

## Short note

## Facile and rapid preparation of platinum counter electrodes for dye-sensitized solar cells

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## ABSTRACT

Here, we report on the deposition of platinum nanoparticles (PNPs) on fluorine-doped tin oxide (FTO) substrate by synthesizing PNPs through chemical reduction of potassium tetrachloroplatinate with formic acid, and subsequently depositing the PNPs on FTO substrate at 70 °C; and application of the chemically reduced Pt electrodes (CRs) as the counter electrodes (CEs) of dye-sensitized solar cells (DSSCs). The surface morphology and catalytic activity of the prepared CRs were studied along with conventional thermally decomposed Pt electrodes (TDs). Electrochemical study showed that the catalytic performance of the CRs toward the reduction of I<sub>3</sub><sup>-</sup> was comparable to that of TDs. Also, the photovoltaic performance of the DSSCs with CRs were similar to that with TDs. The method of preparing Pt electrodes through chemical reduction is so fast that the whole process of preparing a set of CRs, after pre-cleaning of the FTO substrates, takes less than 30 min. Most importantly, the present method enables low temperature fabrication of Pt electrodes even on flexible substrates.

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## 1. Introduction

The present form of dye-sensitized solar cells (DSSCs) was developed by O'Regan and Gratzel in 1991 [1]. Since then DSSCs emerged as a promising technology in the field of photovoltaics [2,3]. In general, a DSSC is composed of a panchromatic dye loaded nanostructured semiconducting metal oxide on fluorine-doped tin oxide (FTO) glass substrate as a photoelectrode, an iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) based electrolyte solution as a redox mediator, and a platinum (Pt) coated FTO substrate as a counter electrode (CE) [4–8]. Even though Pt is expensive and scarce in nature, developing new methods to fabricate Pt based electrode materials is still common due to its superior performance [9–16].

Pt-CEs for DSSCs may be prepared by depositing Pt nanoparticles or composites of Pt on conducting substrate through thermal decomposition [12], chemical reduction [9,13], electrochemical deposition [17], and sputtering [18]. Most of the processes require either sophisticated tools or long processing time. Size-controllable uniform nanoparticles of Pt can be synthesized by chemical reduction of Pt precursor such as potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>) [16,19], and

chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·2H<sub>2</sub>O) [20] with formic acid (HCOOH) as a reductant. Aziz and Oyama showed that thermally driven attachment of nanoparticles on tin-doped indium oxide (ITO) could be a simple route to modify ITO surfaces [21]. Thus, deposition of Pt nanoparticles on FTO substrates could be performed through chemical reduction of Pt precursor at elevated temperature.

Here, we have fabricated Pt CEs by synthesizing Pt nanoparticles (PNPs) through chemical reduction of K<sub>2</sub>PtCl<sub>4</sub> with HCOOH at 70 °C and subsequently depositing the PNPs on FTO substrate in the same reaction vessel. The surface morphology and catalytic activity of the chemically reduced Pt electrodes (CRs) were studied along with conventional thermally decomposed Pt electrodes (TDs). The photovoltaic performance of the DSSCs fabricated with the CRs was compared with that with TDs.

## 2. Experimental

All reagents and solvents were purchased from Sigma–Aldrich unless otherwise mentioned. A mesoporous layer of nanocrystalline TiO<sub>2</sub> with an active area of 0.25 cm [2] was deposited on cleaned FTO ( Pilkington TEC8, 8 Ω/square) substrates by screen printing a TiO<sub>2</sub> paste (TTP-20N, ENB Korea) followed by sintering at 500 °C for 30 min in an electric muffle furnace. The average thickness of the TiO<sub>2</sub> film was 8 μm. The TiO<sub>2</sub> electrodes were

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immersed in a 0.3 mM ethanolic solution of a ruthenium dye (N719, Solaronix SA, Switzerland) for 16 h.

Chemically reduced Pt electrodes, CRs, were prepared by immersing cleaned FTO substrates in 20 mL of aqueous solution of potassium tetrachloroplatinate ( $K_2PtCl_4$ ). Then the temperature of the solution was raised to 70 °C in a water bath and an excess amount of formic acid (HCOOH), ten times of the molar concentration of Pt precursor, was added to the solution with shaking. The reaction mass was kept for 15 min at the same temperature to facilitate the deposition of Pt nanoparticles on the FTO substrate. Finally, the Pt-loaded FTO substrate was washed with water, and dried with nitrogen flow followed by heating at 80 °C for several minutes. For optimization, the concentrations of the Pt precursor used were 0.1 mM, 0.5 mM, 1.0 mM, and 2.5 mM. In the order of increasing concentration of the Pt precursor, the chemically reduced Pt electrodes were labeled as CR-1, CR-2, CR-3, and CR-4.

