Artifact-Metrics Using Photoluminescence Imaging of Single-Walled Carbon Nanotube Composite Paper

Masahiro Ito and Yoshikazu Homma*

Department of Physics, Faculty of Science, Tokyo University of Science, Shinjuku-ku 1-3, Tokyo 162-8601, Japan

Makoto Akiba

Department of Physics, Electrical and Computer Engineering, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

Takahide Oya

Division of Intelligent Systems Engineering, Faculty of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

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Composite paper containing single-walled carbon nanotubes (SWNTs) has been employed for artifact-metrics authentication using Raman mapping images for authentication keys. To make the most of SWNT properties for authentication, it is desirable to use the diversity of chiralities for authentication keys. In this study, we explored the application of photoluminescence (PL) imaging of SWNT-composite paper to artifact-metrics authentication. SWNTs were wrapped with carboxymethyl cellulose to activate PL and embedded in paper. PL mapping images of different chiralities were examined for authentication. The authentication accuracy was greatly improved by using three-chirality keys. An estimated error rate as small as 10^{-12} was achieved.

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I. INTRODUCTION

Artifact-metrics techniques have been advanced by using intrinsic physical feature patterns of paper [1–3] or silicon microstructures [4]. Artifact-metrics is an information security technology that utilizes physical artifacts based on their measurable intrinsic characteristics, such as random patterns emerging inherently during the manufacturing process. One of the most widely used authentication technologies today is biometric authentication. However, there are privacy concerns associated with this type of authentication. Furthermore, it has been reported that artificial fingers made of gelatin were accepted with high rates [5]. Therefore, there is a need to improve assembly of foundation and method of the evaluation for authentication accuracy. In particular, it is important to enhance the difficulty of cloning authentication metrics. In the case of paper, several authentication methods have been developed using optical images of physical feature patterns [2, 3], waveforms from magnetic fibers embedded in paper [1, 6], or Raman spectra from single-walled carbon nanotube (SWNT) composite paper [7]. Here, SWNT-composite paper was made from a mixture of a pulp suspension and a dispersed SWNT suspension [8, 9]. Because SWNTs are cylindrical nanomaterials with a variety of diameters and structures defined by chiral indices (n, m), i.e., chirality. When SWNTs are embedded in paper randomly, we can use not only physical feature patterns of SWNT distribution, but also data on the distribution of diameter or chirality. Thus, it is impossible to fabricate clones by using SWNT-composite papers. In the previous work, the G mode from physical feature patterns and radial breathing mode (RBM) from SWNT diameter distributions were used as authentication keys using Raman spectroscopy, and an authentication accuracy of 5.0 \times 10^{-10} was obtained [10]. Further complexity can be added by utilizing chiralities of SWNTs as authentication keys. For chirality specific imaging, photoluminescence (PL) spectroscopy can be employed [11]. However, no PL signals are obtained from pristine-SWNT-composite papers. SWNTs need to be wrapped with biomolecules such as DNA [12, 13] and carboxymethyl cellulose (CMC) [11] in order to activate PL under the dry condition [15–17].

In this work, we obtained PL mapping images from CMC-SWNT-composite paper in which CMC-SWNTs were embedded in the pulp, and verified that PL of CMC-SWNT-composite paper was useful for artifact-metrics. We used CMC as a dispersant of SWNTs, because the principal component of pulp is cellulose and CMC is more stable than DNA.

II. EXPERIMENTAL

We used HiPco SWNTs (Unidym, length: 100–1000 nm, diameter: 0.8–1.2 nm) and CMC (Daicel Fine Chem Ltd., molecular weight: 60000). SWNTs with a total weight of 10 mg were placed in a CMC solution containing 10 mg of CMC in 10 mL of pure water and sonicated using an ultrasonic homogenizer at 20 W in an ice bath for 0.5 h. To remove bundled SWNTs, the solution was centrifuged at 163,000 G. The SWNT concentration for fabricating composite paper was 1 wt% with respect...
to the pulp weight. CMC-SWNT-composite paper was fabricated by the method used in a previously reported study [7]. Pulp was soaked and dispersed in pure water. The pulp solution and CMC-SWNT solution were mixed.

