

IN SITU SYNTHESIS OF GOLD NANOPARTICLES ON ZINC OXIDES PRELOADED INTO A CELLULOSIC PAPER MATRIX FOR CATALYTIC APPLICATIONS

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This article describes a facile method for the preparation of cellulosic catalyst paper: the *in situ* synthesis of gold nanoparticles (AuNPs) on zinc oxide (ZnO) whiskers, the preferential support for AuNPs, preloaded into a paper matrix. The ZnO paper composites were fabricated using a high-speed and low-cost paper-making technique, and immersed in an aqueous solution of HAuCl₄. After drying, fine 5 nm AuNPs were successfully formed on the ZnO whiskers inside the paper matrix. As-prepared AuNPs@ZnO whisker-containing paper (AuNPs@ZnO paper) is similar to ordinary paper products, being flexible, lightweight, and easy to handle. The AuNPs@ZnO paper exhibited a high catalytic efficiency towards the reduction of 4-nitrophenol to 4-aminophenol in aqueous media. Furthermore, the addition of a polyamideamine epichlorohydrin resin provided a wet strength to the AuNPs@ZnO paper, which enables several catalyst recycles with no significant losses in catalytic activity.

Keywords: Paper; Catalyst; Gold nanoparticle; Zinc oxide; On-paper synthesis; Catalytic reduction

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INTRODUCTION

From papyrus to more up-to-date products, paper is a widely used and highly familiar material, and continuous technological efforts are ongoing to prepare paper products with further advances to meet ever-increasing demands (Mocchiutti et al. 2011; Pathak et al. 2011; Sang et al. 2011). Paper is a class of bio-based material originating mainly from wood cellulose fibers, i.e. pulp. It is fabricated using a well-established technique, where a water suspension of pulp and various additives is dewatered via suction on a forming fabric, followed by pressing and heat-drying. Although such paper-making techniques are very simple, precise three-dimensional porous structures are robustly formed due to the large number of hydrogen bonds present between the pulp fibers (Tajedo and Van de Ven 2010). The physicochemical and biological properties can be tuned by tailoring the reagents and the preparation conditions (Yokota et al. 2009; Gao et al. 2011). Numerous researchers have recently devoted significant attention to the development of intriguing paper properties and rational paper-making processes. Researchers have focused on the functional design of paper materials for novel applications, such as cell culture systems (Derda et al. 2009; Egusa et al. 2009), energy storage

devices (Hu et al. 2009), microfluidic processes (Martinez et al. 2008), and analytical devices (Wang, H. et al. 2010).

Metal catalysts play an important role in many chemical reactions, e.g. reforming, oxidation, and hydrogenation (Aguilera et al. 2011; Rafiq and Hustad 2011; Zhang et al. 2011). Thus, considerable efforts have been devoted to the development of high-performance catalysts that are highly active, stable, easy to handle, reusable, and simple to separate from the reaction media. In last decade, metal nanoparticles (NPs) have proven to be promising catalysts, which exhibit excellent activities due to their large specific area to volume ratios (Koga et al. 2010a; Firsova et al. 2011). Although remarkable catalytic activity enhancements can be achieved by controlling the catalyst morphology on a nanometer scale, metal NP catalysts are not widely used in industrial applications due to the practical difficulties associated with handling and stability. Also, for expensive precious metals, reusability becomes a very important issue. The ultrafine particles can also agglomerate and form larger, less active particles. To overcome these problems, one currently adopted approach involves immobilizing metal NPs onto solid supports, such as metal oxides (Patil et al. 2004) and organic polymers (Wang, Y. et al. 2010).

We have previously reported another strategy: the effective immobilization of metal NPs onto an inorganic paper-like fibrous matrix to utilize the highly active metal nanocatalysts in the form of easy-to-handle cardboard (Koga et al. 2008, 2010b; Koga and Kitaoka 2011). The key to our approach is to preload zinc oxide (ZnO) whiskers, which act as the preferential support for the metal NPs, into an inorganic paper matrix prior to NP synthesis. An inorganic fiber/ZnO whisker matrix was firstly prepared via a paper-making technique. Metal NPs, such as copper and platinum were successfully synthesized *in situ* onto the ZnO whiskers through immersion into a metal ion solution with simultaneous reduction. For gold (Au) and silver, NPs could be synthesized without the need for any reductant, thanks to the photo-induced reduction promoted by the ZnO whiskers (Koga et al. 2009a, 2009b). These paper-like catalysts are not only practically convenient, but they also offer excellent catalytic activities in a number of gaseous and liquid phase reactions. This simple method to synthesize paper-like nanocatalysts opens a wide range of potential applications for organic cellulosic paper. Research into reusable paper catalysts, using bio-based cellulose fibers could make a great contribution to wider applications for paper products prepared via environmentally friendly processes.

