPs on the surfaces of TEMPO-oxidized cellulose nanofibers (TOCNs) was achieved, and active nanoparticles were highly dispersed on the outer surface of the TOCN supports, which enabled effective contact with reactants, resulting in high catalytic activities (Koga *et al.* 2010; Azetsu *et al.* 2011). However, there is much room for further improvement of the handling of nanofibers, which were used as a viscous suspension. Paper is also a biomass-based material with a layered fiber-network structure, and is used in daily life as a writing, printing, and packaging commodity. Paper materials have good practical utility, *e.g.*, they are lightweight, flexible, and easily handled, and thus researchers have developed new paper materials with unique functions, such as a flexible energy storage device (Pushparaj *et al.* 2007) and a portable bioassay system (Martinez *et al.* 2007). Optically transparent nanofibril paper was also developed as a matrix for solar cells (Nogi *et al.* 2009), and paper-like AuNPs catalysts composed of pulp fibers and zinc oxides (Miura and Kitaoka 2011).

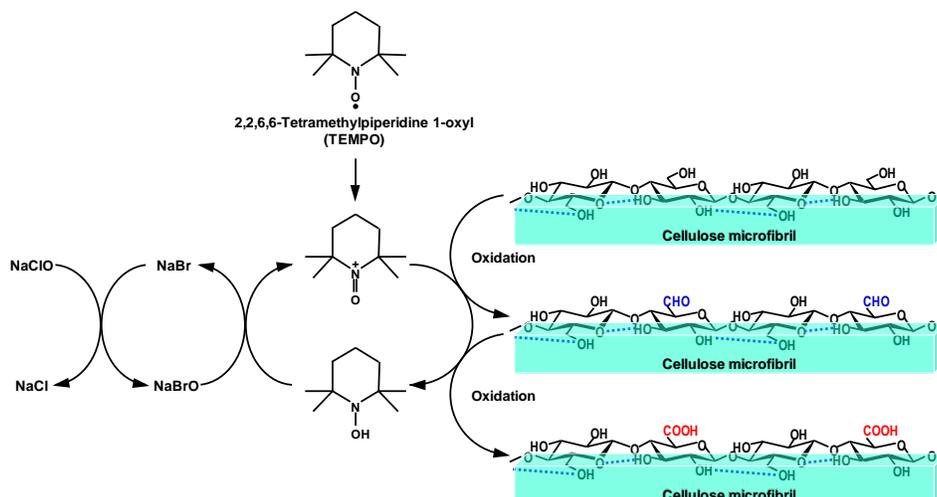


Fig. 1. Schematic illustration of the TEMPO oxidation process of cellulose pulp fibers

In this work, the direct, *in situ* synthesis of AuNPs on TEMPO-oxidized pulp paper (TOPP), not TOCN in a nanofiber form, was achieved without any external reducing reagents and heat treatments. The TEMPO-oxidized pulp has aldehyde groups as an intermediate, as illustrated in Fig. 1, and the aldehydic moieties in carbohydrates can act as a reducing reagent of metal ions (Kotelnikova *et al.* 2002; Li *et al.* 2011). Thus, it is expected to synthesize metal NP catalysts by *in situ* reduction *via* aldehyde groups on the surface of TEMPO-oxidized pulp fiber in paper. From the viewpoint of green chemistry, less harmful chemicals and the saving of energy are strong requirements (Vargas-Hernandez *et al.* 2010). Besides, paper materials are more promising as a catalyst support for practical use than viscous TOCN suspension. TOPP matrix was immersed in an aqueous solution of Au ions at room temperature and subjected to characterization and catalytic reaction tests.

EXPERIMENTAL

Materials

Tetrachloroauric(III) acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was purchased from Tanaka Kikinzoku Kogyo (Japan). TEMPO-oxidized softwood kraft pulp (COOH; 1.18 mmol g^{-1} , CHO; $0.349 \text{ mmol g}^{-1}$) was provided by Nippon Paper Industries (Japan). The COOH content was quantitatively determined by an electroconductive titration method, and the CHO content was obtained using the difference in the COOH contents before and after post-oxidation with NaClO_2 , according to the reported protocol (Saito and Isogai 2004). Polyamidepolyamine epichlorohydrin (PAE; WS-4020) was obtained from Seiko PMC (Japan). The water used in this study was purified with a Milli-Q system (Millipore, Japan). Sodium cyanoborohydride (NaCNBH_3) and other chemicals were reagent grade and were used without further purification.

