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Kinetic spraying of silver nanowire blended graphite powder to fabricate transparent conductive electrode and their application in electrochromic device

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ABSTRACT

A transparent conductive electrode (TCE) using the mxiture of graphite and silver nanowires (AgNWs) powder was fabricated with a nanoparticle deposition system (NPDS), a facile dry deposition approach using a graphite-AgNW powder mixture. The deposited film formed a composite structure with few-layered graphene, single layered graphene sheets, and AgNWs forming a fused junction under optimal heat treatment at 80 °C. The sheet resistance of the deposited film was measured to be 24–28 Ω/□, in accordance with values measured for commercial TCEs. Transmittance of 58–67% was measured for the deposited sample, which was lower than the 20–30% measured for conventional TCEs, due to scattering of incident light by few-layered graphene and AgNWs within the deposited film. An electrochromic (EC) cell with fabricated TCE performed well, showing a transmittance change of 15% at its wavelength of 630 nm. CV measurements were conducted for 500 cycles to confirm the stability of the EC device and TCE, and no performance degradation was observed for the device after 500 cycles, which represents good cyclic stability. Therefore, a TCE using graphite and AgNWs was successfully fabricated using the facile NPDS process, which represents a new fabrication process for TCEs based on graphene and AgNWs.

1. Introduction

Transparent conductive electrodes (TCEs) with high transparency and good electrical conductivity are necessary components in many devices such as displays, transistors, touch panels, and solar cells. They form a thin film on various substrates such as glass, polyethylene terephthalate, and polyethersulfone for device fabrication, and exhibit high conductivity and excellent transmittance in the visible light region. TCEs can be used for various applications such as antennae, optical filters, and antistatic films, and etc., due to its low sheet resistance [1]. Transparent conductive oxides (TCOs) such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO), have been widely used as TCE materials [2]. A sputtering method has typically been used to fabricate TCOs, with the substrate heated to 300 °C to form a highly crystallized film. However, TCOs have several drawbacks relating to both material properties and cost. Since TCOs are ceramic materials, they can crack upon mechanical stimulation and fracture at relatively low strains [3–5]. These cracks and fractures can propagate, finally leading to a decrease in electrical conductivity [6]. Moreover, indium is a fairly rare earth metal, and is therefore costly, and the sputter deposition process is inefficient with ITO residue remaining during ITO target fabrication and deposition. To overcome these problems, several nanoscaled materials such as silver nanowires, carbon nanotubes (CNTs), graphene, and conducting polymers as well as other nanostructured metals have been studied intensively [7–11]. Among those, carbon-based materials, including CNTs and graphene, have shown great promise as TCEs because of their excellent mechanical, electrical, thermal, and optical properties [12]. Graphene is single atomic layer of pure graphite and an allotrope of carbon in the form of a two-dimensional structure. Owing to its unique atomic structure, it shows potential in TCE applications, and could be a substitute for ITO- or FTO-based TCEs [13]. Initially, Geim et al. used Scotch tape to peel off a layer of graphite from its block and obtained single-layer graphene by repeated peeling, and this peeling method has been widely used to obtain

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graphene layers with good structural stability and a large grain size (1 mm) [14]. However, this method is not suitable for mass production. Another approach for the synthesis of graphene layers was developed by Kim et al. using chemical vapor deposition (CVD), which is one of successful method of producing large area graphene layers, resulting in relatively cheaper graphene controlling the thickness of sheets. They reported that a graphene-based transparent electrode layer with transmittance of 80% and sheet resistance of 280 Ω/□ was fabricated using a catalyst such as Ni or Cu for graphene layer growth [15]. However, compared with conventional ITOs, the sheet resistance is relatively high, and there are several disadvantages such as the high equipment cost and high processing temperature [16].

To overcome these problems, a nanoparticle deposition system (NPDS), which is a kinetic spray technique, has been used to fabricate a TCE. NPDS is a recently developed dry-deposition technique capable of kinetically depositing both nano- and sub-micron-sized metal and ceramic particles at room temperature under low vacuum with low-cost compressed air as the carrier gas. In NPDSs, nanoparticles are accelerated through a converging/diverging nozzle at supersonic velocities stemming from the pressure difference between the deposition chamber and the powder feeder [17,18]. The deposition mechanisms of metal and ceramic particles have been studied. In the case of metal deposition, the bonding mechanisms proposed for the metal particles are plastic deformation on the particle/substrate interface, and a rising temperature below the melting temperature that softens the material [19]. However, in the case of ceramic deposition, the mechanism of deposition is considered to be the fragmentation of submicron ceramic particles into nanoparticles and the subsequent impact of submicron particles, which provides sufficient bonding energy by means of shockwaves that impart heat and high pressure [17]. This NPDS deposition mechanism has been widely used to coat metals and ceramics including Cu, TiO_2, ATO, Fe_2O_3, and graphite on various substrates including glass, Si, and polymers [20–24]. Commercial powders can be directly deposited by NPDS, thereby simplifying the fabrication process for transparent conductive electrodes using carbon-based materials, such that neither pre- or post-processing steps nor precursors are required.

