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PAPER-BASED ELECTRONICS AND SENSORS FABRICATED BY USING PRINTING TECHNOLOGY

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ABSTRACT

Paper is seen as a potential substrate for devices such as electronics and sensors because of environmental friendliness, being a dualistic material with flexibility and rigidity, and a possibility for mass production at low cost. In this study, two such applications as devices will be introduced. First, a power generator has been developed to convert sonic vibration into electric energy. Secondly, a corona discharge-treated polytetrafluoroethylene sheet, as an electret, was attached to a paperboard with a back electrode. Another paperboard with a counter electrode was mechanically vibrated to simulate a sound. During vibration, electric power was successfully generated by electrostatic induction. Insertion of nano-cellulose paper furthermore enhanced the output voltage. A simple, quick, sensitive and ion species-selective paper-based sensor with a quinone derivative dye ink-jet printed has been developed to detect Cu^{2+} ions at 2 ppm, a maximum allowed for drinking water, by colour change observation. A fluorescence spectrum of the dye provided higher resolution to permit quantitative detection of Cu^{2+} concentrations.

Keywords: Copper ion sensor, Paper electronics, Power generation.

1 INTRODUCTION

Due to the recent development of electronic media, such as smartphones and tablets, paper has evolved as a medium that is attractive to readers' sensibility and not as the primary means to communicate information. Paper is thus a product not only for information propagation but also for many other purposes. Characteristic functionalities of paper are lightness and absorbency owing to its porous structure, flexibility and processability to facilitate layering and folding, high elasticity like a speaker cone, moisture absorption and desorption for stabilizing humidity, light scattering for brightness and opacity, product quality stability owing to mass-production, recyclability and disposability, long lifetime like historical documents, and so on. Those properties may be combined to develop new types of paper products: "paper devices", as represented by paper electronics and sensors.

As for paper-based energy source devices, there are some applications to chemical, biological, and physical batteries and capacitors. Among those, physical batteries are the furthest along in developing from the viewpoint that a large area system is advantageous to power generation and achieved easily by using paper [1]. Solar panels with a large area would collect more solar energy. In addition, capacitor-type devices with a large area would be able to store more electricity. One of pioneering work of those types is a conductive paper sheet prepared from a conductive polymer and cellulose fiber mixture to create a battery [2]. Prototype light and thin paper batteries alternative to button cells were also developed by many researchers. Studies on paper batteries were reviewed to details elsewhere [3]. Other physical batteries acquire energies from heat, electromagnetic waves, and vibration that can be categorized into energy harvesting technology. As vibration resources, vibration energy of automobiles and bridges is converted to electricity by electromagnetic or electrostatic inductions. Electrostatic induction uses a dielectric material called electret that has quasi-permanent electric charge or dipole polarization. When an electrode crosses the electric field created by an electret, an electric current flows inside the electrode. Various types of power generator can be produced by modifying the relative position between the electret and electrode to conform to any generator shape and vibration direction. A concentric dual cylinder containing a spiral electrode and electret was designed to function with both translation and rotation [4]. A prototype self-powered frequency monitor for motor operations was produced [5].

This article reports two paper devices: (1) a paper-based power generator based on electrostatic induction and its improvement by use of nano-cellulose paper with a high dielectric constant, and (2) a paper-based copper ion (Cu^{2+}) sensor using a quinone derivative dye with strong adsorption to cellulose and copper ions.

2 PAPER-BASED POWER GENERATOR

2.1 Fabrication of the paperboard triboelectric generator (out-of-plane motion)

2.1.1 Experimental

This study [6] focuses on electrostatic induction using paper vibration caused by environmental noise, voice, and sound as an energy source. Figure 1 shows a structure of the triboelectric generator TriboEG. In the system, a triboelectrically-charged polytetrafluoroethylene sheet, as an electret (a dielectric material with permanent electric charge), was attached to a paperboard with a grammage of 736 g/m^2 and an area of 90 × 209 mm^2 laminated with a back electrode of copper foil. Another paperboard with a counter electrode was mechanically vibrated to simulate noise, voice, and sound.

