

FABRICATION AND CHARACTERIZATION OF SUPERCAPACITOR ELECTRODE BY 3D PRINTING

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Abstract. 3D printing technology has emerged as a unique platform for rapid prototyping of various applications at low cost. Herein, we present a study on the fabrication and characterization of supercapacitor electrode by 3D printing. A colloidal suspension containing carbon nanotubes (CNTs) and cobalt ferrite nanoparticles (CoFe₂O₄ NPs) was used as ink. The ink was successfully printed on nickel foam and graphite paper substrates using a modified 3D printer followed by solvent evaporation to form a porous CNTs/CoFe₂O₄ aerogel film. The characterization results show that the film has porous surface, high electrical conductivity and good electrochemical properties, indicating its promising application as supercapacitor electrode for energy conversion and storage.

Keywords: 3D printing, electrode, supercapacitor, hybrid nanomaterials.

Classification numbers: 2.4.4; 2.8.2

1. INTRODUCTION

The economic and social development of modern society is increasingly dependent on energy supply, which makes energy conversion and storage becoming important. Batteries are widely used in industrial applications because of their high energy density. In recent years, supercapacitors have attracted much interest due to their superior properties such as short charge/discharge time, high power density and long life [1-4]. However, the energy density of commercially available supercapacitors is still lower than that of traditional batteries. Supercapacitors have a specific energy density of 5-80 Wh/kg (energy density ≤ 10 Wh/kg with commercial products), much smaller than traditional batteries are widely used in the market (about 170 Wh/kg). Therefore, the size of supercapacitor is higher than that of rechargeable

batteries at the same energy level [3, 4]. In order to improve the energy density of supercapacitors, most researches are now focused on the development of new electrode materials that will yield better performances [2].

The charge is stored in supercapacitor in the form of electrochemical double layers or electrochemical energy. To be used as supercapacitor electrode, a material must have high specific surface area and high electrical conductivity. Low-cost and abundant carbon-based materials such as activated carbon and graphite meet these requirements, and have been widely used in commercially available supercapacitors [2, 5]. Recently, it was reported that carbon materials of nanoscale such as carbon nanotubes (CNTs) and graphene exhibited superior performance as compared to activated carbon or graphite. However, carbon-based materials only store charge in the form of electrochemical double layer. To provide additional electrochemical energy (faradaic pseudocapacitance), various metal oxides such as nickel oxide (NiO), ruthenium dioxide (RuO₂), manganese oxide (MnO₂), iridium oxide (IrO₂) have been used due to their high pseudocapacitance and electrochemical stability. The combination of a carbon material with a metal oxide may offer enhanced properties as compared to lone ones, because both physical and chemical charge storage mechanism are provided in a single electrode [2]. Moreover, novel phenomena such as synergic effects can be observed, which greatly improve electrode performance [2]. Recently, rational designs of supercapacitor electrodes based on hybrids of CNTs and metal ferrites/oxides have been reported [6-10].

In addition to material design, the development of large-scale manufacturing techniques for fabrication of supercapacitors is critical for realizing their practical applications. Recently, 3D printing, or additive manufacturing (AM) [11, 12], has been emerging as promising solution for future manufacturing. The powerful capacity of 3D printing for rapid prototyping makes it a unique but ubiquitous platform for a vast range of applications, from mechanical engineering, medicine, to materials science. Notably, 3D printing technologies renovates the manufacturing as a whole, from design to fabrication, at a significantly lower cost [12].

In this study, we investigate the possibility of fabricating supercapacitor electrodes using 3D printer and colloidal ink made of CNTs and CoFe₂O₄ nanoparticles (NPs). The 3D printer was built by modifying commercially available 3D printer so that it is compatible with CNTs/CoFe₂O₄ NPs nanohybrid ink. The printed film was characterized using various techniques to assess its suitability for supercapacitor electrode.

