Engineering nanoinks and photonic manufacturing for printable electronics

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ABSTRACT

We have developed various nanoinks, including silver nanowires, silver nanoplates, Cu-Ag core-shell nanoparticles, graphene oxide and graphene. Gram level nanoplates are successfully synthesized through a polymer controlled hydrothermal growth. Core-shell structures are synthesized through a microwave-assisted reduction and galvanic metal displacement. Graphene is fabricated through laser reduced graphene oxide. We show that these inks are enabling for direct writing on various substrates. Also, we displayed high viscous nanopastes can be developed by further concentration of these inks and metallic nanopastes can be used for low temperature packaging of flexible electronics and power electronics operating at high temperatures. For curing printed nanoinks and nanopastes, we compared three kinds of methods: thermal sintering, photonic sintering with flash light and athermal sintering with ultrafast fiber laser irradiation. It is possible to build 3D structures by combining ink printing, flash light nanosintering and/or laser reduction.

Keywords: nanoink, nanowire, graphene, inkjet printing, laser writing

1 INTRODUCTION

Inkjet printing and laser writing are two well-establsihed manufacturing methods for various printable devices for wearable electronics, biomedical sensors, optoelectronic applications and low-cost, disposable and portable components for Internet of Things (IoT). Both enable pattern development and circuit-directed writing without using photolithography, which involves in complicated chemical etching with poisonous chemicals.[1,2] For inkjet printing, a uniform, stable ink with proper viscosity is desired. For the laser writing, material-laser interaction is essential for hiqh quality manufacturing and control. Some fundamental material-relevant issues have to be clarified to bring nanomaterials into the market, such as, large-scale low-cost synthesis of nanomaterials, appropriate parameters for nanoink development, size and shape effects in nanosintering (i.e., the sintering of nanomaterials), and liquid pahse nanojoining during low temperature packaging and laser writing.[3-7]

In this work, we reported our latest research progresses on these fields. Metallic nanoinks were developed for both printing and low-temeprature packaing purposes. Graphene-nased ink was developed for printable energy device. The nanosintering and nanojoining were investigated throuhg chemical activated, local self-triggered, plasmonic- assisted and femtosecond laser induced mechanisms. Some prototype devices were successfully demonstrated including paper-based touch-pad sensors, paper-based antenna, and paper-based supercapcitors.

2 NANOINK DEVELOPMENT

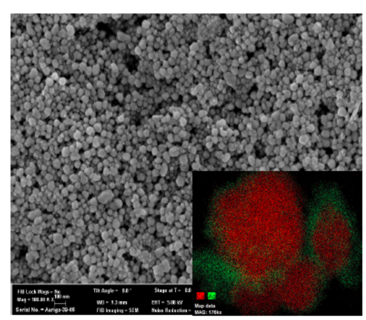

Figure 1 SEM imaging of as-prepared Cu-Ag core-shell nanoparticle inks. Inset: EDS mapping

Silver nanoparticle, nanowire and nanoplate inks were developed through a modifed polyyol (nanoparticle and nanowire) and hydrothermal method (nanoplates) with various molecular weight polymer as the capping reagent (polyvinylpyrrolidone, PVP).[4,7] Decrease the polyyol reaction temperature to 110°C silver nanoparitcle solution were obrained.

Copper nanoparticles were intially synthesized through a modified polyol method with sodium hypophosphte monohydrate as the strong reduction reagent.[8] Recently, we develop an enviromentally-benigned microwave-assisted method for Cu nanoparticle synthesis.[9] The anti-oxidization of Cu ink was realized with anti-oxidization reagent, such as ethylenediamine or silver shells through a metallic electroless displacement coating. Fig. 1 shows the Cu-Ag core-shell nanoparticle ink. The core-shell structure was evident by a energy dispersive spectroscopy mapping (inset to Fig.1). The green shell is Ag and the red core is Cu. These Cu-Ag core-shell nanoparticle ink was stable in air for a couple of months without significant oxidization.