Preparation of TEMPO-oxidized Pulp Paper

TEMPO-oxidized pulp paper (TOPP) as a matrix for AuNPs synthesis was prepared with a papermaking technique. As-received TEMPO-oxidized pulp fibers (*ca.* 10% consistency, 1.2 g by dry weight) were suspended in filtrate water (800 mL) and stirred for 5 min. Then, the suspension was mixed with PAE (20 wt% per solid) with gentle stirring for 3 min. After suction on a 200-mesh wire, the wet web was pressed at 350 kPa for 5 min, followed by drying in an oven at $105 \text{ }^\circ\text{C}$ for 30 min. PAE-free TOPP, aldehyde-free TOPP with PAE, softwood bleached kraft pulp (SBKP) paper, and SBKP paper with PAE were prepared for use as control samples. Aldehyde-free TOPP was prepared from the TEMPO-oxidized pulp fibers post-treated by additional oxidation using sodium chlorite (NaClO_2). Each paper sample was cut into circular pieces (*ca.* $7.0 \times 10 \text{ mm}^2$, *ca.* 60 g m^{-2} of basis weight) and subjected to AuNPs synthesis, analytical characterization, and catalytic reduction tests.

On-paper Synthesis of Gold Nanoparticles

The prepared papers were simply immersed in an aqueous solution of HAuCl_4 (0.05 mM) for 12 h at room temperature. The circular paper pieces were separated from the solution using tweezers, immersed in MilliQ water for more than 5 h for rinsing, and air-dried at room temperature.

Analytical Characterization

The paper samples were stained in a 0.05 wt% aqueous solution of toluidine blue to confirm the fixation/leaching of TOCN fractions. X-Ray diffraction (XRD) patterns were recorded on an XD-D1 X-ray diffractometer (Shimadzu, Japan) with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning angle (2θ) regions were between 5° and 50° at a voltage of 30 kV and a current of 40 mA. Surface observation of paper samples was conducted using a field emission scanning electron microscope (FESEM, ULTRA55, Zeiss, Germany). Elemental analysis was carried out using an energy dispersive X-ray spectrometer (EDS, SII-nanotechnology, Japan). The Au content of paper composites was determined by atomic absorption analysis using a Shimadzu AA-6600F apparatus as follows: The concentration of Au ions eluted from the samples with a 3:1 mixture of 36% hydrochloric acid and 69% nitric acid was quantitatively determined.

Catalytic Reduction Test

Aqueous reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was carried out in a batch mode. An aqueous solution of 4-NP (0.05 mM, 60 mL) was initially mixed with NaCNBH_3 (0.60 mmol). A piece of AuNPs@TOPP composite was then added to the solution, and the reaction was started at 25°C with gentle stirring. At set intervals, small aliquots of the solution were analyzed using a UV-vis spectrometer (U-3000, Hitachi, Japan).

RESULTS AND DISCUSSION

Characterization of TEMPO-oxidized Pulp Paper

The TOCNs composing pulp fibers have a high density of carboxyl groups on their crystalline surfaces. Toluidine blue dye molecules electrostatically bind to TOCNs and form self-aggregates on the TOCN surfaces *via* intermolecular interaction, resulting in characteristic metachromasia, specifically, a clear shift in the visible light absorption from *ca.* 630 to *ca.* 540 nm (Saito *et al.* 2011). Figure 2 shows the optical images of paper samples stained with toluidine blue dyes. Original paper samples of TOPP (Fig. 2a) and SBKP (data not shown) were white regardless of PAE addition. SBKP papers were clearly stained to show a blue color (Fig. 2b and Fig. 2c), whereas TOPP samples with or without PAE exhibited a purple color, revealing the high density of carboxyl groups of TOCNs on the TOPP surfaces.

