

# Polyacrylonitrile-based electrospun nanofibers carrying gold nanoparticles in situ formed by photochemical assembly

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**Abstract** Polyacrylonitrile (PAN) nanofibrous fabrics carrying gold nanoparticles (AuNPs) were prepared via the combination of electrospinning of PAN solution containing  $\text{HAuCl}_4$  and in situ gold formation induced by ultraviolet (UV) irradiation. The factors to control the diameter of AuNPs were first investigated, and then their applicability to catalytic reaction using the obtained fibers was presented. The initial contents of Au ranging from 3 to 21 wt% did not exert a significant effect on the size of AuNPs formed in/on the PAN fibers, giving 4.7–5.4 nm in diameter, for 5 days of UV irradiation. On the other hand, the sizes of formed AuNPs were found to change from 5.2 to 2.7 nm with varying UV irradiation time from 5 to 1 day. The first-order rate constants obtained for the reduction of 4-nitrophenol increased from  $1.1 \times 10^{-3}$ ,  $3.5 \times 10^{-3}$  to  $4.0 \times 10^{-3} \text{ s}^{-1}$ , under a fixed volume of the fibers with AuNPs as catalysts, with increasing content of Au from 3, 13 to 21 wt%. The PAN catalysts with decreased size of AuNPs obtained through 1 day of UV irradiation gave a higher rate constant of  $2.7 \times 10^{-2} \text{ s}^{-1}$ . The highest rate constant per Au content and turnover frequency obtained in this study were  $8.3 \times 10^{-2} \text{ s}^{-1} \cdot \mu\text{mol-Au}^{-1}$  and  $71 \text{ h}^{-1}$ , respectively.

## Introduction

Electrospinning is a facile and cost-effective method for the production of nanofibrous fabrics with diameters ranging from several micrometers to hundreds nanometers or less. The fabrics have the potential usefulness for various applications in the fields of filtration [1], textile manufacturing [2], biomedical devices [3], electronics [4], and catalysis [5]. For the use in catalysis, electrospun nanofibrous materials enjoy the priority over the other materials due to their attractive features of structural characteristics such as high porosity and interconnectivity, which are of benefit to the diffusion of substrate or product molecules onto/from active sites [6, 7]. Therefore, intensive attention has been attracted for supporting highly active catalysts like noble metal nanoparticles onto electrospinning nanofibers [8, 9].

Gold-based materials have become of interest because of their unique catalytic activities [10, 11]. The most simple and intensively investigated formula of gold-based materials is use of a suspension of gold nanoparticles (AuNPs) in aqueous or organic solvent. For preparing the AuNP catalysts, smaller particles are desired due to their size-dependent catalytic activity [11]. It was reported that the AuNPs of less than 5 nm showed a significantly higher catalytic activity compared with larger ones [12]. However, the naked small AuNPs are difficult to handle and apt to agglomerate with lowering of their catalytic activity. Therefore, it is a great technical challenge to develop an effective way of preventing the agglomeration during AuNP preparation in/on the materials with stabilizing properties [6–9, 13–17].

The polymers possessing the functional groups with a high affinity to gold element or ion such as amine, cyano, and mercapto groups have been reported as promising materials for the purpose. Polyacrylonitrile (PAN) is a

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polymer rich in cyano groups. In addition, PAN has been reported as the material suitable for electrospinning [8, 9, 16]. Anka et al. [16] proposed a method of AuNP preparation in electrospun PAN fibers. In their method, the AuNPs were successfully formed in situ by photo-reduction of Au ions in/on electrospun PAN nanofibers subjected to UV irradiation. The PAN fibers containing Au ions were obtained from a gold salt/PAN mixture solution. These preceding reports only dealt with the photochemical preparation of AuNPs or catalytic applications of AuNPs over PAN fibers prepared through wet chemistry.