2.1.2 Results and Discussion

During mechanical vibration, electric power was generated by electrostatic induction. The voltage generated by forced vibrations of 0 to 55 Hz from the vibrator was recorded and analysed using the fast Fourier transform (FFT) to determine the natural frequency of the paperboard and separate the generated electricity from the electric noise sourced by the power outlet in the room. Figure 2 shows FFT spectra calculated from those generated voltages. The TriboEG system tended to be practically ineffective at forced vibration frequencies of 10 and 20 Hz; the highest peak voltage for both was only 0.1 V. From the 30 Hz forced vibration, the 1-mm gap configuration generated 1.1 V, which was more than double that of the 2-mm gap (0.4 V), as predicted by capacitor theory. The TriboEG system achieved the highest peak voltage of 3.6 V at 47 Hz by a 46-Hz forced vibration. The peak voltage decreased for forced vibrations greater than 46 Hz to 2.8 and 1.9 V at 50 and 55 Hz, respectively.

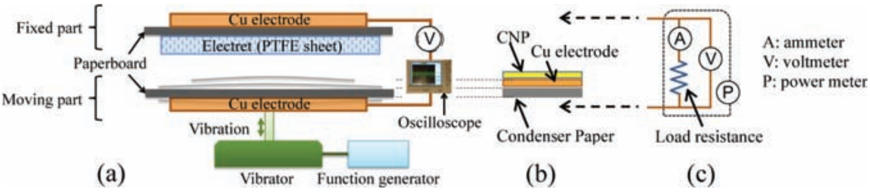

Figure 1. Design configuration of (a) paperboard TriboEG (out-of-plane motion), (b) layers of CNP, Cu foil electrode and CP, and (c) power measurement option.

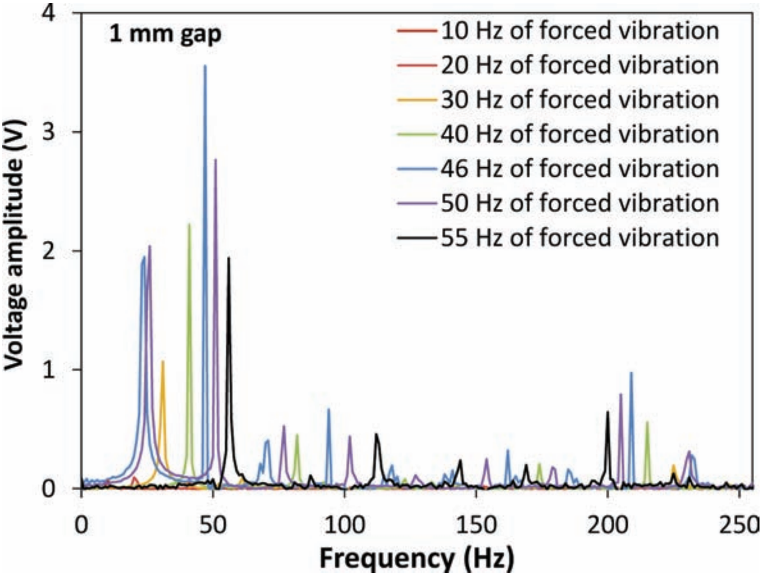

Figure 2. Voltages generated by paperboards at a gap of 1 mm with amplitude of background noise removed.

2.2 Fabrication of the paperboard triboelectric generator (in-plane motion)

2.2.1 Experimental

The propagation of a longitudinal wave was considered, and a paperboard triboelectric generator with an in-plane motion mechanism was designed using comb-shaped electrodes as shown in Figure 3. The moving part illustrated at the top of this figure moves horizontally on a pair of guide-rails with bearings on both sides for smooth linear motion (not shown in the figure), keeping a constant distance from the fixed part at the bottom. In the experiment of power generation, the moving part was quickly moved back and forth twice by hand.