Herein we report the facile synthesis of active gold nanoparticles (AuNPs) inside a cellulosic paper matrix containing ZnO whiskers, as the preferential support for AuNPs. These novel organic–inorganic hybrid catalysts are composed of organic pulp fibers (major constituent) and inorganic ZnO whiskers (minor one), being much different in kind from inorganic paper-structured catalysts as reported in our previous studies (Koga et al. 2008, 2009a, 2009b, 2010b; Koga and Kitaoka 2011). As-prepared AuNPs@ZnO paper, a novel biomass-based catalyst paper, was subjected to the aqueous reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), and was investigated with regard to both catalytic activity and reusability.

EXPERIMENTAL

Materials

A commercial bleached hardwood kraft pulp was beaten to 300 mL of Canadian Standard Freeness (TAPPI Test Methods T227 om-09) using a Technical Association of the Pulp and Paper Industry (TAPPI) standard beater (TAPPI Test Methods T200 sp-06). ZnO whiskers purchased from Matsushita Amtec, Ltd. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (99.9% purity, Aldrich, Ltd.) were used as the precursor for the Au catalyst. Sodium borohydride (NaBH_4) was obtained from Kishida Chemical, Ltd. Polyamideamine epichlorohydrin (PAE) (WS-570, Seiko PMC, Co.) and anionic polyacrylamide (A-PAM) (HH-351; molecular weight ca. $4 \times 10^6 \text{ g mol}^{-1}$; Kurita, Ltd.) were used as the wet-strength agent and flocculant, respectively. All other chemicals were of reagent grade and used without further purification.

Preparation of AuNPs@ZnO Paper

ZnO whisker-preloaded paper was prepared using a paper-making technique according to the TAPPI Test Methods T205 sp-95, as follows. Pulp (3.0 g) and ZnO whiskers (1.5 g) were suspended in water and mixed with PAE (1.5% per solids) and A-PAM (0.5 wt% per solids). After suction on a 200-mesh wire, the wet web was pressed at 350 kPa for 3 min, followed by drying in an oven at 105°C for 1 h. As control samples, additive-free paper was prepared by adding ZnO whiskers, and ZnO whisker-free paper was prepared with PAE and A-PAM.

The resultant white ZnO paper was cut into disk-shaped pieces ($8 \times 10^2 \text{ mm}^2$) using scissors and immersed in an aqueous solution of HAuCl_4 (0.1 mM, 100 mL) for 6 h at room temperature. The paper disks were then separated from the solution using tweezers, rinsed thoroughly with distilled water, and dried at 105°C for 3 h.

Catalytic Performance Test

The 4-NP reduction reaction was carried out in batch mode. An aqueous solution of 4-NP (0.05 mM, 30 mL) was initially mixed with NaBH_4 (1.5 mmol). A piece of AuNPs@ZnO paper ($8 \times 10^2 \text{ mm}^2$) was then added to the solution, and the reaction proceeded at 25°C with gentle stirring. At set intervals, small aliquots of the solution (1.0 mL) were taken and analyzed using a UV-Vis spectrophotometer (U-3000, Hitachi, Japan).

Analyses

Au content was determined via atomic absorption spectrophotometry using a Shimadzu AA-6600F apparatus. The Au ion concentrations as eluted from the AuNPs@ZnO paper with a 3:1 mixture of 36% hydrochloric acid and 69% nitric acid were quantified using a flame atomic absorption method. Surface analysis of the paper samples, after carbon coating was performed using a scanning electron microscope (SEM; JSM-5600, JEOL, Ltd.). Transmission electron microscopy (TEM) was also conducted using a JEM1010 instrument (JEOL, Ltd.) with an 80 kV accelerating voltage. The chemical states of the component elements were analyzed by X-ray photoelectron spectroscopy (XPS; AXIS-HSi spectrometer, Shimadzu/Kratos, Ltd.). The XPS spectra