In the current study, we investigated the factors to control the diameter of in situ-formed AuNPs over resultant PAN nanofibers by photochemical process and demonstrated possibility of the AuNP-carrying nanofibers as catalysts. The factors were evaluated by changing the concentration of Au ions in electrospinning polymer solution and the irradiation time of UV light. The catalytic property of the fibrous mats was determined by employing the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) as a model reaction [8, 9, 17]. This study is the first report concerning the application of the AuNPs prepared by photochemical assembly to catalysis.

## Materials and methods

### Materials

Polyacrylonitrile (PAN, MW150,000),  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{NaBH}_4$ , 4-nitrophenol (4-NP), and *N,N*-dimethylformamide (DMF) were purchased from Polysciences Inc. (Pennsylvania, United States), Kanto Chemical Corp. (Tokyo, Japan), Sigma-Aldrich (Missouri, United States), and Wako Pure Chemical Industries Ltd. (Osaka, Japan), respectively.

### Electrospinning of PAN and $\text{HAuCl}_4$ composite nanofibers and photo-reduction

A solution of 14 wt% PAN was prepared by heating a suspension of PAN powder in DMF at 50 °C until the solution turned transparent. Subsequently,  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  powder was dissolved in DMF solution at 1, 5, and 10 wt%. The prescribed amount of  $\text{HAuCl}_4$ /DMF solution was blended with the PAN solution. Other conditions for electrospinning were conducted shown elsewhere [18]. The mixture solution was electrospun at tip-to-collector distance of 15 cm, applied voltage of 20 kV, and volumetric rate of 2.0 ml/h from a 5-ml plastic syringe. The resultant fibers were stored in the dark until being used in subsequent experiments. The PAN/ $\text{HAuCl}_4$  composite fibers electrospun from the solutions containing gold at 3, 13, and

21 wt% on a total solute basis were denoted as Au3, Au13, and Au21, respectively. The fibers were exposed to ultraviolet (UV) light with a peak wavelength of 253.7 nm (UV-lamp GL15, Toshiba Corp., Tokyo, Japan) at 51 mW/cm<sup>2</sup> under ambient conditions for 1–5 days after vacuum drying of the fibers for 48 h to remove the residual solvent.

### Characterization

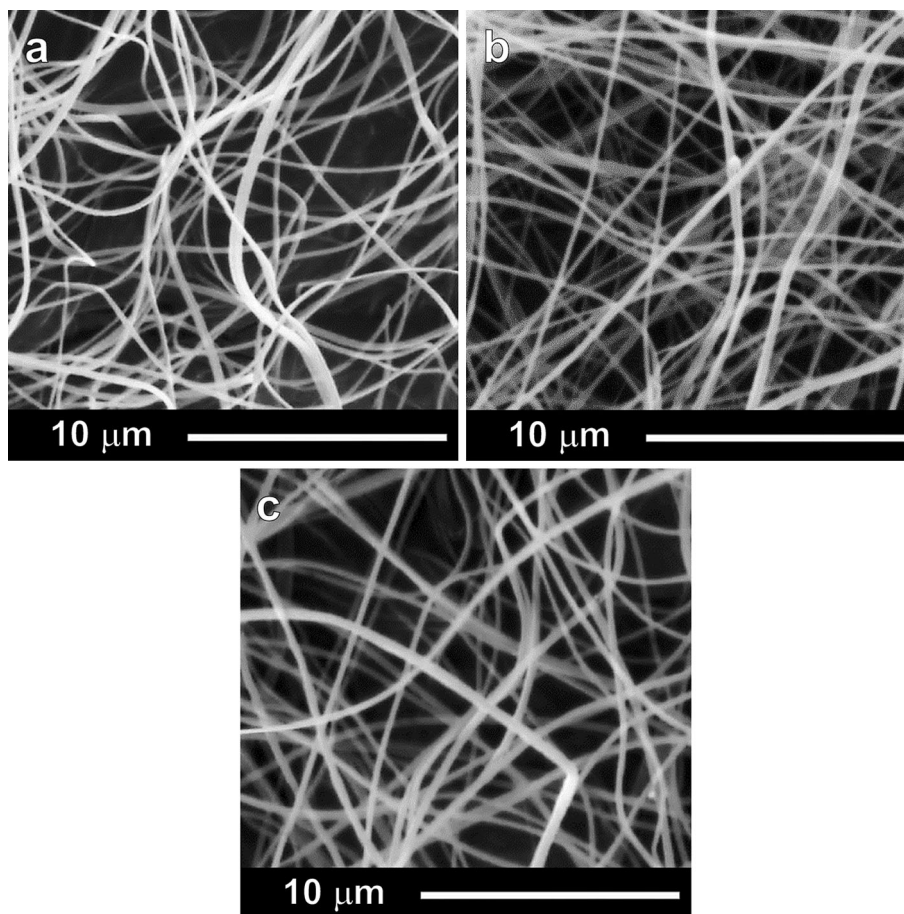
Morphologies of the electrospun PAN nanofibrous mats were observed using a scanning electron microscope (SEM, Model S-2250N, Hitachi Ltd., Tokyo, Japan). Particle diameters and their distribution of AuNPs in/on the fibers were determined from the measurements of over 300 individual particles on more than 5 images taken with a transmission electron microscope (TEM, Model H-800, Hitachi Ltd.) operating at 200 kV. To evaluate diameters, larger particles than ones observed in the fibers without UV irradiation were excluded from the measurements of the photochemically formed AuNPs.