2.2 Results and Discussion

The paperboard triboelectric generator system for in-plane motion generated voltage with a sliding action by hand as shown in Figure 4 with a gap of 1 mm between the paperboards. In the generated voltage wave to the left of the figure, each of the four distnct pulse waves were found to consist of 12 oscillations, corresponding to the number of teeth of the comb-shaped electrodes during the two round trips. The generated voltage momentarily reached 8.2 V. The FFT

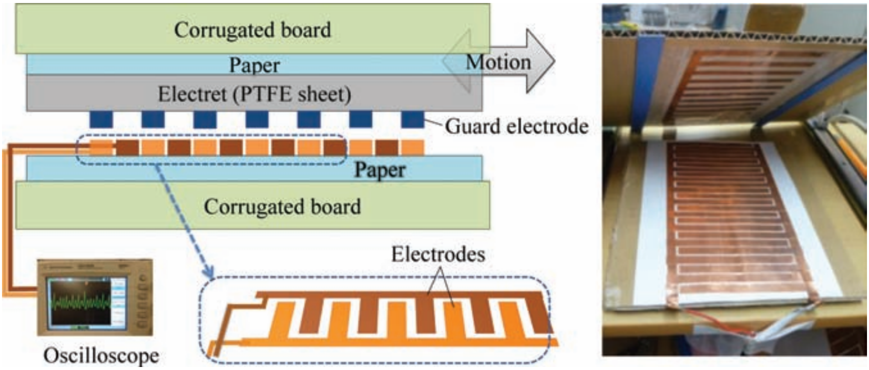

Figure 3. Design configuration of the paperboard TriboEG (in-plane motion) and photograph of apparatus.

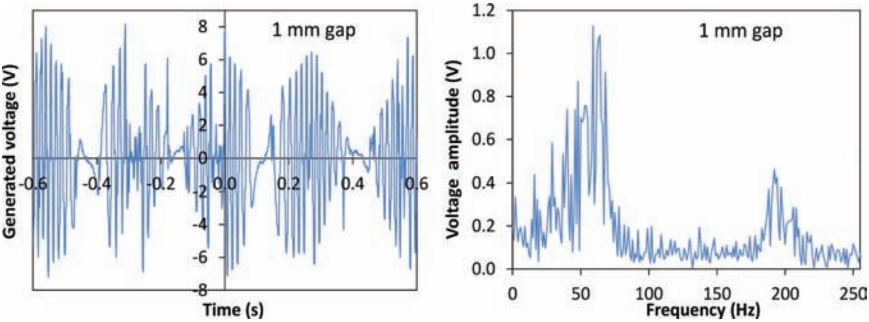

Figure 4. Voltage generated by paperboard TriboEG (in-plane mode) and voltage amplitude spectrum.

amplitude to the right shows the highest peak at approximately 60 Hz. This frequency depended on the moving speed of the examiner's hand and the interval of the electrode teeth. This result proved that in-plane displacement could generate electricity and further indicated that microscopic electrodes and electret printed on two sheets of paper with smoothly finished surfaces at a high resolution could be an electric power source for microscopic electronics.

2.3 Improvement of power generator using highly dielectric nanopaper

2.3.1 Introduction

To make the sheet of paper more prone to to vibrate, a fluoropolymer resin was coated on the paper sheet so that the resin film thickness would be as thin as possible. Furthermore, to obtain high output power, a material with a high dielectric constant was inserted between the electret and electrode.

2.3.2 Experimental

Materials:

Perfluoropolymer resin (Teflon®) with a thickness of 514 μm, referred-to as "PTFE" hereafter, and amorphous perfluoropolymer resin (CYTOP, Asahi Kasei Corp.), referred-to as "APFP" hereafter, were applied. APFP achieves higher surface charge density than conventional perfluoropolymer resins. In addition, coated APFP adheres to paper surfaces strongly by forming hydrogen bonds with end carboxyl groups. Figure 5 shows the chemical structures of the electret materials used.

As a substrate for conveying vibration energy, condenser paper (OFS100P, TOMOEGAWA, 90 g/m^2, 100 μm), referred to as "CP" hereafter, was used. As a material with a high dielectric constant (k), we prepared cellulose nanopaper from cellulose nanofibers with a small amount of silver nanowires dispersed in the structure [7]. This silver nanowire/cellulose nanopaper composite had a k value as high as 202 at 1.1 GHz, compared to $k = 3$ for conventional paper. This composite will be referred to as simply "CNP" hereafter. This CNP had a diameter of 75 mm and a thickness of 48 μm.