were obtained using a monochromatic AlK α X-ray source (1486.6 eV) with a 12 kV voltage and a 10 mA current. The pass energy and step width in the detection of photoelectrons were set at 10 and 0.05 eV, respectively. X-Ray diffraction (XRD) patterns were recorded on an XD-D1 X-ray diffractometer (Shimadzu, Ltd.), using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) with an Ni filter. Scanning angle (2θ) regions between 10° and 80° were explored with a 30 kV voltage and a 40 mA current. Dry and wet tensile strengths were measured according to TAPPI Test Methods T220 sp-10, using an AGS-1kNG tensile tester (Shimadzu, Ltd.). Prior to the wet strength measurement, samples were soaked in distilled water for 10 min.

RESULTS AND DISCUSSION

Characterization of AuNPs@ZnO Paper

In this study, we prepared cellulosic catalyst paper via a two-step process (Fig. 1a): (i) ZnO whisker-containing paper was prepared using an established paper-making technique, and (ii) AuNPs were synthesized *in situ* onto the preloaded ZnO whiskers by soaking in an HAuCl $_4$ solution. As-prepared ZnO paper composites are sufficiently strong and easy to handle, rendering them practical and convenient. The ZnO paper composite could then be immersed in an aqueous HAuCl $_4$ solution, washed with deionized water, and heat-dried, whilst retaining its original state. Through this procedure, the color of the paper composites changed from white to pink-red (Fig. 1a). This suggests that the AuNPs were successfully synthesized on the paper, since metal Au on a nanometer scale appears as a reddish purple color due to the surface plasmon resonance effect (Si et al. 2007). Even after the wetting and drying process in the AuNPs synthesis, the paper composites preserved their original flexibility and showed mechanical robustness upon bending (Fig. 1b). Furthermore, the paper composites could be cut into various shapes using scissors (Fig. 1c), and displayed a homogeneous red color in their cross sections, implying a uniform distribution of AuNPs inside the paper (Fig. 1d).

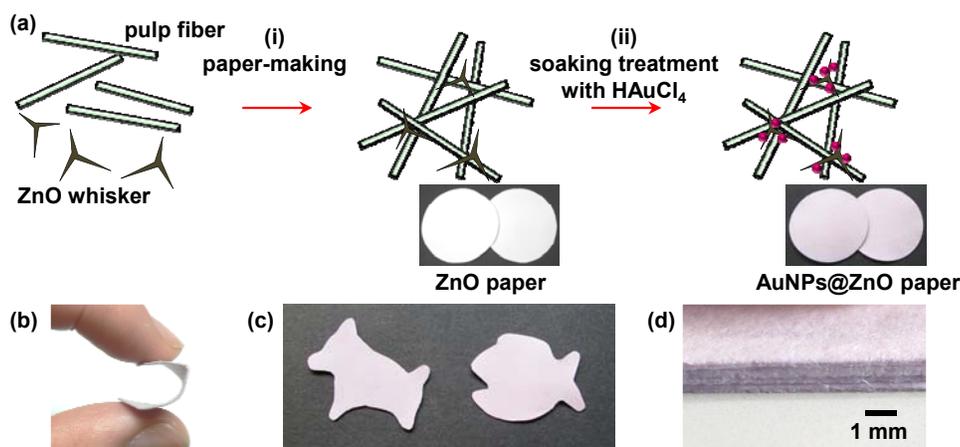


Fig. 1. Schematic illustration of the AuNPs@ZnO paper: (a) synthesis outline and sample color changes; (b) optical images of the AuNPs@ZnO paper upon bending; (c) after cutting into dog and fish forms of length ca. 30 mm; and (d) the cross sections of stacked AuNPs@ZnO papers