2. MATERIALS AND METHODS

2.1. Design and fabrication of printer for colloidal ink

The printer for printing electrode was designed based on robocasting technology or direct ink writing [12] to utilize the simplicity and low cost of the method. The overall structure of the printing system is shown in Fig. 1, which consists of three parts. Software part consists of some required PC-based softwares which are used to design objects, generate G-code and send them to electronic part. Electronic part gets commands and controls the mechanical part to perform necessary tasks to print the designed objects.

The moving bed style is applied to the mechanical part. Moving bed-style printer moves the print bed as one of the axes (Y-axis). The print head mounted on the ZX gantry is moved in the Z-axis. This is a mechanically simpler design in which the X-axis and Y-axis are managed independently using entirely linear motion. The mechanical structures of the printer were designed using SolidWorks, a 3D design software. Materials for this design were chosen from

commercial components available on the market. The parameters are selected to match these components to make advantages in design and fabrication. The NEMA 17 two phase stepper motors with A4988 stepper motor controller modules are chosen to drive the motion of the axes and the extruder. An Arduino Mega 2560 board and a RAMPS module are the most common and useful electronic components for 3D printer. A smart controller which contains a SD-card reader, a rotary encoder and a LCD display can be added to the printer. The mechanical parts needed to build the printer include a 20×20 aluminum profile, linear motion shafts, linear ball bearings, lead screws and nuts, and GT2 pulleys and belts. All support parts were designed in SolidWorks and printed by a commercial 3D printer. The firmware was configured and modified from the free Repetier firmware to be suitable with this printer. Repetier-Host software was used to give full control of the printer, slicer and printing process if needed.

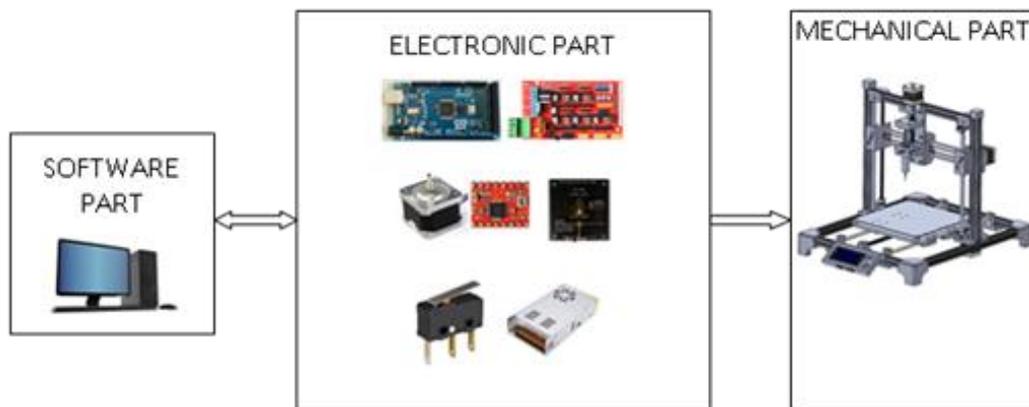


Figure 1. The overall structure of the printing system.

2.2. Fabrication of porous CNTs/CoFe₂O₄ aerogel film

The CNTs/CoFe₂O₄ aerogel film was fabricated using freeze gelation method [13]. CNTs were synthesized using chemical vapor deposition method by the Laboratory of Carbon Nanomaterials [14]. CoFe₂O₄ NPs were synthesized by thermal decomposition of organometallic precursors of corresponding metals (Fe (III) and Co (II) acetylacetonate) in octadecene using oleic acid/oleylamine as surfactant and 1,2-hexadecanediol as accelerating agent [15]. Then the surfactant of NPs was replaced by nitrosonium tetrafluoroborate (NOBF₄) by ligand exchange reaction [16]. The weight ratio of CoFe₂O₄ NPs over CNTs was kept at 2 %. Typically, 76 mg powder mixture of CNTs and CoFe₂O₄ NPs and 4 mg of poly (vinyl alcohol) (PVA) were mixed in 2 mL of phenol in liquid form at 60 °C for 30 minutes, using sonication to form a stable dispersion. The suspension was then filled in the print head to be used as ink. A designed pattern was printed on the substrates (nickel foam or graphite paper) to form electrodes with the process shown in Figure 2. Firstly, a designed sample of 20×10×0.8 (all dimensions are in mm) was printed on the substrates (nickel foam and graphite paper) to form electrodes. The CNTs/CoFe₂O₄ ink was filled in the print head. Then the print-head was controlled to extrude the ink onto the substrate. The printed electrodes were then cooled down in an ice bath until the solidification of phenol was completed. The electrode was taken out and stored at room condition. The CNTs/CoFe₂O₄ aerogel film on the substrate was obtained when the sublimation process of phenol was completed. The printed electrodes are denoted as CNT-NP-GP (printed on