Methods:

An APFP solution was coated on an A4 size CP sheet with a bar coater. Subsequently, the coated sheet was dried at 80°C and then 180°C each for 1 hour for hardening. Then, copper foil was attached to the uncoated side of the CP sheet as an electrode. The APFP layer was corona discharge-treated with a charging gun (GC50S, Green-Techno) negatively. A PTFE sheet was also attached to another CP sheet with a double-sided tape to be subjected to the same tests for comparison.

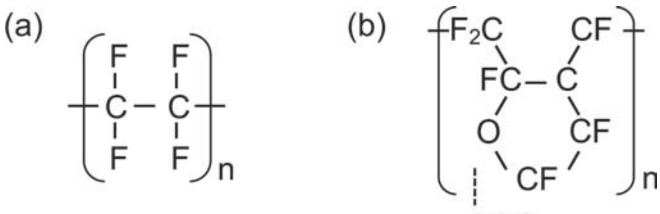

Figure 5. Chemical structures of (a) PTFE and (b) APFP.

The counter electrode was prepared by attaching copper foil to paperboard with a grammage of approximately 300 g/m^2. The layered structure of the power generator is shown in Figure 1(b).

Some 150 mm by 150 mm sheets were cut out and mounted on a mechanical vibrator (U56001, 3B scientific Physics). After the relative positions among the components of the power generator was adjusted so that maximum output voltage and power values would be obtained, measurement was performed using the power measurement option shown in Figure 1c as the load resistance was varied from 1 to 10 MΩ.

To examine CNP effects, the CNP sheet was laminated with a copper foil as a counter electrode. This laminate CNP was further attached to paperboard with a double-sided tape for vibration.

2.3.3 Results and discussion

Figure 6 shows the output power as a function of load resistance. Both PTFE and APFP exhibited maximum power values at approximately 2 MΩ. The maximum power values were 11.8 μW and 12.1 μW for PTFE and APFP, respectively. Those power levels were very close; however, the thickness was 514 μm and 10 μm for PTFE and APFP, respectively, suggesting that APFP is much more useful to achieve flat power generators.

Figure 7 shows the CNP effects. The insertion of CNP enhanced the power generation function by 34% on a voltage basis. Theoretically, the output voltage is inversely proportional to the dielectric constant of the electret [8]. For the same

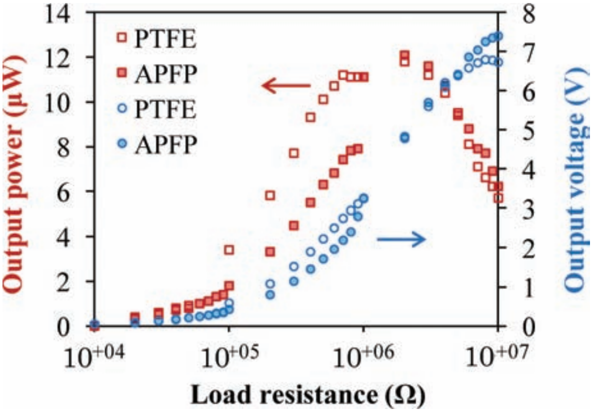

Figure 6. Power and voltage output from vibration-induced generator with perfluoropolymer electret vs. load resistance.

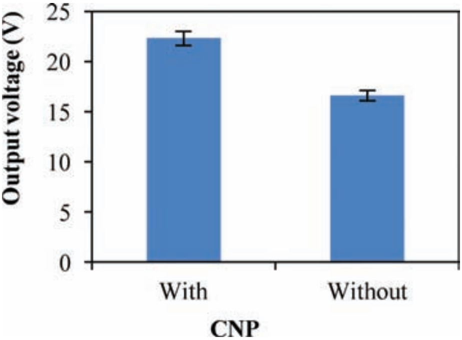

Figure 7. Effect of CNP with a high dielectric constant on output voltage.

reason, the strength of an electric field between the two parallel plates (electrodes) decreases with an increase in dielectric constant of the inserted electric material when the generator system is assumed to be a capacitor. Thus, the decreased dielectric field was likely to result in decreased output voltage. Therefore, the unexpected increase in output voltage might be due to other mechanisms such as prevention of discharging of the electret by inhibiting a direct contact.