The compound in solution was scooped up using a wire net. Then, the CMC-SWNT-composite paper was dried. The thickness of the composite paper was ~100 μm. For PL measurements, a Ti:sapphire laser (690–850 nm) was used as the excitation laser. PL imaging patterns were detected with a 2D InGaAs array detector through an acousto-optic tunable filter. The laser spot was 14–16 μm in diameter, and the laser power was 0.4 mW. The exposure time was 1 s, so we could obtain one PL imaging pattern (Fig. 1) per second. We used 20×20 pixels as enrolment data. Positional displacement was allowed by using 10×10 pixels as verification data, i.e., an authentication key.

We evaluated the similarities between each pair of PL mapping images using pattern-matching and correlation-coefficient scores in verification [7]. Pattern-matching is a method for specifying whether and where a specific pattern appears. Using pattern-matching, resemblances can be calculated stably, regardless of brightness changes. We used Eq. (1) to calculate the pattern matching,

\[
R_{ZNCC}(k, l) = \frac{\sum_{i=1}^{10} \sum_{j=1}^{10} \{(I_{(i+k)(j+l)} - \bar{I}) - (T_{ij} - \bar{T})\}}{\sqrt{\sum_{i=1}^{10} \sum_{j=1}^{10} (I_{(i+k)(j+l)} - \bar{I})^2 \times \sum_{i=1}^{10} \sum_{j=1}^{10} (T_{ij} - \bar{T})^2}},
\]

(1)

where \(k\) and \(l\) are integer number; \((k, l) = (1, 2, \ldots, 10)\), and \(I_{(i+k)(j+l)}\) and \(T_{ij}\) are the peak strengths in coordinates of enrolment data (20×20 pixels) and verification data (10×10 pixels). The point \((k, l)\) was determined when \(R_{ZNCC}\) was maximized. The correlation-coefficient was calculated for the point \((k, l)\) as

\[
R = \frac{100 \sum_{i,j=1}^{10} P_{ij} T_{ij} - \sum_{i,j=1}^{10} P_{ij} \sum_{i,j=1}^{10} T_{ij}}{\sqrt{\{100 \sum_{i,j=1}^{10} (P_{ij})^2 \} \{100 \sum_{i,j=1}^{10} (T_{ij})^2 \} - \{\sum_{i,j=1}^{10} P_{ij}\}^2}}
\]

(2)

where \(P_{ij} = I_{(i+k)(j+l)}\) and \(T_{ij}\) are the peak strengths in coordinates of segmented enrolment data (10×10 pixels) and verification data (10×10 pixels).

Furthermore, evaluating indices of false match rate (FMR): rate of classifying counterfeit into genuine incorrectly) and false non-match rate (FNMR: rate of classifying genuine into counterfeit incorrectly) were calculated to determine the authentication accuracy as follows (actual examples can be found in Figs. 3 and 4). A histogram of the correlation-coefficient values between genuine and genuine (G-g), and genuine and counterfeit (G-c) was obtained for an authentication key. Then, FRM for a given threshold value was obtained as the ratio of the number of G-c data over the threshold value to the total number of G-c data. Similarly, FNMR was obtained as the ratio of the number of G-g data under the threshold value to the total number of G-g data. The equal error rate (EER) was estimated as the point where the FMR was equal to the FNMR, i.e., the intersection point of FMR and FNMR extrapolation lines. It is assumed that if the EER is small, the authentication accuracy is high.

Figure 2 shows PL maps from CMC-SWNT-composite paper. PL peaks of (9, 4), (8, 6), and (8, 7) SWNTs are obtained with an excitation wavelength of 730 nm and those of (10, 2) and (12, 1) SWNTs are obtained with 750 nm and 800 nm, respectively. Thus, the PL imaging patterns from different chiralities could be used as multiple keys. The diameters of (10, 2), (9, 4), (8, 6), (12, 1), and (8, 7) SWNTs are 0.87, 0.90, 0.95, 0.98, and 1.02 nm, respectively.

III. RESULTS AND DISCUSSION

A. Authentication key with only (9, 4) SWNT

Verification data of the (9, 4) SWNT were compared with PL mapping images at different positions and PL mapping images of (8, 6), (8, 7), (10, 2), and (12, 1) SWNTs at the same position. We calculated correlation-coefficients from the authentication key, and determined the authentication accuracy. The number of enrolment data was 100. Figure 3(a) shows a histogram of
correlation-coefficients. In the case of patterns at different positions, (G-g) was high, while (G-c) was not so low. However, the EER estimated by FMR/FNMR curves was small, $7 \times 10^{-12}$, as shown in Fig. 3(c). On the other hand, there was only a small difference between the correlation-coefficient values of G-g and G-c (see Fig. 3(b)), when verification data were compared with enrolment data of different chiralities at the same position. The number of enrolment data was 50. Although the threshold value is somewhat unclear (see Fig. 3(d)), it is clear enough to help distinguish the (9, 4) SWNT from other chiralities. Thus, it is expected that the authentication accuracy will improve by using a combination of data for the (9, 4) SWNT and SWNTs with other chiralities as multiple keys.