graphite paper) and CNT-NP-NF (printed on nickel foam). Besides, a sample denoted as CNT-GP was also printed on graphite paper with the CNTs ink (without CoFe_2O_4 NPs).

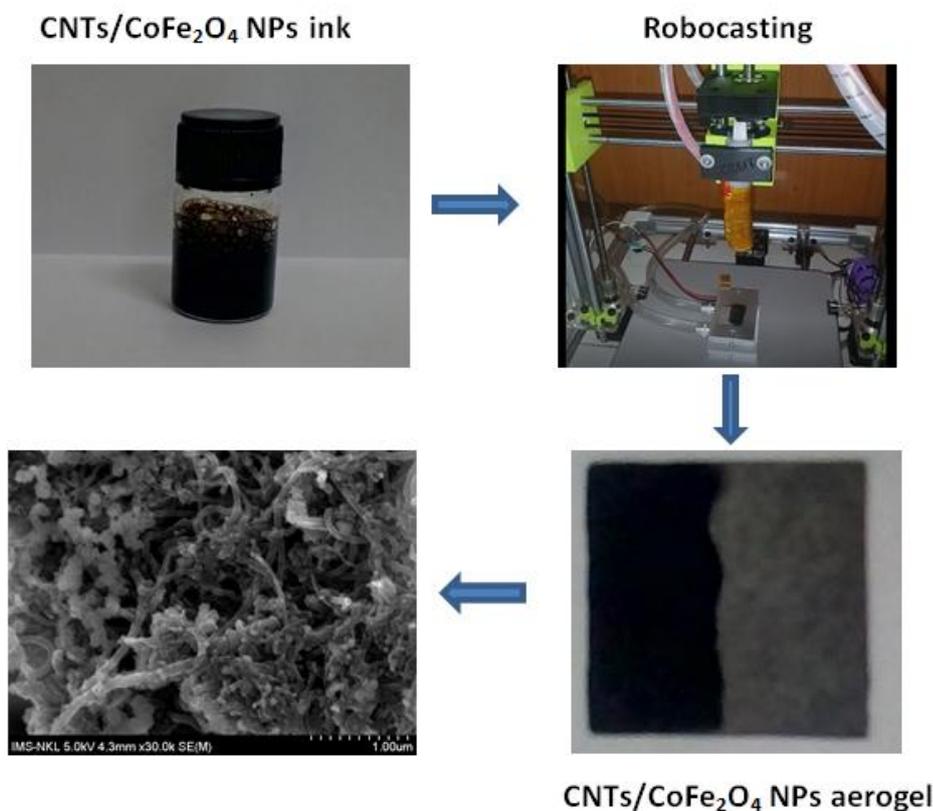


Figure 2. The process of printing supercapacitor electrodes.

2.3. Analytical methods

The morphology of CNTs and printed CNTs/CoFe₂O₄ aerogel film were observed by scanning electron microscopy (SEM, Hitachi S-4800 microscope) and transmission electron microscopy (TEM, Jeol JEM-1010 microscope). Electrochemical property of the printed CNTs/CoFe₂O₄ aerogel film was characterized by cyclic voltammetry (CV) method in 0.1 M tetraethylammonium tetrafluoroborate (TEABF₄, Sigma Aldrich) in acetonitrile (Xilong Scientific) using a Bio-Logic VSP-300. A platinum rod was used as counter electrode. Ag/AgCl in saturated KCl as a reference electrode and working electrode was CNTs/CoFe₂O₄ aerogel film printed on graphite paper substrate.