In consideration of multiple potential uses in various reaction situations, the mechanical properties of the paper composites were evaluated using a tensile strength tester. Table 1 shows the tensile strengths of the paper samples in both dry and wet states. The dry tensile strength of the ZnO paper was reduced by about one third in comparison to a paper sheet with no ZnO whiskers. The lower dry strength for the ZnO paper is attributed to the reduced level of hydrogen bonds between the pulp fibers, due to high level of ZnO fillers. However, the remaining strength is still sufficient for practical handling. In a wet state, weaker paper strength was observed in both cases, but PAE addition led to a drastically improved wet tensile strength. The cationic PAE molecules used here are adsorbed on negatively-charged pulp fibers at the wet end, and can reinforce the pulp fiber network via covalent ester bonds between the fibers (Espy 1995; Obokata and Isogai 2007). On the other hand, dual-polymer retention chemistry through the combined use of PAE and A-PAM increased the retention of ZnO whiskers from 70.7 to 84.0%, possibly resulting in the decrease in the dry strength of paper composites, since the ZnO fillers interfere with the formation of hydrogen bonds between the fibers. Nevertheless, these results indicate that the ZnO whisker-containing paper with PAE is sufficiently workable in both cases. In addition, when the ZnO paper in water was subjected to 100-W ultrasonic treatment, negligible ZnO whiskers were detached from the paper, even after 5 min. This suggests that the preloaded ZnO whiskers are strongly integrated within the fiber-network matrix.

Table 1. Dry and Wet Tensile Strengths for the Paper Samples

Additives	Dry tensile strength (N m g ⁻¹)	Wet tensile strength (N m g ⁻¹)
None	96.0 ± 0.7	n.d.
ZnO whisker	60.0 ± 2.7	n.d.
PAE and A-PAM	106.4 ± 5.6	15.8 ± 0.7
ZnO whisker, PAE and A-PAM	54.8 ± 1.3	9.4 ± 0.2

Figure 2a shows an SEM image for the surface of H₂AuCl₄-treated ZnO paper, having a porous structure composed of cellulosic pulp fibers and ZnO whiskers. The pulp fibers are entangled with each other, and the ZnO whiskers have a tetrapod-like nanostructure that sticks into the pulp fiber network. TEM images for the ZnO whiskers in the original and the H₂AuCl₄-treated ZnO paper are shown in Fig. 2b-d. A low-magnification TEM image of the ZnO whisker (Fig. 2b) also shows the tetrapod-like structure, consistent with the SEM observations (Fig. 2a). A high-magnification image of the ZnO whisker, after treatment with H₂AuCl₄ reveals the formation of numerous NPs (ca. 5 nm in diameter) on the ZnO whisker (Fig. 2d). No NPs were observed on the smooth surface of the ZnO whisker before H₂AuCl₄-treatment (Fig. 2c).

The XRD patterns for the original ZnO paper and AuNPs@ZnO paper are shown in Fig. 3a. Typical diffraction peaks for crystalline ZnO were observed in both samples. After AuNP synthesis, new broad peaks were observed at ca. 38° and 44°, which correspond to the Au(111) and Au(200) crystalline planes, respectively, of a metallic Au face-centered cubic structure. This suggests the successful formation of very small Au nanocrystals. These results reveal that AuNPs spontaneously form on the ZnO whiskers

and eventually the AuNPs@ZnO whiskers are well scattered on the pulp fiber network upon soaking in an HAuCl_4 solution, without the need for any reductants.

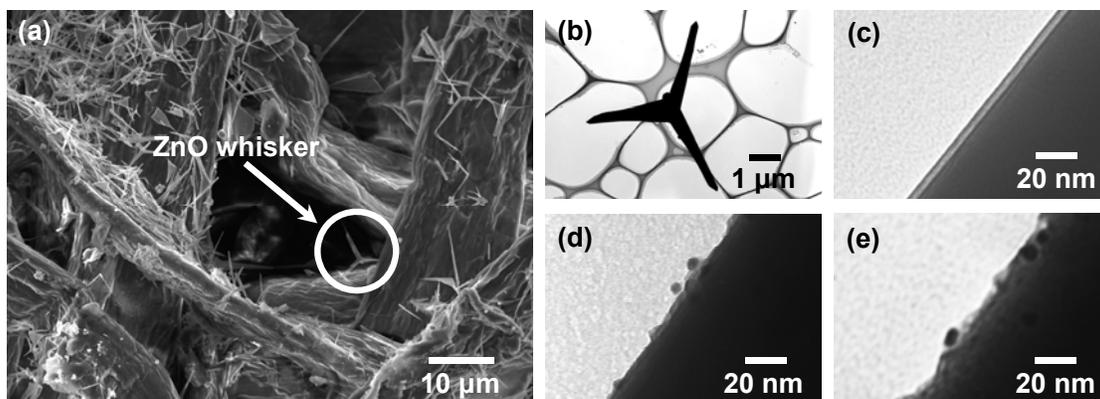


Fig. 2. (a) SEM image of HAuCl_4 -treated ZnO paper; (b, c) TEM images of the original ZnO whisker; (d) the as-prepared AuNPs@ZnO; and (e) the AuNPs@ZnO whisker after five cycles of 4-NP reduction. Each ZnO whisker was scraped from the paper samples.