### Catalytic activity measurement by reduction of 4-nitrophenol

The catalytic activity of the prepared fibers with AuNPs was evaluated by photometrically monitoring the reduction of 4-NP to 4-aminophenol (4-AP) in the presence of an excess amount of  $\text{NaBH}_4$ . The AuNP-carrying fibers were freeze-dried after washing with distilled water. The freeze-dried preparations were weighed and dispersed in water again by sonicating for 30 min with an ultra-sound homogenizer. In a quartz cuvette with a 1-cm light path length, 1.46 ml of water, 12.2  $\mu\text{l}$  of 10 mM 4-NP aqueous solution, and 24.4  $\mu\text{l}$  of freshly prepared 2 M  $\text{NaBH}_4$  aqueous solution were added. Then, after introducing 150  $\mu\text{l}$  of catalyst suspension into the reaction mixture, the absorption spectra were recorded in the range of 200–500 nm with a spectrophotometer (Model V-630BIO, JASCO Co., Tokyo, Japan). The concentrations of the catalysts, Au3, Au13, and Au21, were 0.07, 0.14, and 0.20 mg-fibers/ml, respectively, to give a fixed total volume of catalysts calculated from the densities of PAN (1.18 g/cm<sup>3</sup>) and gold (19.3 g/cm<sup>3</sup>), when comparing the activities of catalysts containing the different gold concentrations at 3, 13, and 21 wt%, respectively. In the same manner, the catalyst suspensions were prepared at 0.2 mg-fibers/ml using Au21 fibers, to examine the effect of UV irradiation time on the activity.

The reaction exhibited a profile of pseudo-first-order kinetics in the existence of an excess amount of  $\text{NaBH}_4$ . Turnover frequency (TOF) was defined as the number of substrate molecules reacted per Au mol and per hour, and

**Fig. 1** SEM images of Au3 (a), Au13 (b), and Au21 (c) fibers



calculated from the concentration of remained Au weight after washing the fibers.

