

Platinum nanoparticles immobilized on CVD-grown graphene as a transparent and efficient counter electrode materials for dye-sensitized solar cells

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The dye-sensitized solar cell (DSC) has attracted considerable attention as a next-generation solar cell because of its many virtues such as low fabrication cost, environmentally benign process, glossy transparency, and relatively high energy conversion efficiency.^[1] One of the issues with DSCs is the need to improve the transferring of electrons into the redox system and activating electrolyte reduction at the counter electrode (CE). Platinum (Pt) is traditionally the most popular material for the CE of DSCs^[1-4] and numerous substitutes such as carbon nanotube (CNT),^[5] CNT-TiN,^[6] and CNT-Pt^[7] have been developed to replace or reduce the use of expensive Pt.

Owing to its unique 2D structure, large specific surface area, high electrical conductivity, and robust mechanical strength, graphene has been known as one of the best supports for metal nanoparticles (NPs) for the application to energy conversion/storage devices. Graphene-metal composites have been mostly synthesized through either chemical methods or physical methods. However, extreme conditions such as high temperature, low pressure, liquid environment, and chemical toxicity become drawbacks for the application of graphene-metal composites to large scale productions. Recently, we developed a new process of efficiently synthesizing supported Pt-NPs using dry plasma reduction (DPR) at near room temperature under atmospheric pressure. The aim of this technique is to overcome the process restrictions previously mentioned.

Herein, we demonstrate the DPR to synthesize Pt-NPs on chemical vapor deposition (CVD)-grown graphene under atmospheric pressure without using any toxic chemicals at near room temperature. The aim of this study is to develop a transparent and efficient DSC, which is crucial for realizing building integrated photovoltaic (BIPV), through synergistically combining a high transparency of CVD-grown graphene and a low charge transfer resistance of supported Pt-NPs while considering methods to keep production cost low.

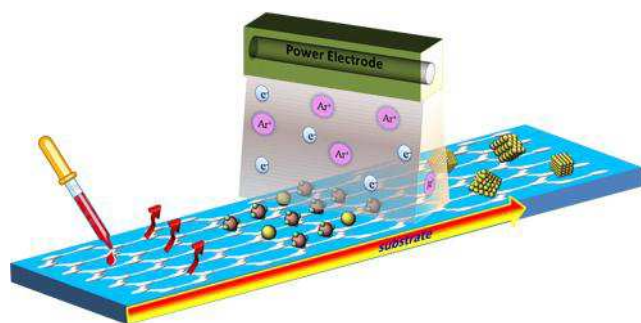


Figure 1. Synthesis of Pt-NPs hybridized on CVD-grown graphene using dry plasma reduction

The synthesis of Pt-NPs hybridized on CVD-grown graphene is achieved by using a DPR as shown in Scheme 1. First, a drop of precursor solution is loaded on the substrate, followed by a process of completely drying solvent at 70 °C for 10 min. During this drying process, $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ is partially reduced to Pt atoms through alcoholic reduction. The remaining salts on the dried

surface are then further reduced to Pt-NPs through the irradiation of RF atmospheric pressure plasma with Ar gas under previously optimized conditions. As shown in Figure 1, the DPR can also be well adapted to develop an economic continuous process for immobilizing metal NPs on the surface of various substrates, including thermoplastic films as well as a CVD-grown graphene layer.

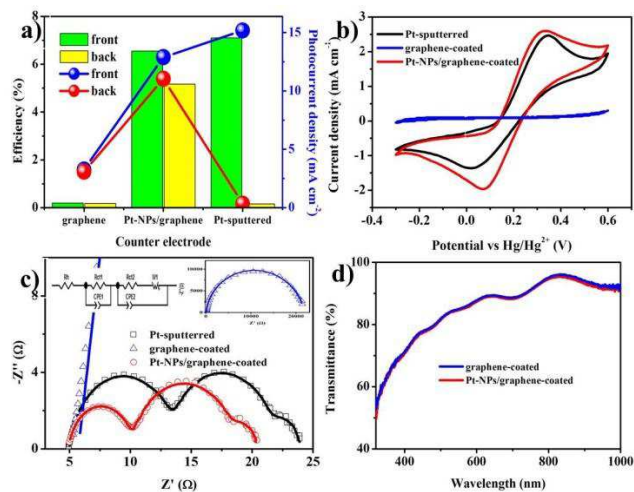


Figure 2. (a) The relationship between front-side illumination, back-side illumination, and photocurrent density with different CEs; (b) Cyclic voltammograms of Pt-sputtered, graphene-coated, and Pt-NPs/graphene-coated; (c) Nyquist plots of three DSCs equipped with Pt-sputtered, graphene-coated, and Pt-NPs/graphene-coated CEs. The inset image shows the equivalent circuit diagram used to fit the observed impedance spectra in this figure and the Nyquist plot of DSC equipped with graphene-coated CE; (d) Transmittances of graphene-coated and Pt-NPs/graphene-coated FTO glass with respect to wavelength.

Ultrafine crystalline Pt-NPs/graphene-coated electrode was successfully fabricated using DPR at low temperature. TEM results showed Pt NPs with the size of 1~2.5 nm, most of which were 1.5 nm, dispersed on the surface of a graphene-coated electrode with a high areal density of $66,875(\pm 550)$ particles/ μm^2 . The many small Pt-NPs with enough spacing for light penetration also provided a sufficiently active surface area for catalytic activity without losing the optical transmittance of the FTO glass. The Pt-NPs/graphene-coated electrode used as the CE of DSC reached the conversion efficiency of $6.55 (\pm 0.21)\%$ for front-side illumination and $5.17 (\pm 0.22)\%$ for back-side illumination due to the low charge-transfer resistance and high optical transmittance of the Pt-NPs/graphene-coated electrode, as shown in Figure 2.

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