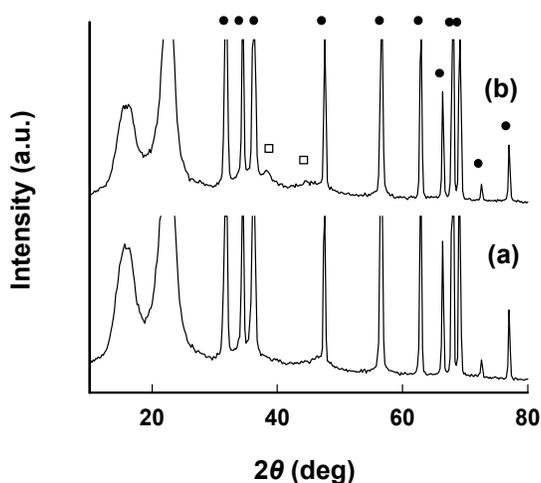


Fig. 3. XRD patterns for (a) the original ZnO paper and (b) the HAuCl_4 -treated ZnO paper: ◻: Au, ●: ZnO

To gain further insight into the formation of the AuNPs, XPS analysis was also carried out. The XPS data for the ZnO paper, before and after HAuCl_4 -treatment, are shown in Fig. 4. The ZnO paper showed no photoelectron peak corresponding Au4d. On the other hand, the ZnO paper after HAuCl_4 -treatment displayed a clear Au4d_{5/2} peak at ca. 334-335 eV, which is in agreement with the characteristic peak for Au(0). Furthermore, after AuNP formation, the Zn2p peak shifted slightly towards a higher binding energy, as reported in our previous work (Koga et al. 2009a). The proposed mechanism is summarized as follows: (1) the substitution of OH^- ions for the coordinated Cl^- ions of $[\text{AuCl}_4]^-$, (2) the hydroxylation of outer surface of ZnO whiskers in aqueous solution of Au(III) complex, (3) spontaneous approach of anionic $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ ions

to $\text{Zn}(\text{OH})_2$ positively charged in the acidic solution due to an electrostatic interaction, (4) the formation of Zn-O-Au bonds through a condensation reaction between Au-OH and Zn-OH , and (5) the reduction of $\text{Au}(\text{III})$ to $\text{Au}(0)$ due to the large difference in the ionization tendency between Au and Zn . Consequently, electron transfer from the $\text{Zn}(\text{II})$ on the ZnO whiskers to the $\text{Au}(\text{III})$ complex ions may occur. The slight shift of the $\text{Zn}2\text{p}$ peak suggests that the $\text{Zn}(\text{II})$ in the outermost layer of the ZnO whiskers becomes further oxidized after soaking in the HAuCl_4 solution, which results in the reduction of any Au species.

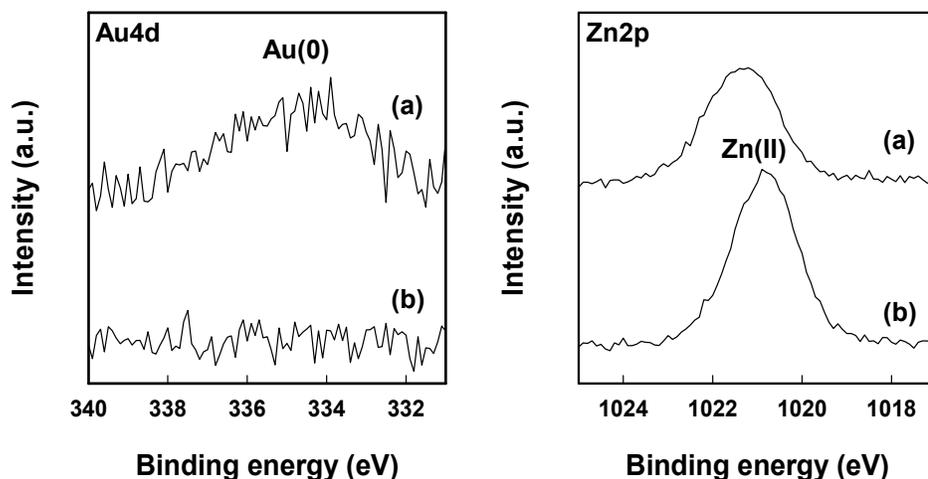


Fig. 4. XPS spectra for the ZnO paper (a) with and (b) without soaking treatment in HAuCl_4