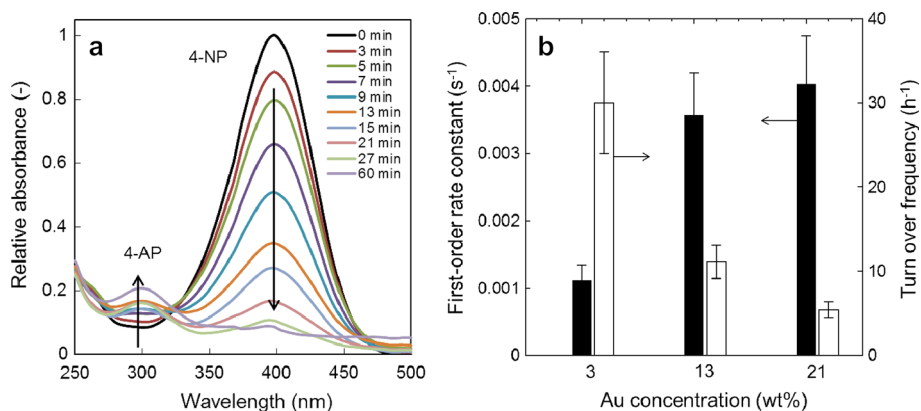
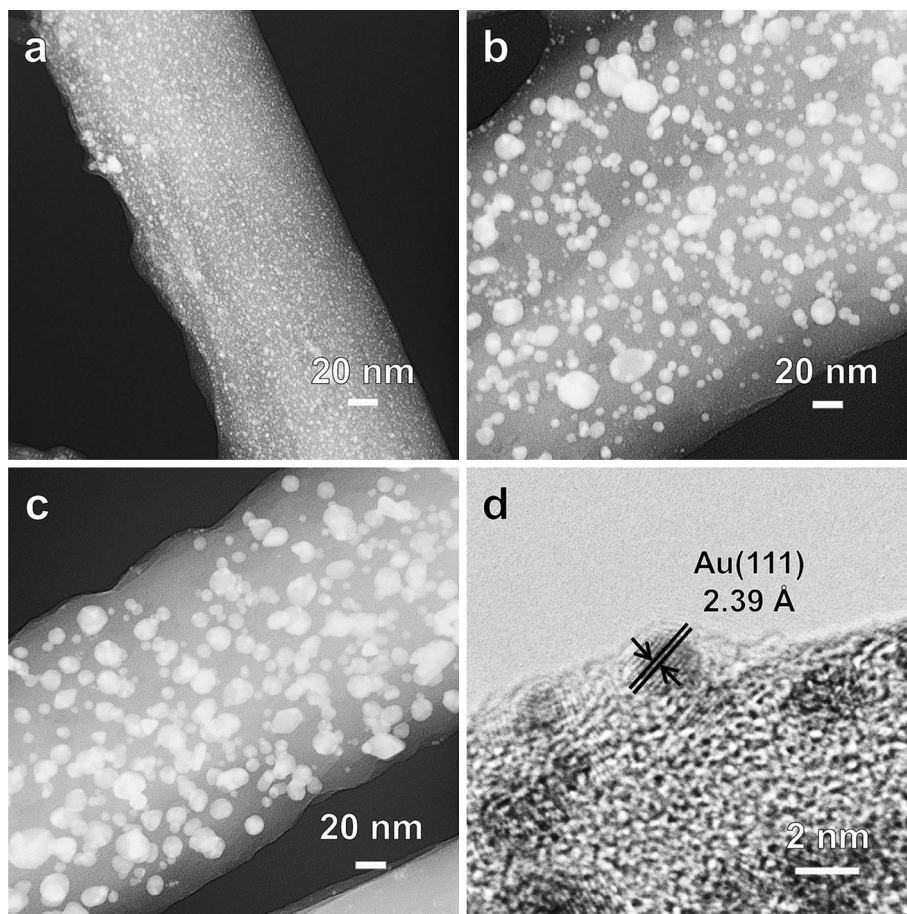
## Results and discussion