3. RESULTS AND DISCUSSION

3.1. The assembled printer for colloidal ink

The printer was completely assembled and calibrated in order to achieve a good printing quality. The printer was assembled easily from parts and can be applied for printing electrode as shown in Fig. 3. The main specifications of the printer are Travel range: 190×190×120 (all dimensions are in mm); Control: Repetier - Host, Smart controller; Print materials:

CNTs/CoFe₂O₄ NPs colloidal ink.

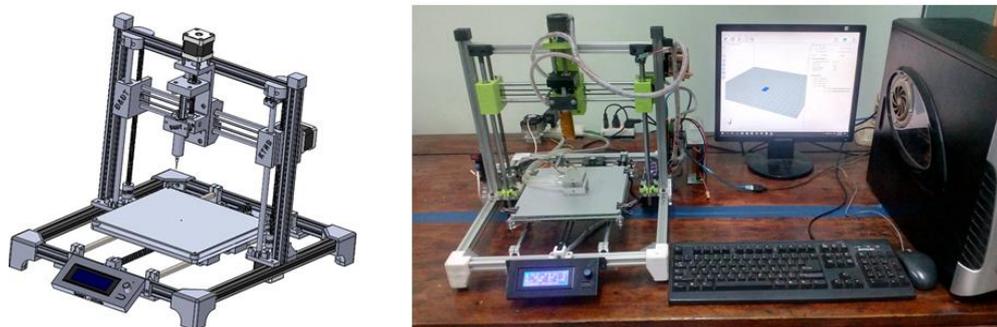


Figure 3. The perspective design (left) and real image of assembled printer (right).

3.2. Morphology of the printed electrodes

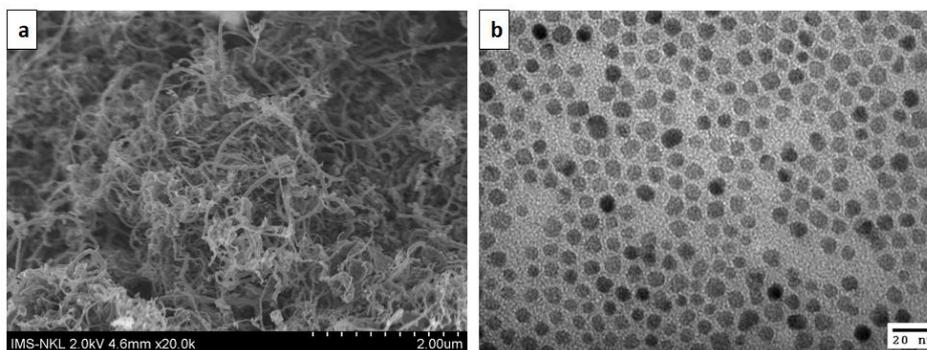


Figure 4. SEM image of CNTs (a) and TEM image of CoFe₂O₄ NPs (b).

The SEM image of CNTs (Fig. 4(a)) shows that all CNTs are in the form of long tube, indicating their good electrical conductivity. TEM image of CoFe₂O₄ NPs (Fig. 4(b)) shows that CoFe₂O₄ NPs are in uniformly spherical shape with an average diameter of ca. 10 nm. Figure 5 shows SEM images of CNT-NP-GP (a, c) and CNT-NP-NF (b, d). In comparison with CNTs (Fig. 4(a)), the morphology of CNTs before and after printing is well preserved. The morphology of single CoFe₂O₄ NPs is not well observed due to the limited resolution of the scanning electron microscope we used. However, the formation of aggregated nanoparticles on CNTs in various shapes (mainly, spheres) can be evidenced on the CNTs/CoFe₂O₄ hybrid film. Due to the sublimation of phenol, the film becomes more porous, which is beneficial for the diffusion of electrolytes during charge/discharge of the printed electrode. From Fig. 5, it is realized that the obtained film has not got the uniform distribution of CoFe₂O₄ NPs on CNTs. The morphology and distribution of CoFe₂O₄ NPs on CNTs in the obtained film can affect on the electrochemical properties of electrode and it will be discussed in the next section.