In this research, graphite particles as a source material were used to form a graphene layer by the colliding and shattering of graphite particles via NPDS. Additionally, the graphite powders were used as a deposition complement, to be used with silver nanowires (AgNWs) as this deposition complement; i.e. the particles assisting the deposition of other particles that are otherwise hard to deposit solely, as this concept has been reported previously [25]. Using small amount of AgNWs, TCE using graphite/AgNWs powder mixture can be fabricated by NPDS with low cost and good electrical conductivity.

We investigated the microstructure of the deposited layers using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy to confirm the transition to graphene layers from graphite source particles. Moreover, the graphite-graphene-AgNWs-based TCE was characterized by measuring electrical conductivity and transmission spectra. Our results establish that the NPDS could be used as a new and facile fabrication process for TCE and TCE layers using graphite-AgNWs.

2. Experiment

2.1. Material preparation and deposition conditions

To fabricate the graphene-silver nano wire (AgNW) electrode using the NPDS (Fig. 1(a) and (b)), AgNWs (1 wt% in ethanol; Nanopyxis, South Korea), with its mean diameter and length to be 27 ± 3 nm and 22 ± 5 μm, respectively, was prepared with its weight ratio of 30%, to be mixed with graphite (< 20 μm; Sigma-Aldrich, St. Louis, MO, USA) flakes. Furthermore, the minimum amount of powder required for deposition via NPDS is 5–15 g depending on the density of powder. However, since it is hard and expensive to prepare 5–15 g of AgNWs powder itself from the AgNWs suspension, we have prepared powder mixture of graphite and AgNWs instead. Moreover, AgNWs itself was not deposited via NPDS. This powder mixture was then deposited on soda lime glass. Fig. 1(a) shows a schematic diagram of the NPDS, which consisted of an air compressor for the carrier gas, a powder cartridge, a nozzle, a vacuum chamber, a vacuum pump, and *x*-, *y*-, and *z*-axis translation stages. Pressurized air was supplied via a compressor, and the particles were aerosolized using a fluidized bed of powder (3400A; TSI, USA). It is straightforward to apply other materials using a powder cartridge, and the material in the fluidized bed powder feeder can be changed. The particles were sprayed into the vacuum chamber at supersonic speeds at room temperature, such that they impinged on the substrate. To facilitate formation of a thin, transparent coating, the substrate was translated along the *x*-axis at a high speed of 10–100 μm s^{-1} during deposition. The deposition area was 10 × 10 mm in size, obtained using a slit nozzle with a size of 10 × 0.3 mm. The gas flow rate through the slit nozzle (outlet cross-section: 10 × 10 mm) was fixed at 17.5 L min^{-1}. The jet pressure was 0.3 MPa, while the chamber pressure was measured to be 0.01 MPa according to the gauge pressure. Finally, the stand-off distance (i.e., the separation between the nozzle and the substrate) was fixed at 3 mm. Then, the fabricated sample was heated to form a fused AgNWs junction in a coating layer under varying temperature conditions from room temperature to 150 °C.

2.2. Characterizations

The surface morphologies and microstructures of the deposited films using graphite and AgNWs were characterized using SEM (Mira 3; TESCAN, Czech Republic). The sheet resistance of the TCE film was measured using a four-point probe (CMT-SR1000N; Changmin Tech Co. Ltd., South Korea), and Raman analysis (NRS-3100; JASCO, Japan) was performed to confirm the transition of the graphene layer from graphite particles. The microstructure of the exfoliated graphene was investigated by high-resolution transmission electron microscopy (TEM, 2100F; Jeol, Japan) at an acceleration voltage of 200 kV. Finally, the optical transmittance spectra of the graphite-graphene-AgNWs TCE films were measured using a UV–Visible spectrophotometer (VS650; JASCO, Japan) from 30 to 900 nm. To confirm the possibility of operating the graphite-graphene-AgNWs TCE in a device, an PEDOT:PSS-TiO_2 EC cell was fabricated. Optical transmittance spectra of the colored and bleached PEDOT:PSS-based EC films were measured using a UV spectrophotometer (V650; JASCO, Japan) over the wavelength range of 350–900 nm. To investigate the cyclic transmission change and charge balance, a rectangular wave of ± 1.5 V for 120 s per cycle was applied to the EC devices for 1 h using a potentiostat (Versa STAT4; Princeton Applied Research, USA), and the transmittance change was measured using a UV spectrophotometer (V650; JASCO, Japan). For CV measurements, the cyclic potential was scanned at a rate of 50 mV s^{-1} over the range −1.5 to +1.5 V for 500 cycles to measure the cyclic stability of each device. Fig. 1 shows a schematic diagram of the NPDS method and the fabrication process for the TCE.

3. Results

Fig. 2(a) shows SEM images of the graphite-AgNWs powder mixture deposited by NPDS. Prior to deposition, it seems that a very small number of AgNWs were blended with the graphite powder. After deposition, the microstructure of the films deposited at different annealing temperatures was observed using second and back-scattered electron microscopy (SE & BSE). In contrast to the microstructure before deposition, the AgNWs (white contrast areas) were uniformly deposited and the large graphite particles (dark contrast areas) were broken and fragmented by collisions on the glass substrate, forming thin layers of graphene sheets, as shown in Fig. 2(b). AgNWs, which are