### Preparation of PAN nanofibers carrying AuNPs

Photochemical assembly of AuNPs in/on PAN nanofibers is expected to bring a practical advantage to AuNPs-based catalysts by realizing an easy and fast preparation process with less chemical waste and high loading of AuNPs, as compared with a traditional wet chemical process [6, 8, 9]. According to literatures [15, 16, 19], the in situ formation of AuNPs in/on nanofibers can result in highly uniform dispersion of AuNPs over the fibers only by combining electrospinning and reduction processes. To prepare AuNPs through in situ formation in/on nanofibrous mats, in the present study, the mixture of PAN/HAuCl<sub>4</sub>/DMF solution was first electrospun. The resultant fibrous mats were yellowish and composed of smooth individual fibers (Fig. 1). No significant difference was observed among Au3, Au13, and Au21 fibers. These yellowish fibrous mats turned into purplish ones after 1 day of photo-reduction process with

UV irradiation. This change in color indicates the formation of AuNPs in/on the fibers from Au ions existing in the PAN fibers [16, 17]. The purplish color heightened with increasing UV irradiation time from 1 day to 3 and 5 days. The formation of AuNPs in the PAN fibers was also estimated from the change in weight of fibrous mats before and after washing with distilled water. The weight decrease detected for Au21 after 1, 3, and 5 days of UV irradiation was less than 5 % of enclosed HAuCl<sub>4</sub>. In the case of specimen without UV irradiation, on the other hand, the weight loss after water washing reached 34 %. For determining the size of gold particles formed in/on the PAN fibers, we observed the fibers using TEM. The TEM images clearly showed the existence of AuNPs and growth of them with increasing UV irradiation time (Fig. 2a–c). The average diameters of AuNPs were estimated to be  $2.7 \pm 1.4$ ,  $5.0 \pm 1.4$ , and  $5.2 \pm 1.6$  nm for the fibers receiving the UV irradiation for 1, 3, and 5 days, respectively. This increase in the size of AuNPs with increasing UV irradiation time can be explained by the agglomeration of the small particles generated in advance. In contrast with the effect of UV irradiation time, Au concentration was found to be a minor factor affecting the diameter of AuNPs, from the results that the diameters lied in 4.7–5.2 nm when Au concentrations varied from 3 to

**Fig. 2** TEM images of AuNPs in/on Au21 fibers prepared by UV irradiation for 1 (a), 3 (b), 5 days (c). **d** High-resolution TEM image of AuNPs in/on Au21 fibers prepared by UV irradiation for 1 day



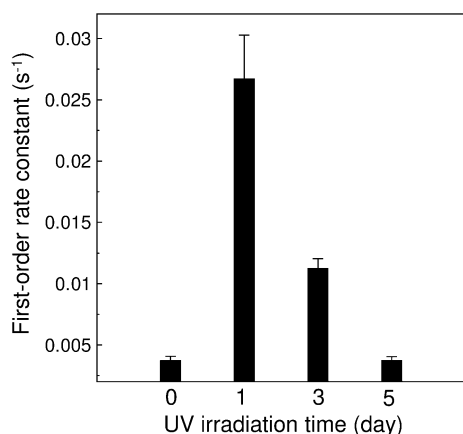
**Fig. 3** **a** UV-Vis spectra of 4-NP aqueous solution catalyzed by AuNPs in/on Au21 fibers prepared by UV irradiation for 5 days. **b** Effect of Au concentration on first-order rate constant in reduction of 4-NP with AuNPs in/on Au3, Au13, and Au21 fibers prepared by

21 wt% under a fixed UV irradiation time of 5 days. In addition to the size information, the high-resolution TEM observation revealed that AuNPs mainly existed in a state of nanoparticles of Au crystals (Fig. 2d) [6, 8]. Further characterization by UV-Vis and XPS spectra as well as XRD pattern measurement supported the formation of crystalline AuNPs after the UV irradiation (Fig. S1).