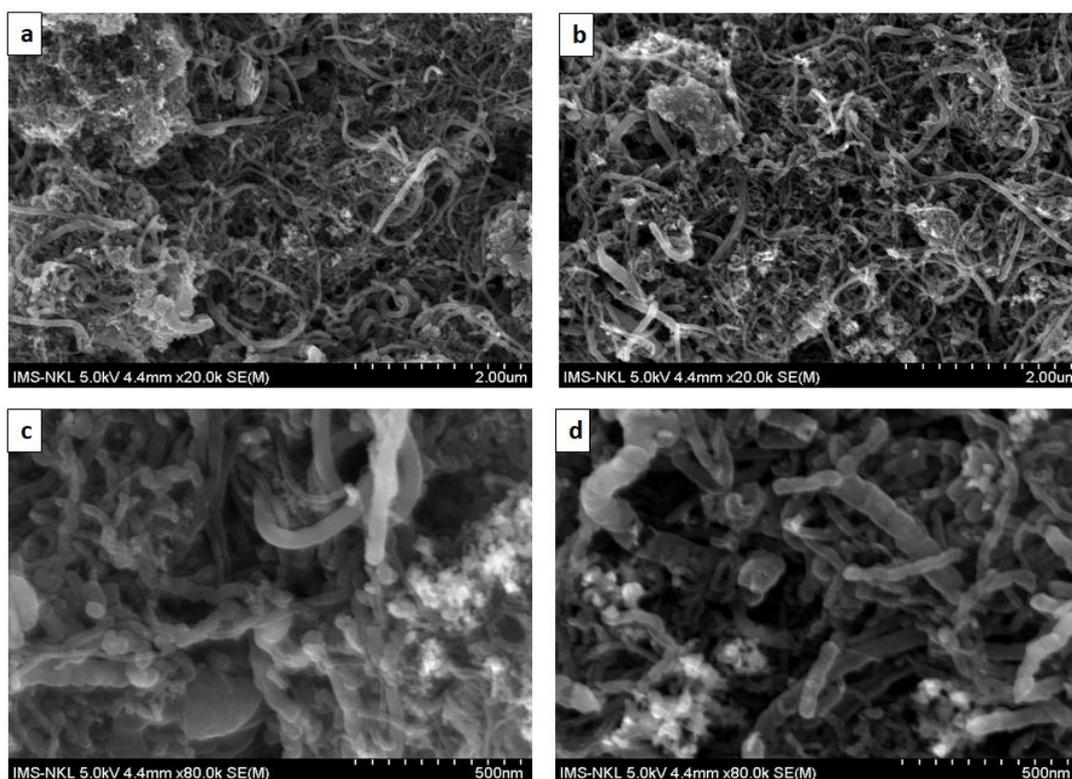


Figure 5. SEM images of CNT-NP-GP (a, c) and CNT-NP-NF (b, d) at different magnifications.

3.3. Electrochemical property of the printed electrode

Figure 6 shows the CV curves of CNT-GP (a) and CNT-NP-GP (b) at a scan rate of 50 mV/s with 200 cycles. The calculated specific capacitances at the third cycle of CNT-NP-GP and CNT-GP in the potential range from -1.0 V to 1.5 V are 13.9 F/g and 5.0 F/g, respectively. This result shows that adding nanoparticles can increase the performance of the electrode. It is possible that the porosity of the CNTs film was changed after adding nanoparticles. The formation of aggregated nanoparticles on CNTs made them split apart instead of being stacked together as without nanoparticles. Thus, the surface area of the electrode is increased leading to enhance specific capacitance as the result of CV test. In addition, ferrite NPs are materials storing charge based on pseudocapacitance mechanism, the presence of the materials in the CNT-NP composite is also the reason for the improvement of the capacitance.

