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Ni–P and TiO_2 codeposition on silk textile via supercritical CO_2 promoted electroless plating for flexible and wearable photocatalytic devices

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ABSTRACT

This study reported integration of Ni–P/TiO_2 incorporated structure on silk textiles to produce a flexible, highly reliable, and photocatalytic composite material toward applications in functional wearable devices. Supercritical carbon dioxide (Sc–CO_2) promoted electroless plating was utilized to codeposit photocatalytic TiO_2 and electrically conductive Ni–P metallization layer on silk textile. Silk was chosen as the substrate for its flexibility and stretchability. Ni–P was utilized due to its high corrosion resistance, electrical conductivity, and high wear resistance. TiO_2 was selected for its photocatalytic activity and acting as a reinforcement filler to fulfill requirements for applications in wearable devices. Surface morphology, composition, crystal structure, electrical resistance, corrosion resistance, adhesive test, and photocatalytic activity assessments were conducted to evaluate the practicability for wearable photocatalytic devices. With the assistance of sc–CO_2, palladium (II) acetylacetonate catalyst was successfully embedded into the silk substrate at around 330 nm in depth. The coatings on the silk were confirmed to be amorphous Ni–P phase and TiO_2 anatase phase. Uniform Ni–P/TiO_2 composite layer with strong adherence was successfully co–deposited on the silk textile. Ni–P/TiO_2 composite layer deposited with 30 g/L of TiO_2 (critical concentration) in the electrolyte showed higher corrosion resistance while comparing to those of TiO_2–free specimen. The Ni–P/TiO_2 composite layer deposited with the critical concentration of TiO_2 in the electrolyte performed the highest photocatalytic activity.

1. Introduction

Wearable devices have been developed rapidly over the last decade [1]. To fulfill the requirements of the modern technique, wearable devices have been further diverted into different functional applications such as photocatalytic and photovoltaic applications [2,3]. Flexible, electrically conductive, and functional materials are the essential requirements for wearable devices equipped with different functions.

Firstly, flexible silk textile, a common cloth material, is an ideal material for wearable devices to realize the requirement of flexibility. Silk also shows stitchability, which indicates that it can be combined with items commonly used in daily life such as watches, bags, furniture and so on. Secondly, metal–based composite has been widely investigated over the last decades for its chemical property and the mechanical property enhancement effects to perform different functions for the modern techniques [4–8]. Especially, Ni–P can be the electrically conductive layer to produce the electrical conductivity due to its high corrosion resistance [9], simple deposition procedures [10], and low cost [11]. Hence, Ni–P is considered to be a promising material for wearable devices. Lastly, TiO_2, a well–known material as reinforcement filler, photocatalyst, and photovoltaic materials [12], can be included into the Ni–P layer to equip the composite material with photocatalytic activity as well as improve its corrosion resistance and wear resistance. This study integrated flexible silk textile, electrically conductive Ni–P, and photocatalytic TiO_2 together to meet the requirements of wearable devices.

The greatest difficulty in fabrication of flexible functional

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materials for wearable devices is integration of materials with different properties. There are many techniques that can integrate different types of materials such as hydrothermal method [13], chemical vapor deposition [14], physical vapor deposition [15], electrodeposition [16], and electroless plating. Electroless plating is a promising technique to integrate different materials together due to its low cost, simple operation procedures, and process without vacuum system [17]. The greatest advantages of electroless plating is the ability to handle non–electrically conductive materials with sophisticated surface structure such as silk textile in this study. There are three major steps in electroless plating, including pretreatment, catalyzation, and deposition. The substrate is cleaned and roughened in the pretreatment step, and catalysts are deposited onto the substrate in the catalyzation step as active sites for the next deposition step. Lastly, materials are deposited on surface of the substrate in the deposition step. Electroless plating technique was used in this study to equip the flexible silk textile with electrically conductive Ni–P and photocatalytic TiO_2 materials together by introducing TiO_2 particles into the Ni–P metallization electrolyte to form a suspension solution.