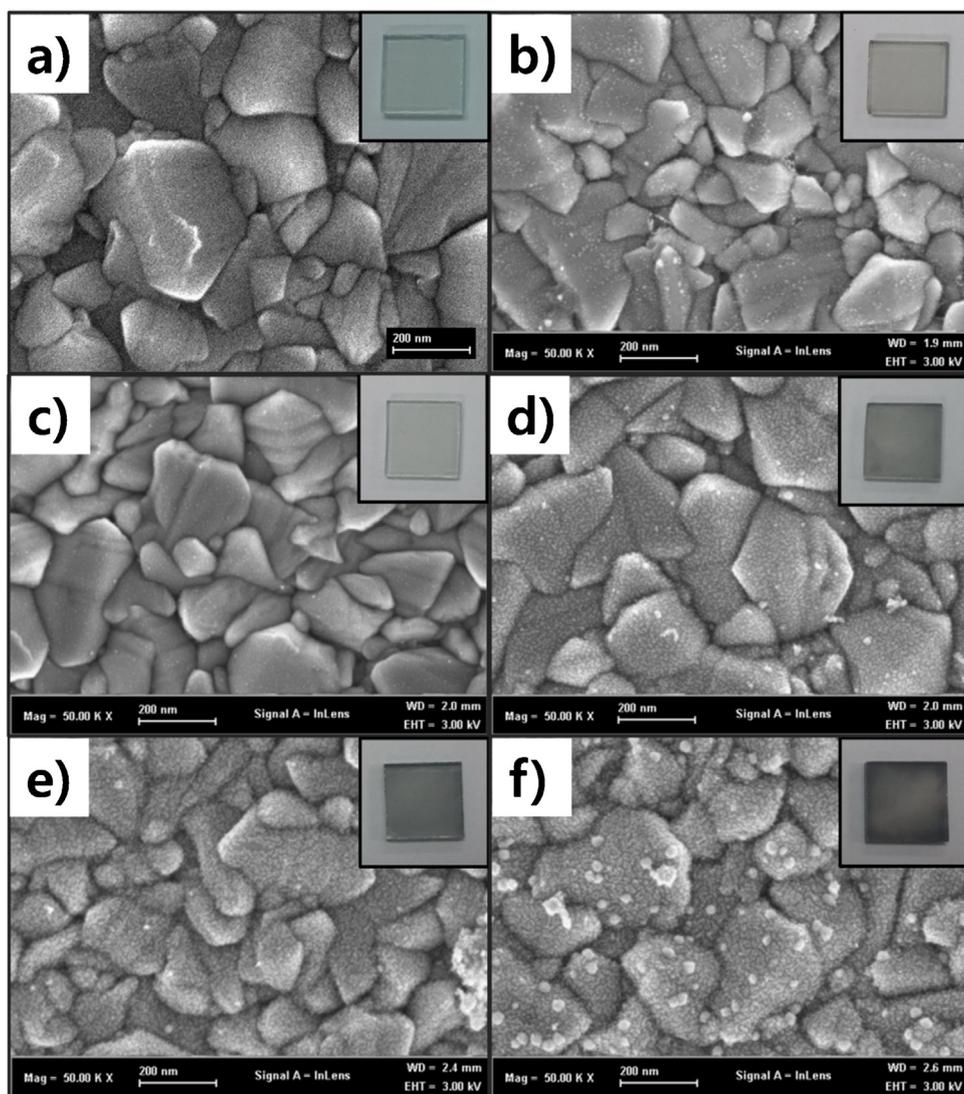
Thermally decomposed Pt electrodes, TDs, were prepared following a procedure as reported elsewhere [22]. Briefly, cleaned FTO glass substrates were spin-coated with an ethanolic solution of

50 mM chloroplatinic acid hexahydrate ( $H_2PtCl_6 \cdot 6H_2O$ ) and then sintered at 380 °C for 20 min in an electric muffle furnace.

The dye loaded  $TiO_2$  photoelectrodes and the platinumized CEs were put together with a piece of 60  $\mu$ m-thick Surlyn film (Meltonix 1170-60, Solaronix SA, Switzerland) as a spacer and sealing agent. A drop of liquid electrolyte solution composed of 0.6 M 1-butyle-3-methylimidazolium iodide (BMII), 0.1 M  $I_2$ , 0.1 M guanidinium thiocyanate and 0.5 M 4-*tert*-butylpyridine (TBP) in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15) was directly injected into the cell through the drilled holes at the counter electrode and the holes were sealed with a piece of scotch tape. Also, symmetric dummy cells of the configuration Pt/electrolyte/Pt were fabricated following the same procedure.

Surface morphology and the elemental analysis of the Pt electrodes were studied by high-resolution field emission scanning electron microscope (E-SEM, FEI Quanta 400 FEG, USA) equipped with detector for energy dispersive X-ray spectroscopy (EDS).

Photovoltaic measurements were performed employing a solar simulator (XES-40S1, San-Ei Electric Co., Ltd., Japan) with an AM 1.5 filter. The intensity of the light was adjusted to simulate one sun



**Fig. 1.** SEM images at a magnification of 50,000 $\times$  of the surfaces of (a) bare FTO, (b) TD, (c) CR-1, (d) CR-2, (e) CR-3, and (f) CR-4. Insets show photographs of the corresponding electrode surfaces (1.5 cm  $\times$  1.5 cm).

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