# Platinum coating on silk by a supercritical $CO_2$ promoted metallization technique for applications of wearable devices

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### A B S T R A C T

Highly reliable Pt coating on silk textile was practiced by supercritical carbon dioxide (sc-$CO_2$) promoted electroless plating in this study. Electroless plating is a facile method to integrate polymeric and metallic materials, and sc-$CO_2$ was introduced to the process to enhance the electroless plating characteristics. Firstly, the palladium organometallic complex was inlaid into the silk substrate without damaging the silk structure in the catalyzation step. Secondly, a smooth and compact Pt layer was realized in the metallization step. Mechanisms involved in the sc-$CO_2$-assisted metallization step were focused and discussed in this study. The lowest electrical resistance was found at 50 m$\Omega$ in the sample metallized with the optimized conditions. The adhesive test showed robustness of the composite material. Corrosion resistance results revealed the applicability of this silk-Pt composite materials prepared by the sc-$CO_2$-assisted electroless plating in wearable device technology.

## 1. Introduction

Supercritical carbon dioxide (sc-$CO_2$) specifies when $CO_2$ goes beyond its critical point (304 K and 7.4 MPa) possessing the properties midway between a gas and liquid state. Sc-$CO_2$ shows non-polar property [1], high self-diffusivity [2], and low viscosity [3]. Owing to these advantages, sc-$CO_2$ is considered as a promising candidate for the development of polymer [2]. Polymer developments are important topics among the critical wearable devices issues due to the highly demand of next generation technology, which is strongly connected to our daily life such as cloth materials [4]. Sc-$CO_2$ is non-polar and non-corrosive to most of polymers, which makes sc-$CO_2$ an ideal solvent in polymer development processes. In this study, we will demonstrate a sc-$CO_2$-assisted polymer development process for applications in fabrication process of wearable devices.

Electroless plating, which can metallize non-conductive polymer substrates with a thin metal or alloy layer, is utilized for the functionalization of polymers due to the requirement of electrical conductivity in wearable device applications. Electroless plating [5,6] is also known as auto-catalytic plating or chemical plating. This technique can be accomplished by simple procedures and is operated without external electrical power. In addition, unlike electrodeposition and sputtering, electroless plating is less restricted by the equipment, and the

metallization shows conformal properties. Accordingly, electroless plating is considered as a powerful technique to deposit materials on sophisticated structure and non-conductive substrate. There are three major steps in electroless plating, cleaning and roughening the substrate are carried out in the pretreatment step firstly, activation sites are settled on the substrate to complete the catalyzation step secondly, and the last step is the metallization on the substrate.

Sc-$CO_2$ is introduced into the catalyzation and metallization steps in the electroless plating system to enhance the properties [7–9]. Since the roughening step can be excluded with the help of sc-$CO_2$, this technique can simplify the procedures. In the meanwhile, due to the introduction of sc-$CO_2$, the usage of catalyzation solutions and electrolytes can be reduced [10]. Structure of the polymer substrate is often damaged during the conventional (CONV) catalyzation step, and the catalyst is merely settled on the substrate surface [11]. Due to the low viscosity and non-corrosive property, sc-$CO_2$ can bring non-polar organometallic complexes to go into the substrate while remains the substrate structure intact after the catalyzation step. This enhancement solves the most challenging issue in the CONV catalyzation step, which settles the catalyst on the substrate surface only by using a corrosive solution [12]. On the other hand, in CONV metallization, reactions are usually accompanied with hydrogen evolutions, which could lead to defects in the metallization layer [13]. In this study, sc-$CO_2$ is introduced into the

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metallization step to enhance the metallization properties. A surfactant is introduced into the aqueous metallization bath to emulsify the aqueous bath and form sc-$CO_2$ micelles [14]. With the help of sc-$CO_2$ micelles, it can carry the hydrogen bubbles away from the substrate due to its non-polarity and high self-diffusivity. The metallization layer turns out to be compact and smooth by elimination of the hydrogen bubbles. Therefore, a sc-$CO_2$-assisted method was further introduced into the metallization process in this study to enhance the properties of the metal film and solve the difficulties from the CONV metallization.

For applications in wearable devices, making the devices user-friendly and biocompatible are the critical issues since there are frequent interaction between the device and human body. In the metallization point of view, common wearable devices are made of Ni metal or its alloys because of their high corrosion resistance [15,16] and low price. However, there is a high risk that Ni arises the allergy due to the non-biocompatible property [17,18]. Platinum was chosen in this study for having biological inertia [19,20] and high corrosion resistance [21] to avoid the allergy reactions. Furthermore, platinum also performs high electrical conductivity [22] and high thermal stability. Based on the aforementioned interests, electroless Pt metallization assisted by sc-$CO_2$ on silk textile was conducted and evaluated in this study.

## 2. Experimental

### 2.1. Sc-$CO_2$-assisted catalyzation

Palladium(II) acetylacetonate (Pd(acac)$_2$; 99%, Tokyo Chemical Industry Co., Ltd., Japan) organometallic complex and a stir bar were enclosed into a 50 mL stainless reaction cell. Silk substrates with dimensions in 2 cm × 4 cm were hooked from top of the reaction cell. Pd(acac)$_2$ in 25 mg was included into the reaction cell to maintain the Pd(acac)$_2$ concentration at the saturation concentration point throughout the entire catalyzation step. The solubility of Pd(acac)$_2$ in sc-$CO_2$ is $2 \times 10^{-5}$ mol/mol [23]. After sealing the reaction cell, $CO_2$ (99.99%, Nippon Tansan Co., Ltd., Japan) was injected into the reaction cell using a high pressure $CO_2$ apparatus [24] (Japan Spectra Company, Japan). The catalyzation was carried out under $T = 80 \pm 1\,°C$ and $P = 15 \pm 0.1$ MPa with agitation for 2 h. No pretreatments or post treatments were carried out after the catalyzation.