The stability of the working electrodes is evaluated by the reduction of the specific capacitances according to numbers of cycles of CV tested. After 200 cycles, the specific capacitance of CNT-NP-GP retained 88.6 % of the initial value, while the specific capacitance of CNT-GP is also maintained at 86.4% of the original value (as shown in Fig. 7). The obtained values indicate that both samples are relatively high electrochemical stability and they are potential for supercapacitor electrodes. With relatively high stability and wide potential window, the printed electrodes are capable of applying for supercapacitor. However, specific capacitances need improving further by optimizing various parameters during printing process, as well as ink formulation.

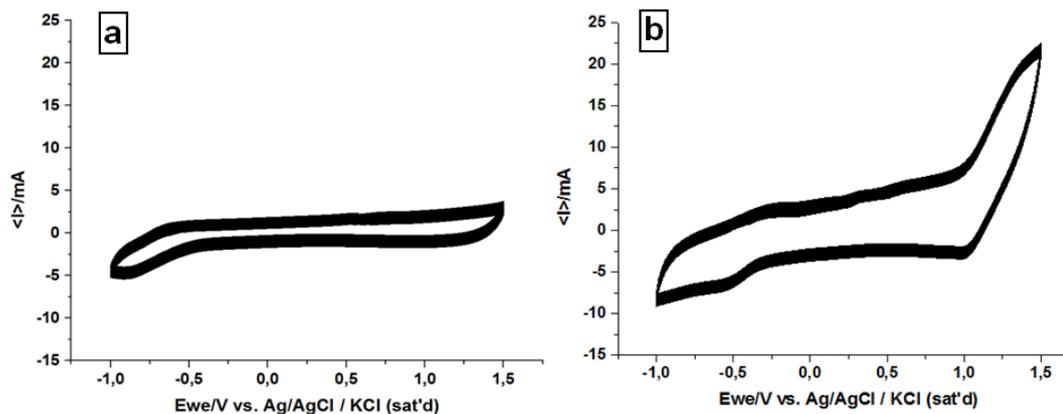


Figure 6. CV curves of CNT-GP (a) and CNT-NP-GP (b).

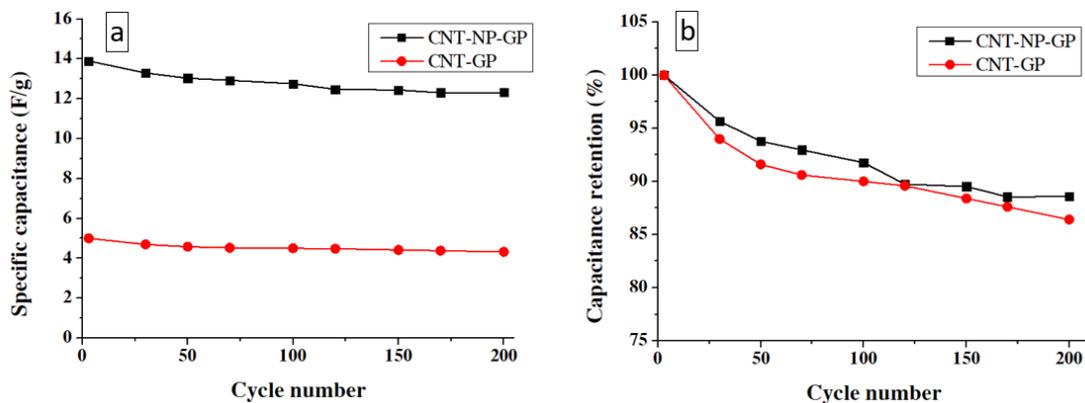


Figure 7. Cycle stability of CNT-GP and CNT-NP-GP during 200 CV cycles at 50 mV/s. Specific capacitance vs. cycle number (a) and Capacitance retention vs. cycle number (b).

4. CONCLUSIONS

A printer for printing colloidal suspension has been designed and assembled successfully with available components and open source software. It can be used to fabricate supercapacitor electrode by printing hybrid materials on different substrates. The initial specific capacitance of CNTs/ $CoFe_2O_4$ hybrid electrode was 13.9 F/g. The hybrid nanomaterials used as ink for this printer need to be improved to get higher performance electrode to widely apply for the fabrication of supercapacitors.

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