Graphene oxide was synthesized through a modifed Hummer's method.[10] Fig. 2 shows typical images of graphene oxide inks. These graphene oxide flacks have an average size of a few micrometers. The concentration of nanoink can be increased by centrifugation. The viscocity of nanoink can be adjusted by adding glycerol. The concentration of metallic nanoparticles over 0.1 M can be used for nanopaste.

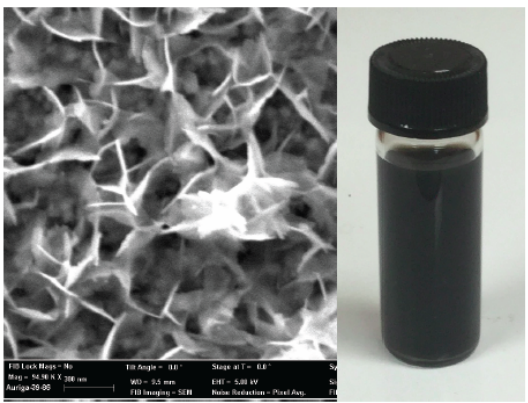

Figure 2 Images of graphene oxide ink

3 NANOSINTERING AND NANOJOINING

There are many methods to sinter nanomaterials and form functional circuits.

3.1 Chemical activated self-sintering

It is well known that the surface energy and diffusion rate of atoms is quite high at the nanolevel. However, the as-grown nanoparticles are usually coated with an amorphous carbon or polymer layer. It is reasonable to deduce that these nanoparticels can be self-sintered if this surface capping layer is removed. Our study shows that silver nanowires can be sintered even at room temperature if surface PVP is washed away.[11] However, due to the heterogeneous thickness of these capping layers, the sintering is selective. For the nanowires the head-to-head joining easily occurs. Alternative methid is to use these organic layers as a reducing reagent to reduce a metal oxide. Our recent studies show silver nanowires can be sintered to Cu by using CuO layers of Cu surface.[12] Although the global heating generated from the reaction of CuO with the organic capping layer is limited they are strongly enough to sinter nanowires locally. These nanojoining methods do not exist at a microsize or larger size. Fig. 3 shows typical joinned Cu nanowires after removing the surface organic layer. The head-to-head feature is evident.

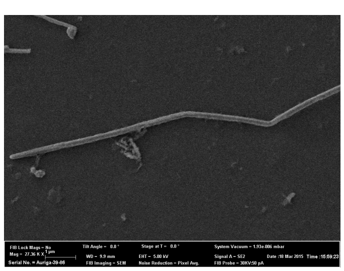

Figure 3 Self-joining Cu nanowires

3.2 Anisotropic nanosintering

Molecular dynamics simulation shows that the edges of nanoplates are more active than the basal plane.[13] This is further evident by experimental investigation of thermal sintering of silver nanoplates.[4] Fig. 4 shows different in-pane and out-of-plane sintering behaviors of silver nanplates. The in-plane nanoplanes can be sintered at a pretty low temperature (around 80^{o}C), however, the out-of-plane sintering has to be carried on at a higher temperatures than 180^{o}C. this difference will be result in anisotripc resistances of sintered silver nanoplate pastes. The sintering behaviors can be more complicated with the influence of surface polymer.

