Laser Direct Writing of Microstructure on Graphene Oxide/Metal Oxide Hybrid Film

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A conductive microstructure consisting of a reduced graphene oxide (rGO) and Cu was prepared by laser direct writing. A hybrid film on a polymer substrate was prepared from a water-dispersion mixture of graphene oxide (GO) and CuO nanorods (CuO NRs) by doctor blade method. A CW 405 nm blue-violet laser beam was scanned on the GO/CuO NRs hybrid film through an objective lens to prepare a microstructure of rGO/Cu on a flexible substrate. The reduction of CuO NRs to Cu was observed by micro-Raman spectroscopy. The surface resistivity of a laser scanned hybrid film was lowered with decreasing laser scan spacing. A hybrid film consisting of rGO/Cu microstructure showed a negative temperature coefficient of resistance ($-1.18\%/^{\circ}\text{C}$), which was extremely larger than those of usual carbon materials. Such characteristics can be applied to an IR photosensor.

Keywords: Graphene oxide, Reduced graphene oxide, Laser-induced reduction, Laser direct writing, CuO nanorods, IR photosensor

1. Introduction

The innovation of electronic device manufacturing process is expected to reduce the cost and energy consumption because the development of Internet of Things (IoT) technology needs huge number of sensors. The printed electronics is widely studied for manufacturing in next generation. The additive manufacturing and on-demand processing are important features in the concept of printed electronics. The laser direct writing gives an on-demand processing with a high spatial resolution. We have studied the laser direct writing of conductive micropattern using metal nanoparticle inks [1-3], where the scanning of a focused laser beam on a metal nanoparticle

coated film enables the sintering of metal nanoparticles and micro-patterning with micron-level resolution. The laser direct writing can be applied to the flexible electronic device fabrication on a polymer substrate because the local sintering process by the irradiation of a laser beam with a small spot size reduces the heat damage of a substrate [2]. The laser-induced reduction of a graphene oxide (GO) is also effective method to prepare a conductive micro-pattern. Because the GO has a structure with oxygen-containing groups on a graphene plane, a solution process using a GO-dispersed solution can be applied to the manufacturing in printed electronics. In previous papers, we have reported a conductive reduced graphene oxide

(rGO) by laser-induced reduction of a GO film and the formation of an rGO/GO/rGO interdigitated microelectrode by laser direct writing [4,5]. The rGO/GO/rGO interdigitated microelectrode can be applied to a humidity sensor based on the changes of C and R parameters by the water molecule adsorption on the GO [4]. In this paper, we studied the laser direct writing using a GO/CuO nanorods (CuO NRs) hybrid film to functionalize a laser-written rGO microstructure. A conductive rGO/Cu structure was obtained by the laser direct writing on a GO/CuO NRs hybrid film, which can be applied to an IR photosensor.

2. Experimental

The 20 mg of few-layer GO powders (Beijing Ding Sheng Xiong Di Technology Co., Ltd.) was dispersed in the water (5 g) to form a GO dispersion. After the ultrasonication in a water bath for 5 min, a gel-like solution was formed. The CuO NRs were synthesized using a plant leaf extract as similar manner reported in previous papers [6,7]. The TEM image showed that the green synthesized CuO has rod-like structure with long axis of ca. 80 nm and short axis of ca. 23 nm. The 2.5 g of CuO NRs was added into the GO water-dispersion and then ultrasonicated for 15 min. A GO/CuO NRs hybrid film was prepared on a polymer (PET, polyethylene terephthalate) film by doctor blade method from a water-dispersion mixture of GO and CuO NRs. The laser direct writing was conducted using a CW (continuous wave) 405 nm blue-violet semiconductor laser. The laser beam with the power of 13 mW was scanned on a GO/CuO NRs hybrid film through an objective lens (OLYMPUS SMLPlan N, 50× N.A. 0.35) using a computer-controlled XYZ auto-stage in air. Raman spectra were measured on a micro-Raman spectrometer equipped with an optical microscope (Olympus BX51), a CW 532 nm DPSS (diode-pumped solid state) laser, a CCD camera (DV401, Andor Technology), and a monochromator (MS257, Oriel Instruments Co.). Surface resistance was measured using a four-point probe resistance meter. X-ray photoelectron spectroscopy (XPS) was performed by PHI5600 (ULVAC- PHI, Inc.).

3. Results and discussion

The optical microscope images of microstructures obtained by the raster scan of a 405 nm

laser beam on a GO/CuO NRs hybrid film are shown in Fig. 1, where the microstructures with the laser scan spacing of 30, 20, 10, and 5 μm are denoted as rGO/Cu-30, rGO/Cu-20, rGO/Cu-10, and rGO/Cu-5, respectively. The change from a dark color of GO and CuO NRs to a bright bronze-color was observed at the laser-scanned line. With decreasing scan spacing, a bronze-colored granular structure became remarkable as shown in Figs. 1g and 1h. The changes of chemical structure by laser beam scanning were studied by micro-Raman spectroscopy. Figure 2 shows the Raman

Fig. 1. Optical microscope images of laser-scanned hybrid films of GO and CuO NRs. (a) (b); rGO/Cu-30, (c) (d); rGO/Cu-20, (e) (f); rGO/Cu-10, and (g) (h); rGO/Cu-5.