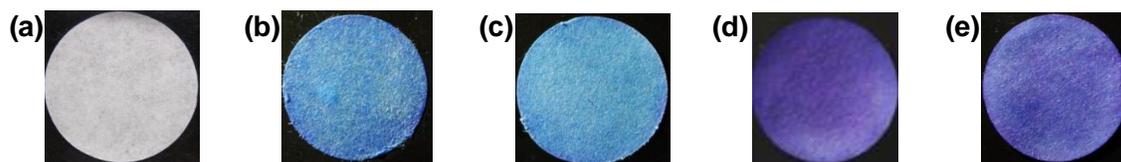


Fig. 2. Optical images of paper samples: (a) TEMPO-oxidized pulp paper with PAE before staining; (b-e) toluidine blue-treated papers: (b) SBKP paper, (c) SBKP paper with PAE, (d) TEMPO-oxidized pulp paper with PAE, and (e) PAE-free TEMPO-oxidized pulp paper

Figures 3 and 4 display the optical images and UV-vis spectra of the supernatant solutions after paper samples were stained with toluidine blue. The dye solution was blue

(Fig. 3a), and the mixture with TOCNs showed a clear purple color (Fig. 3b). Supernatant solutions of stained SBKP papers kept the original blue color (Fig. 3c and Fig. 3d), and in the case of TOPP with PAE, the blue supernatant color also remained unchanged (Fig. 3e). By contrast, the supernatant after staining on TOPP without PAE was obviously purple in color (Fig. 3f). UV-vis spectra supported the visual inspection results, showing a peak shift to *ca.* 530 nm for TOPP without PAE, which roughly corresponded to the absorption peak of the mixture of TOCNs and toluidine blue; in contrast, the only absorption decreases for the other samples were observed at *ca.* 600–650 nm. These results strongly suggested that the TOCN fractions were eluted from the TOPP without PAE, and that the internal addition of PAE could prevent leaching of TOCN fractions from TOPP, possibly due to the covalent bonding between the carboxyl groups of TOCNs on TOPP surfaces and PAE molecules.

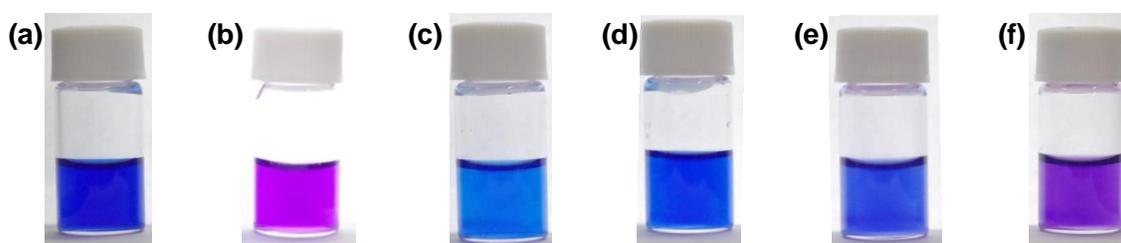


Fig. 3. Optical images of the supernatant solutions of toluidine blue-treated paper samples: (a) toluidine blue, (b) mixture of toluidine blue and TEMPO-oxidized cellulose nanofiber, and (c-f) the supernatant solutions after staining with toluidine blue; (c) SBKP paper, (d) SBKP paper with PAE, (e) TEMPO-oxidized pulp paper with PAE, and (f) PAE-free TEMPO-oxidized pulp paper