UV irradiation for 5 days. Relative absorbance was standardized by the absorbance (wavelength=400 nm) at 0 min. The bars represent standard deviations ( $n = 3$ )

Catalytic activity evaluated by reduction of 4-nitrophenol

The catalytic properties of AuNP-containing PAN nanofibrous mats were evaluated from the conversion of 4-NP to 4-AP in the presence of  $\text{NaBH}_4$  as a model reaction [6, 17, 20–23]. As seen in Fig. 3a, the appreciable activity of



**Fig. 4** Effect of UV irradiation time on first-order rate constant in reduction of 4-NP with AuNPs in/on Au21 fibers prepared by UV irradiation for indicated periods. The bars represent standard deviations ( $n = 3$ )

AuNPs in/on the PAN fibers was observed from the fast lowering of absorbance at 400 nm, being attributed to the reduction of 4-NP to 4-AP (Fig. 3a), as compared to that detected for the PAN fibers without AuNPs (Fig. S2). Figure 3b shows the effect of Au content on the first-order rate constants of the resultant catalysts, which were calculated from the changes in absorbance at 400 nm under a fixed volume of fibrous mats. The value increased with increasing Au content. The rate constant of  $4.0 \times 10^{-3} \text{ s}^{-1}$  determined for Au21 fibers was about four times larger than that detected for Au3 fibers,  $1.1 \times 10^{-3} \text{ s}^{-1}$ . This result shows the possibility of reducing the volume of the fibrous catalyst bed, when constructing a reactor in practical application, by increasing the concentration of  $\text{HAuCl}_4$  in electrospun PAN solution. On the other hand, TOF decreased with increasing Au content. The value determined for Au21 fibers,  $5.4 \text{ h}^{-1}$ , was about 1/5 of that for Au3 fibers,  $30 \text{ h}^{-1}$ . This result suggests the decrease of AuNPs enjoying the sufficient supply of substrate, 4-NP, from the bulk solution with increasing content of Au, i.e., the necessity of determining an optimal composition suitable for each practical run from a viewpoint of increasing productivity per unit volume of reactor and per amount of Au.

Next, the effect of irradiation time on the catalytic activity was evaluated with respect to the Au21 fibers (Fig. 4). As the irradiation time elongated from 1, 3, to 5 days, the rate constants significantly decreased from  $2.7 \times 10^{-2}$ ,  $1.1 \times 10^{-2}$  to  $3.7 \times 10^{-3} \text{ s}^{-1}$ . This tendency can be explained by an increase in the diameter of AuNPs, as mentioned earlier. The rate constants per amount of Au were  $8.3 \times 10^{-2}$ ,  $3.4 \times 10^{-2}$ , and  $11 \times 10^{-3} \text{ s}^{-1} \mu\text{mol-Au}^{-1}$  and then the TOF values were 71, 29, and  $9.4 \text{ h}^{-1}$  for the preparations treated for 1, 3, and 5 days of UV irradiation, respectively. The values of TOF obtained in this

study were comparable to those reported in the literatures using various supporting materials for AuNPs (Table S1). These results demonstrate the feasibility of electrospun PAN fibrous mats carrying in situ-formed AuNPs through UV irradiation as catalysts. The nanofibrous fabrics are expected to be useful for applying to a continuous flow-through type reaction system.

## Conclusion

The factors to control the size of AuNPs and their catalytic activity in/on electrospun PAN nanofibers in situ formed by the photochemical process were investigated by altering the enclosed Au content and UV irradiation time. The TEM observation determined that AuNPs of  $5.2 \pm 1.6 \text{ nm}$  formed after the UV irradiation for 5 days in/on the PAN fibers and the size decreased to  $2.7 \pm 1.4 \text{ nm}$  by the shortened irradiation of 1 day. The catalytic activity was examined by the reduction of 4-NP as a model reaction. The first-order rate constant of AuNP-carrying PAN catalysts increased with increasing Au content in the fibers under a fixed volume of the catalysts. The rate constant was compared by altering UV irradiation time using the fibers with Au amount fixed at 21 wt%. The rate constants per Au content and TOF decreased from  $8.3 \times 10^{-2}$  to  $11 \times 10^{-3} \text{ s}^{-1} \mu\text{mol-Au}^{-1}$ , and from 71 to  $9.4 \text{ h}^{-1}$ , respectively, with an increase in UV irradiation time from 1 to 5 days.

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