3 PAPER-BASED CU^{2+} ION SENSOR [9]

3.1 Introduction

Water that contains excessive amounts of Cu^{2+} is extremely harmful to human health and the biology of other animals. Therefore, we developed a user-friendly, low-cost, sensitive, and ion-species-selective paper-based sensor to inspect drinking water and industrial waste effluent for excessive Cu^{2+} levels, for use by people, especially in developing countries.

3.2 Experimental

A lab-made ink, comprising a 1 g/L quinizarin acetone solution, was first prepared. An inkjet printer (DMP-2831, Dimatix, Fujifilm, Japan) was applied to fabricate the paper-based sensor by printing this ink in a 20 mm by 30 mm rectangular area on filter paper. After drying for 10 s, quinizarin was adsorbed onto the cellulose fibres through non-covalent interactions. The paper-based sensors were cut out from the filter paper for further experiments.

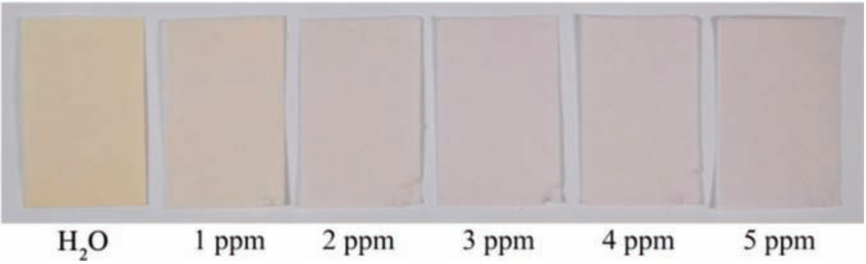

Figure 8. Paper-based sensors after immersion in Cu^{2+} aqueous solutions at different concentrations for 10 min.

3.3 Results and Discussion

In visible detection, the colour of the dye on the paper-based sensor changed from yellow to purple with increasing Cu^{2+} concentration. Figure 8 shows a photograph of paper-based sensors immersed in Cu^{2+} aqueous solutions. This result confirmed that the paper-based sensor was able to detect Cu^{2+} at concentration as low as 2 ppm that is the maximum amount allowed in drinking water according to the World Health Organization. The entire detection process took only 10 min and sensitive detection of Cu^{2+} was successfully achieved.

In fluorescence detection, linear relationships observed between the surface fluorescence intensity and Cu^{2+} concentration in the dilute solution samples, as shown in Figure 6, indicates successful quantitative detection. Furthermore, the accuracy of the Cu^{2+} concentration measurements was proven by comparison with measurements using inductively coupled plasma-optical emission spectroscopy. With regards to detection conditions, pH 7 was optimum and the increase in temperature promoted the detection reaction. Furthermore, although slight colour fading of the paper-based sensor was observed with exposure to strong ultra-violet light, protection from light during storage would prevent this photoredox reaction.

4 CONCLUSIONS

For the next generation with smart systems of Internet of Things (IOT), Industry 5.0, Society 5.0, and so on, we are aiming at paper-based smart tools. One of them is an energy harvesting system from environmental noise and sound to convert to electric energy for an on-site power supply. The basic principle is electrostatic induction brought about by sound-vibrated paper with an electrode and electret. Voltage and power output by two prototype power generators were measured as a counterpart was shaken by a vibrator and by hand back and forth in out-of- plane

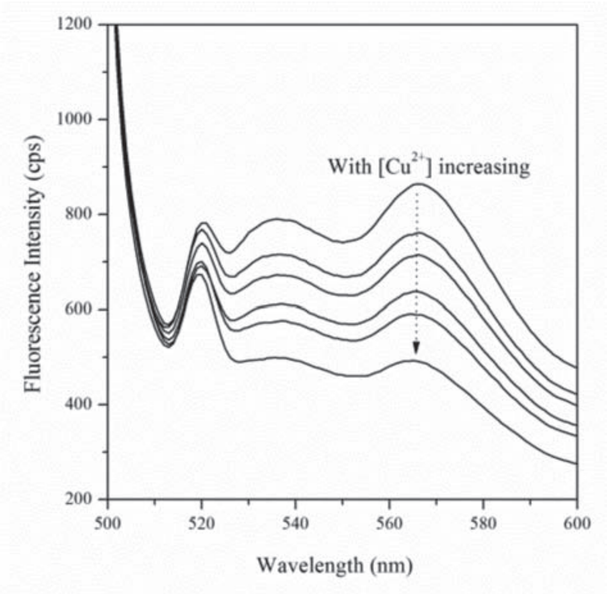

Figure 9. Fluorescence spectra of paper-based sensors after immersion in Cu^{2+} aqueous solutions of various concentrations.