**B. Combination of multiple keys**

First, we integrated the correlation-coefficient data for (9, 4) and (12, 1) SWNTs. Here, the correlation-coefficient of G-c was nearly 0.6 when the verification data for (9, 4) SWNTs were compared with the enrolment data for (12, 1) SWNTs at the same position. The slightly lower PL intensity of (12, 1) SWNTs (see Fig. 1) is thought to be caused by the low correlation-coefficient of G-c at the same position. In order to use multiple keys, PL imaging patterns of different chiralities at the same position were used and data from different positions were compared. The number of enrolment data was 40. Figure 4(a) shows a histogram of correlation-coefficients of (9, 4), (12, 1) and (9, 4)+(12, 1) SWNTs. The EERs for (9, 4) SWNTs and (12, 1) SWNTs were $2.0 \times 10^{-7}$ and $4.0 \times 10^{-8}$, respectively. In the case of the verification data of (12, 1), the threshold value was 0.73. When we used a combination of (9, 4) and (12, 1) SWNT keys, the EER and threshold value improved to $8.0 \times 10^{-9}$ and 0.88, as shown in Fig. 4(c).

We then integrated the data for (9, 4) and (8, 6) SWNTs. Figure 4(b) shows a histogram of the correlation-coefficients of (9, 4), (8, 6), and (9, 4)+(8, 6) SWNTs. Even though the number of samples was 40, the EER es-
FIG. 6. Correlation coefficient vs. focal depth on the basis of (a) the surface of CMC-SWNT-composite paper, and (b) the central depth of CMC-SWNT-composite paper.

eral depth of CMC-SWNT-composite paper.

(8, 6) SWNT was estimated on the basis of the data for the (8, 6) SWNT was happened to be small, $1.0 \times 10^{-13}$. When we used a combination of (9, 4) SWNT and (8, 6) SWNT keys, the EER and threshold value improved to $1.0 \times 10^{-14}$ and 0.89, as shown in Fig. 4(d). Through authentication using two keys, the authentication accuracy was greatly improved.

Finally, we integrated the data for (9, 4), (8, 6), and (12, 1) SWNTs in anticipation of the effect of reducing the EER and threshold value. The number of enrolment data was 60. We succeeded in improving the authentication accuracy for both the EER and threshold value as shown in Fig. 5. The threshold value was 0.75 and EER was $2.0 \times 10^{-12}$.

C. G-g tolerance of authentication in the depth direction

It was necessary to consider the tolerance in the depth direction, because the paper used in this study had a thickness of 100 $\mu$m. First, a PL mapping image was obtained at a certain position and used as verification data. Second, the focal point of the laser was varied every 10 $\mu$m, and nine images were obtained as enrolment data. Finally, a PL mapping image was obtained at the initial depth. Then, each correlation-coefficient was calculated for each enrolment data as shown in Fig. 6 (a). Although the correlation-coefficient became smaller as the depth was varied, it recovered to 0.98 (red circle in Fig. 6(a)) at the initial depth. Furthermore, Fig. 6(b) shows the correlation-coefficient of each data when the focal depth was moved back and forth from the central depth of the paper. In each direction, correlation-coefficient was reduced by a similar extent. From these data, we can conclude that if the depth variation is within $\pm 10 \mu$m, the correlation-coefficient is not largely influenced.

IV. CONCLUSIONS

We succeeded in applying CMC-SWNT-composite paper to artifact-metrics. The variety of keys was increased by using PL spectroscopy, because data on not only diameters but also chiralities could be employed. Note that the difference in diameter between (9, 4), (8, 6), and (12, 1) SWNTs was only 0.08 nm. We confirmed that the authentication accuracy was improved by using multiple keys. The error rate estimate was $10^{-12}$–$10^{-14}$. It might be possible to further improve the authentication accuracy by using a combination of PL mapping images and Raman mapping images.

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