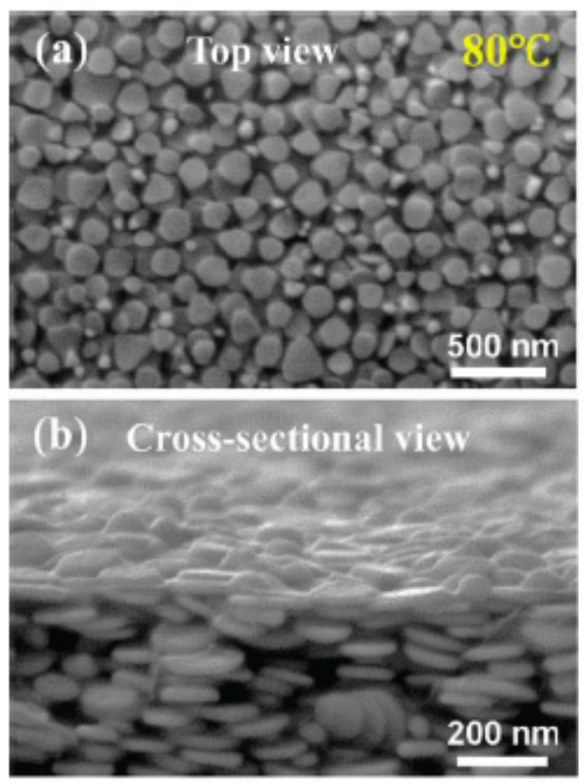

Figure 4 SEM surface and the cross-sectionl images of silver nanopates at 80^{o}C

3.3 Photonic and laser nanojoining

Phononic sintering is a facile method to induce joining of nanoscopic building blocks. Due to plasmoic excitation, the phononic sintering can be highly localized and self-contained.[4,14] The finite elment simulation shows that the optimized wavelength for sintering is infrared light since the plasmonic excitation possesses a dipolar feature, which leads an anisotropic increase of sintered nanoparticles. [4] Fig. 5 shows a successful joining of Cu nanowires with 1030 nm 300 femtosecond laser pulses.

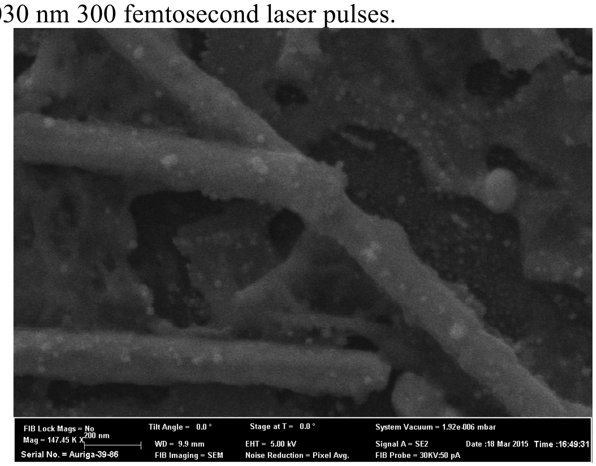

Figure 5 Joinned Cu nanowires by femtosecond laser irradiation

4 APPLICATIONS

We have displayed a paper-based capacitive touchpad sensor written by nanoink prititng. Such a sensor can bear thousand times bending due to superior mechncial properties of nanowire ink, indicating a promising potnetial for wearable electronics.[1] Similarly, we further develop a paper-based antenna with silver nanowire ink. Fig. 6 displays a written narrow-band antenna. The desgined, simulated and measured frequencies are consitent, as 2.45 MHz. Such a anttenna can be also printed on textile for wearable electronics application.

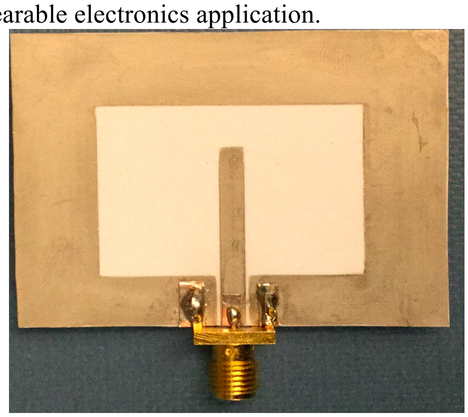

Fig. 6 Printed narrow band antenna with silver nanowire ink

5 CONCLUSIONS

We have successfully developed various metallic and graphene oxide nanoinks. It is demonstred that these metallic inks can be concentrated further and worked as nanopaste for low temperature packaging. Due to the size and shape effects, the sintering of nanoink-printed circuit/devices displays low temperature and anisotropic features. By employing proper photonic sintering various flexible devices are demonstrated. We believe this is a promising field for emerging wearable electronics and IoT applications.

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