and in-plane directions. The highest peak voltage obtained was 3.6 V and 8.2 V, respectively although the values varies with the paper dimension, surface charge density, gap between the two counterparts and so on. The insertion of a silver nanowire/cellulose nanopaper composite with a high dielectric constant into the two counterparts enhanced the output voltage.

RESULTS

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Transcription of Discussion

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Sebastiaan Akerboom NALCO

Thanks for your nice presentation and I guess you have shown that you can indeed convert sonic energy into electricity with your devices, but I was just curious, can you do it also the other way around? So, instead, using this electricity generator as a kind of loud speaker?

Toshiharu Enomae University of Tsukuba

The final purpose is to get energy from a small volume of voice or noise, but it is very difficult to generate enough electricity from a small noise because it has small power only. But, how much energy is required depends on the electricity demand.

Sebastiaan Akerboom

I was thinking the other way around. If you now apply electricity to the device, can you make it emit sound?

Discussion

Toshiharu Enomae

So, maybe it can. If the energy transition is reversed, electricity generates sound like a common speaker. But, there may be lot of loss of energy and poor frequency resolution.

Gil Garnier Monash University

Very interesting work. One question, why do we need paper in the applications?

Toshiharu Enomae

Because a large area of electronics can be made using paper and paper is very compatible with printing. One time use with high disposability and biodegradability are otherwise of importance.

Gil Garnier

In your device you have Teflon, you have electrodes, you have everything, even including a little piece of paper. What is the role of the paper in your device? If you remove the paper, what happens, does it still work?

Toshiharu Enomae

Yes. Paper works as a vibration medium and substrate for layering thin electret and electrode. But, other vibration media can replace the paper like an electret microphone. In my mind the final product is, for example, a paper poster on the wall. If you speak to the poster, the poster responds to your voice and then comes back shouting. In such systems, paper works also as a display media.

Gil Garnier

What are the properties of paper that you need to have your poster talk to you? What are the properties of paper that affect the electrovibration application, what basis weight, what density, what portfolio, what fibres, fibre orientation, filler, chemical content, conductivity, and so on?

Toshiharu Enomae

For example, a larger size makes for more electricity. But, there is paper size limitation in actual situations. The most important parameter is Young’s modulus generally.

Gil Garnier

Why?

Toshiharu Enomae

To transfer energy efficiently.

Gil Garnier

But the other properties of paper that you mentioned are also important because you seek to transfer energy, but you talk about vibration, therefore different wave length. So is there a correlation between wave length and density of paper?

Toshiharu Enomae

Yes, so a high Young's modulus keeps the energy as high as possible compared to the very soft paper. In addition, high amplitude of vibration waves is desired because it makes the distance between the electret and electrode large, but resonance, if it happens, makes the amplitude low. That is why frequency dependence is also important.

Tetsu Uesaka Mid Sweden University

You mentioned about the energy harvesting.

Toshiharu Enomae

Yes.

Tetsu Uesaka

So you tried out here various kinds of power generation systems. What are the numbers for the efficiency of the energy conversion from mechanical to electrical? What is the ballpark figure of the energy efficiency or conversion efficiency in your system? How effective is it for mechanical energy to be converted to electrical energy in this case?

Toshiharu Enomae

There are several types of conversion principles with different efficiencies. Electrostatic induction is one of them. One other method is the electromagnetic system. I don’t know which one is the most efficient, but in the case of the paper, paper is very light and can be a composite with other components. The electret is usually plastic and inhibits paper vibration the least. That is why I used the electrostatic induction.

Tetsu Uesaka

We can discuss more about that later.