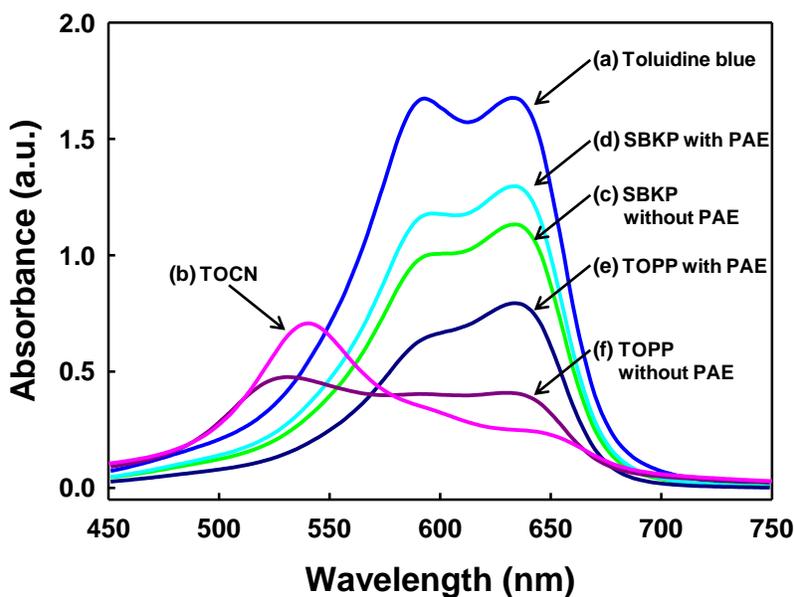


Fig. 4. UV-vis absorption spectra of the supernatant solutions of toluidine blue-treated paper samples: (a) toluidine blue; (b) mixture of toluidine blue and TEMPO-oxidized cellulose nanofibers; and (c-f) the supernatant solutions after staining with toluidine blue; (c) SBKP paper, (d) SBKP paper with PAE, (e) TEMPO-oxidized pulp paper with PAE, and (f) PAE-free TEMPO-oxidized pulp paper

Aldehyde-mediated Synthesis of AuNPs on TEMPO-oxidized Paper

As-prepared TOPP matrix with PAE was immersed in an aqueous HAuCl_4 solution and then thoroughly rinsed with deionized water while keeping its original state. After the immersion treatment, the color of the TOPP matrix changed from white to reddish purple (Fig. 5). This characteristic color change evidently suggested that small AuNPs were successfully synthesized on the paper, since metal Au with a nanometer scale shows reddish-purple color due to the surface plasmon resonance effect (Miura and Kitaoka 2011). As shown in Figs. 3 and 4, a large amount of cationic PAE resin was used to firmly hold anionic TOCNs on the TOPP surfaces, possibly resulting in the positively-charged surfaces. Then, anionic AuCl_4^- ions easily interacted with the TOPP surfaces by an electrostatic attraction, followed by the *in situ* reduction *via* surface aldehyde groups ($\text{Au}^{\text{III}}\text{Cl}_4^- + \text{TOPP-3CHO} \rightarrow \text{Au}^0 + \text{TOPP-3COOH} + 4\text{Cl}^-$). To elucidate the dominant role of TOPP-CHO for the synthesis of AuNPs, we first prepared the aldehyde-free TEMPO-oxidized pulp paper (TOPP-COOH), which was obtained by the post-oxidation of TOPP-CHO with NaClO_2 . Then, the TOPP-COOH was subjected to aqueous HAuCl_4 treatment; but there was no color variation found and its original white color remained unchanged (Fig. 5c). The TOPP-COOH had a carboxyl content of *ca.* 1.53 mmol g^{-1} and the aldehyde content was negligible. Therefore, carboxyl groups present on the TOPP surfaces made no contribution to the synthesis of AuNPs without reducing chemicals, and this is the preliminary evidence that the small amounts of aldehyde groups on the TOPP surfaces play a significant role in the *in situ* reduction of Au ions to form AuNPs.

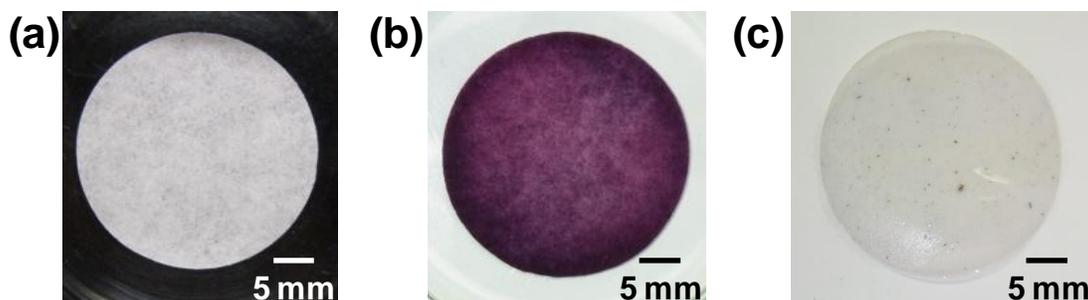


Fig. 5. Optical images of paper samples: (a) TEMPO-oxidized pulp paper (TOPP) with PAE before immersion in an aqueous solution of HAuCl_4 ; (b) TOPP with PAE after HAuCl_4 treatment; and (c) aldehyde-free TOPP with PAE after HAuCl_4 treatment