Fig. 2. Raman spectrum of CuO NRs.

spectrum of CuO NRs. There are three Raman bands at 283, 337, and 616 cm^{-1} , which correspond to the Ag, B1g, and B2g Raman modes of CuO [8,9]. Atomic concentrations of C1s, Cu2p, and O1s obtained from the XPS of CuO NRs were 16.8, 39.16, and 43.63%, respectively. The excess ratio of O1s against Cu2p and a high atomic concentration of C1s suggest residues of organic reducing agent and capping agent in the CuO NRs.

The changes of Raman spectra by laser beam scanning are shown in Figs. 3 and 4, which are corresponding to those at the unirradiated gap and laser scanned line, respectively. The Raman bands assigned to CuO were observed for rGO/Cu-30 and rGO/Cu-20 as shown in Fig. 3. The CuO bands were disappeared with decreasing laser scan spacing as shown in Fig. 3c and 3d for rGO/Cu-10 and rGO/Cu-5, respectively. On the other hand, the Raman bands assigned to rGO were increased in the region from 1300 to 1700 cm^{-1} . The broad increase in intensity at the higher wave numbers may be attributed to the influence of an emission. The Raman spectra at the laser scanning line for rGO/Cu-30, rGO/Cu-20, and rGO/Cu-10 did not show the Raman bands of CuO but those of rGO as shown in Fig. 4. The rGO/Cu-5 showed a new Raman band around 214, which can be assigned to the Raman band of Cu_2O phase [9,10]. The re-oxidation of Cu layer by excess laser irradiation in air must be caused under a narrow laser scan spacing condition.

The reduction of CuO NRs in the composite with GO by laser irradiation was expected by the formation of a bright bronze-color layer in an optical microscope images and the disappearance of CuO Raman bands. The surface resistivities of laser-scanned GO/CuO NRs composite films are summarized in Table 1. The surface resistivity was remarkably lowered from 200×10^3 (Ω/sq) for rGO/Cu-30 to 19.6 (Ω/sq) for rGO/Cu-5 with decreasing laser line spacing. These results are corresponding to the morphology changes as shown in Fig. 1, where the lower resistive film under the narrower laser scan spacing showed the larger grain and the brighter bronze color.

There are several procedures to reduce CuO to Cu. Although the hydrogen direct reduction of CuO is most simple and clean process, it causes the safety problem during the heat treatment in a furnace. The polyol method using ethylene glycol (EG) as solvent and reductant is also effective strategy for the reduction of a metal oxide. The

fabrication of copper electrode by laser-induced direct local reduction of CuO nanoparticles (CuO NPs) has been reported, where a pulse laser beam was scanned on a composite film consisting of

Fig. 3. Raman spectra at unirradiated gap of laser-scanned GO/CuO NRs hybrid films. (a) rGO/Cu-30, (b) rGO/Cu-20, (c) rGO/Cu-10, and (d) rGO/Cu-5.

Fig. 4. Raman spectra at the laser scanning line on GO/CuO NRs hybrid films. (a) rGO/Cu-30, (b) rGO/Cu-20, (c) rGO/Cu-10, and (d) rGO/Cu-5.

Table 1. Surface resistivities of laser scanned GO/CuO NRs composite films.

Sample	Laser scan spacing (μm)	Surface resistivity (Ω/sq)
rGO/Cu-30	30	200×10^3
rGO/Cu-20	20	19.6×10^3
rGO/Cu-10	10	1.28×10^3
rGO/Cu-5	5	19.6

CuO NPs, EG as a reducing agent, and polyvinylpyrrolidone (PVP) as a binder polymer [11]. Direct writing of Cu-based sensors using femtosecond (fs) laser reduction has been reported using CuO NPs mixed with PVP and 2-propanol as a reducing agent [12-14]. The reduction of CuO with carbon by heat treatment is also well known reaction, where the oxygen displacement reaction of CuO with carbon causes the reduction during heat treatment. In this study, the GO was employed as a gel-like binder to form a coating film and as a reducing agent because the GO has a polyol structure on the graphene plane and the carbon structure causes the oxygen displacement reaction with CuO NRs. The oxidized structure of the GO is easily changed into an rGO by laser-induced reduction. Such features of the GO composited with CuO NRs make it possible that the reduction of CuO NRs can be caused even by CW laser irradiation with a rather lower power.

The resistance of an rGO/Cu film showed a large temperature coefficient. For example, the temperature coefficient of resistance for rGO/Cu-30 was -1.18 ($\%/^{\circ}\text{C}$), which is more than 50 times larger than that of graphite. An IR photosensor was developed applying the large temperature coefficient of resistance of rGO/Cu-30. The rGO/Cu-30 sensor with the size of 5×5 mm showed the response to IR light on-off irradiation clearly as shown in Fig. 5.

Fig. 5. Resistance changes by IR light on-off irradiation in vac. (a) and air (b) with an 850 nm long pass filter (102 mW).

4. Conclusion

The laser direct writing on a GO/CuO NRs hybrid film gave a conductive microstructure

consisting of rGO and Cu. The reduction of CuO NRs can be caused even by a small CW 405 nm semiconductor laser with the power of 13 mW. The GO can work as an effective reducing agent and gel-like binder for CuO NRs.

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