There are several literature studied on the inclusion of TiO_2 in metal matrix via electrochemical methods such as electrodeposition and electroless plating to enhance properties of the metal matrix. Gawad et al. [4] synthesized Ni–P–Al_2O_3 and Ni–P–TiO_2 composite layers on Cu substrate from alkaline hypophosphite gluconate baths and studied their properties. This study reported that inclusion of these oxide particles influences structure of the Ni–P matrix. Hardness, corrosion resistance, and coating brightness were enhanced with the TiO_2 inclusions. Thiemig et al. [5] fabricated Ni–TiO_2 composite materials by electro–codeposition via an acidic sulfamate bath and an alkaline pyrophosphate electrolyte. Mechanical properties of the Ni–TiO_2 composite materials were enhanced while comparing to pure Ni electrodeposition in this literature. Parida et al. [6] investigated the ultrafine Ni–TiO_2 composite films by direct current electrodeposition technique on steel substrate from Watt's bath. With the inclusion of TiO_2 in the films, high micro–hardness and high wear resistance were realized while comparing to pure Ni electrodeposition. Benea et al. [7] worked on the electro–codeposition of Ni and TiO_2. The results showed high hardness and high wear resistance. Momenzadeh et al. [8] studied the effect of TiO_2 concentration in the electrolyte on the mechanical properties. They further introduced sodium dodecyl sulfate (SDS) surfactant into the electrolyte to increase the TiO_2 inclusion amount. All the aforementioned literature worked on the mechanical properties and chemical properties such as wear resistance, hardness, and corrosion resistance. In addition, all the composite materials were deposited on rigid substrates. However, flexibility is a critical requirement for wearable devices since the rigid part can be uncomfortable and irritating for active users such as joggers during employment of the device. On the other hand, there is limited literature on decoration of metal–based composite on a flexible substrate and investigating photocatalytic activity of the composite material. Therefore, this study aims at the codeposition of TiO_2 as reinforcing phase into Ni–P metallization layer to improve the basic mechanical and chemical properties such as corrosion resistance and photocatalytic activity.

Results in this study were also compared with a previous article [18] on integration of photocatalytic ZnO with Au metallized silk textile by cathodic deposition. Cathodic deposition is a useful technique to decorate metal oxides on substrates with complex surface condition, however, metal oxides synthesized in aqueous solution often show low crystallinity, and photocatalytic activity of metal oxides is highly dependent on the crystallinity. Although temperature annealing is a strategy to enhance the crystallinity of photocatalysts like ZnO, the flexible polymeric substrate (i.e. silk textile) would be decomposed in the annealing process. In addition, adhesion between the cathodically deposited oxides and the substrate is low, which further limited applicability of the flexible photocatalytic composite. The dilemmas were overcame in this study by the codeposition of Ni–P and TiO_2. Incorporation of TiO_2 with high crystallinity and photocatalytic activity lead to the high photocurrent density.

In order to further enhance reliability (i.e. adhesive property) of the silk/Ni–P/TiO_2 composite in this study, supercritical carbon dioxide (sc–CO_2) is introduced into the catalyzation step [19–22]. Properties directly reflected the practical applicability in wearable devices, such as adhesive firmness, corrosion resistance, and photocatalytic activity of the silk/Ni–P/TiO_2 composite, were investigated.

2. Experimental

2.1. Chemicals

A piece of silk textile (2 cm × 4 cm) was used as the substrate. Palladium (II) acetylacetonate ($Pd(acac)_2$) (98.0%, Tokyo Chemical Industry Co., Ltd., Japan) organometallic compounds were utilized as precursors of the catalysts, and carbon dioxide gas (99.99%, Nippon Tansan Gas Co., Ltd. Japan) was utilized as source of sc–CO_2. A commercially available acidic Ni–P electrolyte (Okuno Chemical Industries Co., Ltd., Japan) consisted of nickel chloride (9.0 wt%), sodium hypophosphite (12.0 wt%), complexing agent (12.0 wt%), and ion–exchanged water (67.0 wt%) was used as the Ni–P metallization solution. A commercially available TiO_2 (average particle size in 20 nm; Degussa, Evonik Industries, Germany) was used as inclusion particles in the Ni–P metallization layer. Sodium sulfate (99.0%, Sigma–Aldrich, USA) was used in the electrolyte for evaluation of the photocatalytic activity.

2.2. Sc–CO_2 assisted catalyzation

No pretreatment was executed before the sc–CO_2 assisted catalyzation step. A piece of silk textile was hooked from the inner ceiling of the reaction cell [23]. Oversaturated $Pd(acac)_2$ (>0.5 mg catalyst/mL reaction cell) were introduced into a 50 mL stainless reaction cell to keep a high concentration throughout the catalyzation process. CO_2 was introduced into the reaction cell after the reaction cell was tightly sealed. A high–pressure apparatus (Japan Spectra Company, Japan) was utilized to pressurize CO_2 into the sealed reaction cell, and the details were shown in our previous studies [23–25]. The sc–CO_2 catalyzation was carried out at 80 ± 1 °C and 15 ± 0.1 MPa with agitation for 2 h. No post treatments were conducted after the sc–CO_2 catalyzation process.

2.3. Codeposition of Ni–P/TiO_2

Different TiO_2 amounts were introduced into 100 mL Ni–P metallization electrolyte individually. Concentrations of TiO_2 in the Ni–P electrolyte were 0, 10, 20, 30, 40, and 50 g/L. Codeposition time was set at 10 min and was conducted under atmospheric pressure. Codeposition temperature was set at 70 ± 1 °C, which was controlled by an isothermal water bath. TiO_2 particles were mixed thoroughly in the electrolyte for 10 min before the codeposition. The electrolyte was agitated throughout the entire codeposition process to establish stable and uniform TiO_2 suspension in the solution.

2.4. Characterization

Surface morphology, cross–section, composition, and elemental