XRD patterns of the TOPP matrix with PAE before and after HAuCl_4 treatment are shown in Fig. 6. Typical diffraction peaks of crystalline cellulose I were observed at 16° and 23° in both samples. After AuNPs synthesis, a new broad peak was observed at *ca.* 38° , which corresponded to the Au(111) crystalline plan of a metallic Au face-centered cubic structure. This suggested the successful formation of very small Au nanocrystals and the maintenance of the original crystalline structure of the cellulose matrix.

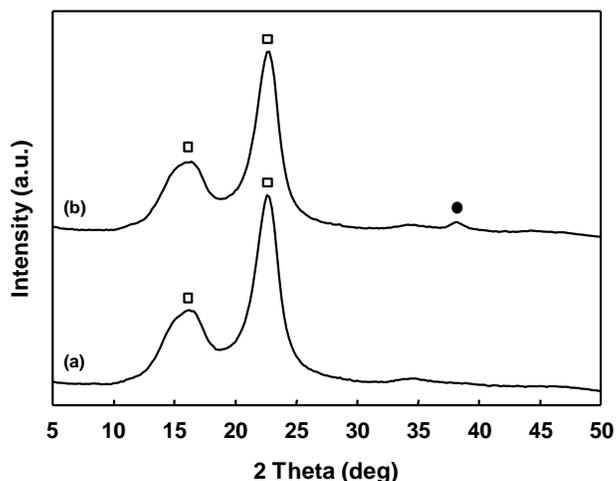


Fig. 6. XRD patterns of TEMPO-oxidized pulp papers: (a) original paper and (b) HAuCl₄ treated; □: cellulose, ●: Au

Figure 7 shows the FESEM images of the surfaces of the original TOPP matrix and AuNPs@TOPP composite. The TOPP surface was very smooth (Fig. 7a); however, the formation of numerous NPs with *ca.* 10 nm in diameter was observed on the TOPP matrix after AuNPs synthesis. The EDS profile of the AuNPs@TOPP composite indicated the existence of Au elements on the pulp surfaces (Fig. 8). Thus, the interaction and *in situ* reaction between metal precursors and aldehyde groups on the crystalline TOCN surface in paper must promote the uniform immobilization of AuNPs on the TOPP matrix. These results also highlighted that AuNPs spontaneously form on the paper without the need for any harmful reductants or high temperatures.

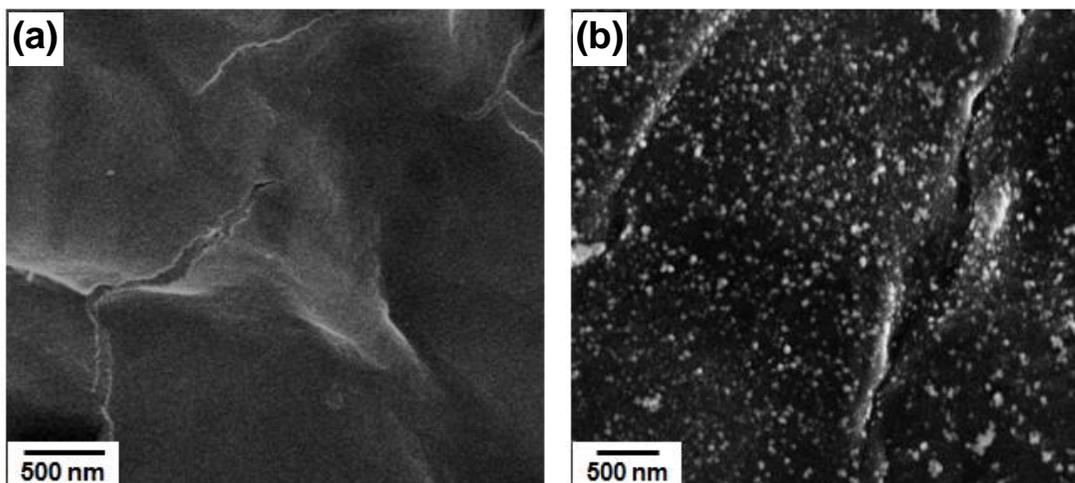


Fig. 7. SEM images of (a) original TEMPO-oxidized pulp paper and (b) HAuCl₄-treated TEMPO-oxidized pulp paper