Catalytic Performance of AuNPs@ZnO Paper

The catalytic activity of AuNPs@ZnO paper was substantiated in the reduction of 4-NP to 4-AP, in the presence of NaBH_4 as the hydrogen source. This reaction is of great significance in both industry and academia. 4-AP is a medicinal intermediate for the production of analgesic and antipyretic drugs, and the reduction also represents a typical model reaction for the evaluation of various metal NP catalysts (Saha et al 2010). No reaction is observed in the absence of catalyst and the decomposition of NaBH_4 is very slow under alkaline conditions. This ensures the hydrogen supply is constant throughout the reaction. NaBH_4 is also environmentally friendly due to the low toxicity of borate.

Typical time-dependent absorption spectra for catalytic reduction of 4-NP, over AuNPs@ZnO paper are shown in Fig. 5a. A significant decrease in peak intensity for the 400 nm band (characteristic band for 4-nitrophenolate ion) was observed with time, with the emergence of a new peak at 293 nm (characteristic band for 4-AP). These results clearly indicate the immediate conversion of 4-NP to 4-AP over AuNPs@ZnO paper. The reaction profiles for the reduction using AuNPs@ZnO paper are shown in Fig. 5b. The reduction follows pseudo-first-order kinetics in the presence of AuNPs@ZnO paper. No conversion of 4-NP was observed with ZnO -free paper. Therefore, the AuNPs@ZnO paper possesses significant catalytic activity towards 4-NP reduction. Furthermore, the AuNPs@ZnO paper has a porous, layered fiber-network structure (Fig. 2a) in which the

AuNPs are homogeneously distributed in the z-direction (Fig. 1d); therefore as-designed catalyst paper is expected to apply for flow-type catalytic reactions.

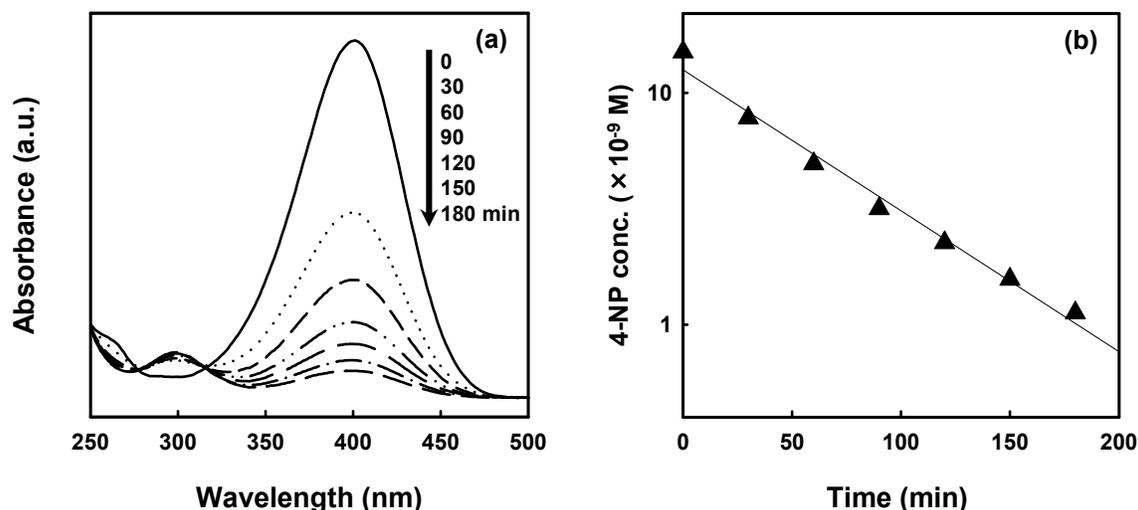


Fig. 5. Time dependent absorption spectra (a) and 4-NP concentration profile (b) for the catalytic reduction of 4-NP over AuNPs@ZnO paper. Initial conditions: [4-NP] = 1.5×10^{-8} M; [Au] = 0.15 mg / 30 mL; [NaBH₄] = 1.5×10^{-4} M