### 2.2. Sc-$CO_2$-assisted metallization

50 mL of an acidic platinum-metallization electrolyte consisted of 0.06 M chloroplatinic acid hexahydrate (≥37.50% Pt basis, Sigma-Aldrich, U.S.A.), 0.15 M $N_2H_4$ reducing agent (24–26%, Sigma-Aldrich, U.S.A.), and 0.2 vol% non-ionic surfactant (polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_{15}OH$, 25%, Toshin Yuka Kogyo, Japan) was added into the 50 mL reaction cell. $CO_2$ was injected into the reaction cell after the cell was tightly sealed. Metallization was carried out in an isothermal furnace controlled at $T = 70 \pm 1\,°C$ and $P = 15 \pm 0.1$ MPa with agitation. Various metallization time periods were performed to examine the relationship between lengths of the metallization time and silk-Pt characteristics. No post treatment was conducted after the metallization. An illustration of the sc-$CO_2$ metallization method is shown in Fig. 1.

### 2.3. Analyses of surface, physical and chemical properties

An optical microscope (OM; VHV-5000, KEYENCE, Japan) and a scanning electron microscope (SEM; JSM-7500, JEOL, Japan) were used to observe morphologies of the silk-Pt. Thicknesses of the Pt layer were estimated by observing cross-sections of the metallized silks via SEM and were analyzed by ImageJ (National Institutes of Health, U.S.A.). Metallized silks were cut into two pieces to unclose the cross section of silk-Pt. One piece of the composite material was fixed

perpendicularly to the SEM holder surface by carbon tape showing the cross section to the electron beam. The composition and coverage of the Pt layer were measured by energy-dispersive X-ray spectroscopy (EDX; EMAX Evolution, HORIBA, Japan). The phases and crystal structures were identified by an X-ray diffractometer (XRD; Ultima IV, Rigaku, Japan).

Electrical resistances of the samples with dimensions at 1 cm × 0.5 cm (length × width) were measured by an in-line four-point probe (Mitsubishi Chemical Analytech Co., Ltd., MCP-T370, Japan) at room temperature. In the adhesive tests, Pt metallized silks with the same dimension (1 cm × 0.5 cm) was evaluated by 3 M tape (3 M adhesive tape #810, 3 M, USA), which a piece of the tape having dimensions large enough to cover entire surface of the silk-Pt composite was used and firmly stuck to the composite. A 1-kg loading was used to ensure complete adhesion between the tape and the composite, then the tape was peeled off afterward. The electrical resistance was measured before and after the adhesive test to evaluate firmness of the Pt metallized layer. The adhesive test with one cycle and two cycles of the sticking–peeling procedure are named as first adhesive test and second adhesive test.

The potentiodynamic polarization curves were measured by a Potentiostat/Galvanostat (1287A, Solartron Analytical, UK). The silk-Pt composite prepared by 140 min of the metallization time, a Pt plate, and a Ag/AgCl reference electrode were used as the working electrode, the counter electrode, and the reference electrode, respectively. The testing solutions were 3.5 wt% NaCl and simulated body fluid (SBF) (r-type) [25]. The 3.5 wt% NaCl was used to simulate artificial sweat. The SBF was used to simulate the human body fluid. Total surface area of the working electrode, which is a piece of the 1 × 1 cm$^2$ silk-Pt composite, was calculated by considering surface area of every bundle of the Pt metallized silk fiber in a piece of the textile, and the value was 9.5 cm$^2$. The Pt counter electrode was cleaned ultrasonically in ethanol and pure water for 1 min, respectively, before the polarization measurements. The scan range was $-0.4$ to $+0.6$ V vs Ag/AgCl at a scan rate of 1 mV/s. Prior to the polarization measurement, the three electrodes were immersed into the solution for 25 min to certify the stability. Similar adhesive tests were also conducted before the polarization measurements to confirm firmness of the Pt layer.

In the immersion test, one piece of the Pt metallized silk composite (1 cm × 1 cm) was immersed into the SBF solution at 37 °C for three months. Then the SBF was drawn out and centrifugated for 2 h to remove the redundant particles. Pd and Pt ion concentrations in the solution were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICPS-8100, Shimadzu Co., Ltd., Japan). Both the electrical resistance and the ICP measurements were carried out at least ten times to provide a reliable average value and calculation of the standard deviation.

## 3. Results and discussion

### 3.1. Structures and phases investigation

Fig. 2 shows the (a) as-received silk and (b) sc-$CO_2$ catalyzation-treated silk. Transparent thread bundles and light yellow flakes seen in the OM images indicate the silk substrate and Pd(acac)$_2$, respectively. With the help of sc-$CO_2$ in the catalyzation step, the Pd(acac)$_2$ was successfully inlaid into the silk substrate without damaging the silk structure (Fig. 2(b)). X-ray diffraction patterns of the (a) as-received silk, (b) sc-$CO_2$ catalyzation-treated silk, and (c) Pt metallized silk are shown in Fig. 3. Silk textiles in Fig. 3(a) shows one broad peak at around $2\theta = 20°$ indicating the amorphous structure of the substrate. After the catalyzation, all the diffraction peaks in Fig. 3(b) can be indexed to Pd(acac)$_2$ (diamond) well suggesting the Pd(acac)$_2$ was successfully deposited. X-ray diffraction pattern of the Pt metallized silk is demonstrated in Fig. 3(c), five diffraction peaks locating at $2\theta = 40.2$, 46.8, 68.4, 82.4, and 84.5 degree can be indexed to (111), (200), (220),