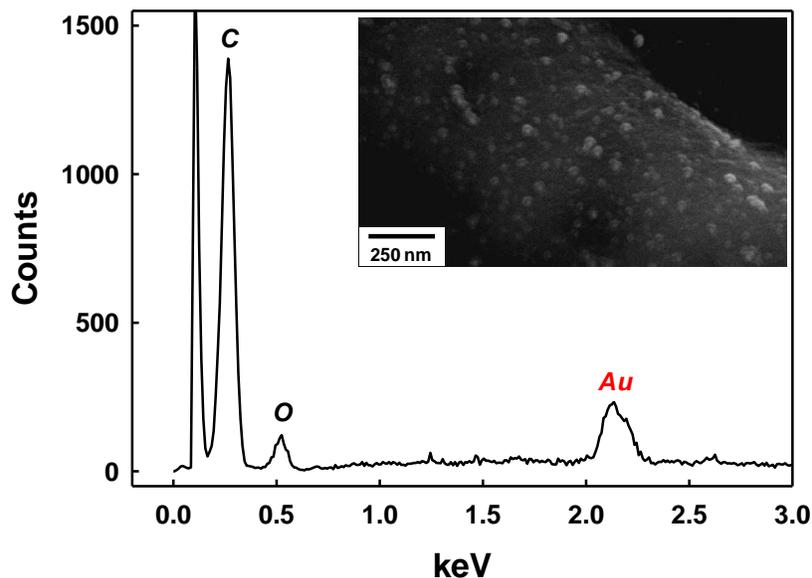


Fig. 8. EDX spectrum and SEM image (inset) of the AuNPs@TEMPO-oxidized pulp paper composite

Catalytic Behavior of AuNPs@TEMPO-oxidized Pulp Paper

The catalytic reaction behavior of the AuNPs@TOPP composite was evaluated by the aqueous reduction of 4-NP to 4-AP, in the presence of NaCNBH₃ as a hydrogen source. This reaction is of significance in both industry and academia, and 4-AP is an intermediate for the production of analgesic and antipyretic drugs; thus, this reduction often represents a typical model reaction to be used for the evaluation of various metal NP catalysts. Upon adding NaCNBH₃ to the 4-NP solution, the color of the solution changed from light yellow to dark yellow due to the formation of the 4-nitrophenolate ion. The reaction progress was monitored by UV-vis spectrometry, and typical time-dependent absorption spectra for the catalytic reduction of 4-NP over AuNPs@TOPP composite are shown in Fig. 9. A decrease in peak intensity for the 400 nm band, *i.e.*, the characteristic band for 4-nitrophenolate ion, was observed with time, with the emergence of a new peak at *ca.* 320 nm, indicating the absorption band for 4-AP. These results clearly indicated the conversion of 4-NP to 4-AP over AuNPs@TOPP composite. No catalytic behavior was observed for SBKP paper or the other control samples without AuNPs (data not shown). Turnover frequency value, which is the catalytic conversion rate per unit mole of catalyst per unit time, for the AuNPs@TOPP composite was estimated to be 1.2 h⁻¹ and was larger than that of one example reported (0.673 h⁻¹) for polymer-supported AuNPs (Zhang *et al.* 2007). In the case of the as-reported polymer, metal NPs are inevitably distributed inside the polymer layers, resulting in poor accessibility of the reactants to the active surfaces of metal NPs. Conversely, in the case of the AuNPs@TOPP composite, active AuNPs are highly dispersed and exposed on the outer surface of the TOPP matrix, which enables an effective contact with the reactants.