From a practical perspective, AuNPs@ZnO paper reusability was assessed. After each cycle, the paper catalyst was removed using tweezers, washed with distilled water, and dried at 105°C for 1 h. The recovered AuNPs@ZnO paper was then employed for the next run under the same conditions. The catalytic activity, with regard to 4-NP reduction is presented in Fig. 6. The initial activity was actually lower than that observed in successive runs. This can be attributed to the undesirable reduction of residual Au species on the pulp fiber during 4-NP reduction with NaBH₄. The catalytic activity for the AuNPs@ZnO paper was maintained, even after five cycles, implying that the as-designed paper catalyst was highly stable in aqueous media. The paper composites were sufficient tough during uses, and easy to be recovered toward the next run. We measured the final Au content in the recovered papers via atomic absorption spectrophotometry. The AuNPs@ZnO paper after five cycles of reaction preserved ca. 100% of original Au content, suggesting a negligible Au leaching in the aqueous phase. The TEM image for the AuNPs@ZnO whisker reused five times reveals that the AuNPs, with an average diameter of 5 nm were well dispersed on the ZnO whisker; furthermore, there was no obvious aggregation of AuNPs in the reused catalyst (Fig. 2e). No apparent damage was observed in the AuNPs@ZnO paper, and it could be handled like ordinary paper. In this study, we have investigated the aqueous catalytic reduction of 4-NP to 4-AP in a wet state; however the AuNPs@ZnO paper would be applicable for other catalytic reactions under dry conditions, e.g. room-temperature CO oxidation (Koga et al. 2009a). In our strategy, preloaded ZnO whiskers act as reducing sites to produce AuNPs on the whisker surfaces without any additional reductants. Besides, highly active AuNPs are allowed to be exposed on the ZnO whiskers distributed beforehand inside the paper. Such a situation is favorable for efficient catalytic reactions in a variety of practical applications.

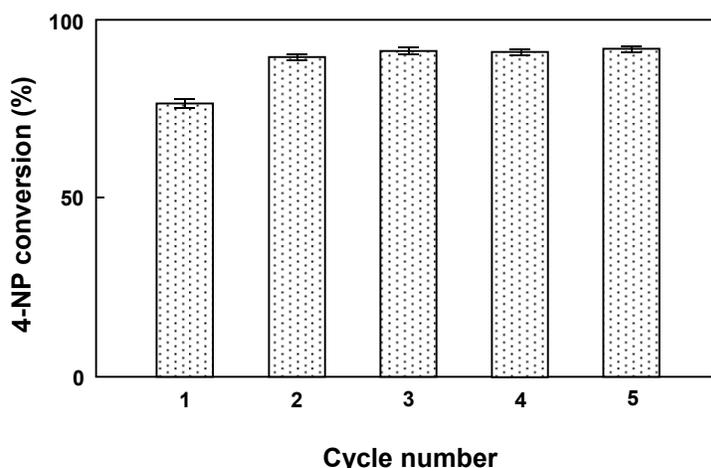


Fig. 6. Final conversion of 4-NP, 90 min after initiation over the AuNPs@ZnO paper, after each repeated use over five cycles

CONCLUSIONS

1. The direct synthesis of active AuNP catalysts onto a cellulosic paper matrix, containing ZnO whiskers as the preferential AuNP support, was achieved via a two-step process: the paper-making of ZnO papers and their subsequent soaking in an aqueous solution of HAuCl₄.
2. The paper catalyst possesses practical utility in terms of handling, even in a wet state and when cut into various shapes.
3. As-prepared AuNPs@ZnO paper shows a high catalytic activity towards the reduction of 4-NP. The paper catalyst is easily recycled and maintains its catalytic activity for up to at least five cycles of reaction.
4. The facile technique described herein, for the on-paper synthesis of a diverse array of metal NPs with catalytic activity, offers great potential for a wide range of applications. Furthermore, the paper has a three-dimensional porous structure, which is a desirable property for flow-type catalytic reactions.

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