At this stage, the catalytic efficiency cannot satisfy industrial levels; complete conversion of 4-NP to 4-AP required a very long time, since the active sites of the AuNPs

were less sufficient than expected. The nano-level surfaces of AuNPs determine the catalytic activity, and moreover, the apparent surfaces of pulp matrix on which the AuNPs are immobilized must influence the accessibility of reactants to the active sites. Therefore, the AuNPs inside the paper matrix might not work efficiently, and further improvement will be required. Nevertheless, even after the wetting process for catalytic application, the paper composite preserved its original flexibility and showed mechanical strength upon bending (Fig. 10). The AuNPs@TOPP was allowed to reuse while keeping catalytic functions to some extent. Therefore, the facile preparation and obtained catalyst paper are promising for potential applications in the catalytic engineering processes.

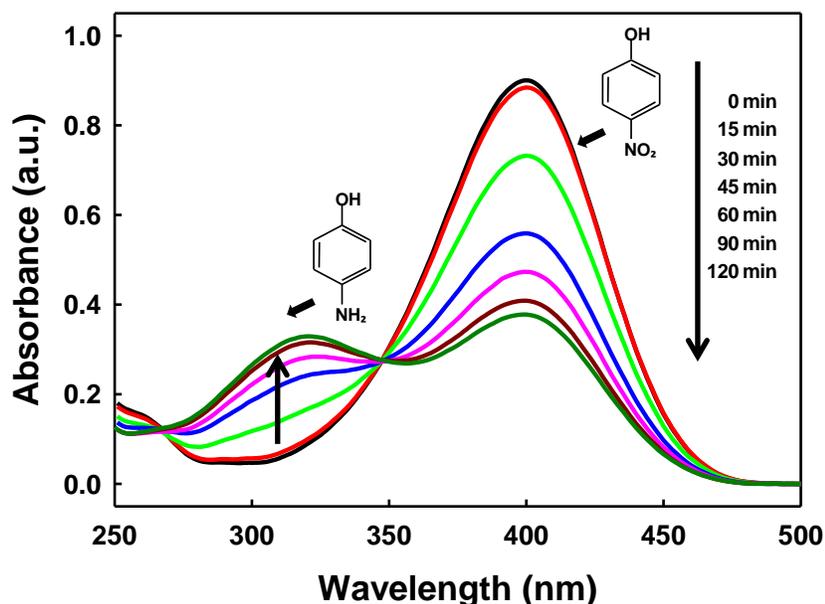


Fig. 9. Time-dependent absorption spectra for the aqueous reduction of 4-NP to 4-AP over AuNPs@TEMPO-oxidized pulp paper

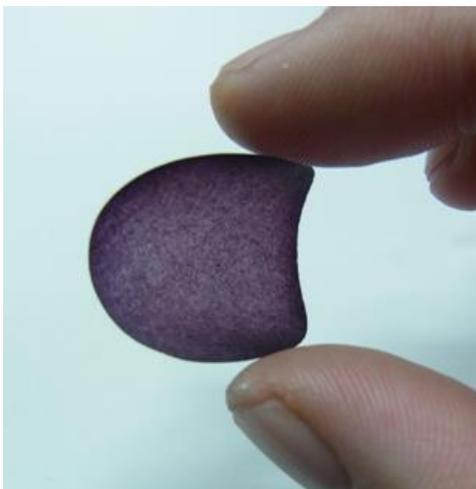


Fig. 10. Optical image of the HAuCl₄-treated TEMPO-oxidized pulp paper upon bending

CONCLUSIONS

This work proposed that the aldehyde groups on the surfaces of TEMPO-oxidized pulp fibers can act as *in situ* reducing sites to produce AuNPs on the paper surfaces without any additional reducing reagents or high temperatures. Conclusions can be summarized as follows:

1. The direct synthesis of active AuNPs catalysts onto the TEMPO-oxidized pulp paper matrix was achieved *via* a simple two-step process: papermaking of TEMPO-oxidized paper and subsequent soaking in an aqueous solution of H₂AuCl₄.
2. The paper-like catalyst containing small AuNPs on the surface possesses practical utility in terms of handling, even when in a wet state and when cut into various shapes.
3. AuNPs on TEMPO-oxidized paper composites show catalytic activity towards the aqueous reduction of 4-NP to 4-AP.
4. The facile technique described here, for the on-paper synthesis of a diverse array of metal NPs with catalytic activity, offers great potential for a wide range of catalytic applications.

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