Encoding Multiple Information into European Article Number (EAN)-13 Codes with Various Chromic Sensing Materials to Construct Intelligent Barcodes

Hui Guan, Hang Liu, Qia Zhang, Jingyu Tang, Jianxiong Zou, Ling Kang, Menghan Hu,* and Jian Zhang*

An intelligent encoding/decoding scheme for barcodes is studied that can realize transformation among different barcodes under external stimuli. The proposed scheme is compatible with the European Article Number (EAN)-13 encoding/decoding system. First, the transformation mechanism among different barcodes is analyzed. Two different transformation strategies, the bar transformation and the background color transformation, are discussed. To demonstrate the possible applications, a temperature-sensitive barcode tag (TSBT) and pH-indicative barcode tag (PSBT) are developed by embedding the corresponding thermochromic and pH-sensitive materials into the traditional EAN-13 barcodes. Except for the conventional identification function, these tags can be used as environmental sensors to sense temperature and pH values. The maximum recognition rates of the TSBT and PSBT are 100% and 98%, respectively. The technology is universal and versatile because different kinds of sensitive tags can be constructed easily. This sensitive barcode technology can be expected to provide an efficient, accurate, and low-cost solution to real-time detection.

1. Introduction

The rapidly increased popularity and the wide application of the Internet of Things (IoT) have affected all fields and are reshaping our lifestyles. The barcode, as the workhorse technology for information storage, transmission, and identification, has penetrated into lots of domains such as transportation, retail, medicine, shopping, catering, financial payment, logistics, and the other industry applications. Conventionally, the barcode can only store static identity information. In all kinds of application scenarios mentioned earlier, there are always more information storage requirements. For instance, in the vaccine transportation and storage processes, the traceability information such as the experienced temperature is always concerned because most of the vaccines are temperature sensitive and need to be stored under low temperature. If the barcode tags attached on these items are designed intelligently so that they can record and monitor the temperature history during these processes, the customer can judge the effectiveness of vaccines accurately and quickly before the injection by scanning the barcode. Therefore, it is an essential topic to expand the barcode theory and application domains and develop the current barcode only with identification function into an intelligent one with multiple sensing capability.

In recent years, some new barcodes based on colorimetric,[1–3] spectral,[4] photonic crystal,[5,6] hydrogel,[7,8] intelligent structural color material,[9,10] luminescent[11,12] and magnetic[13] effects have been studied for their ability to record/transfer different domain information that cannot be supplied by the conventional one. However, these technologies either require complex synthesis techniques or are not compatible with the existing encoding/decoding system. Because these barcodes do not belong to any existing barcode system, they are neither uniform nor universal. Therefore, they are difficult to accept and disseminate widely.

Recently, some novel paper-based or Polydimethylsiloxane (PDMS)-based barcode chips utilizing code-39 code or Codabar code were reported.[14–16] The color-sensitive multiplexed assays were first incorporated into the barcode. A barcode scanner can read the results and realize the multiple target detection successfully. In this technology, the information of multiple targets was directly encoded into the existing barcode system. So, these point-of-care diagnostic devices can offer virtues such as sensitivity, portability, simplicity of operation, and friendliness to nonexperts. Although the character set of
code-39 code or Codabar contains the letters and some special characters, their data density is relatively low. This leads to the limited storage capability. In addition, as the whole chip is embedded into the microfluidic system, the fabrication process is relatively complex.

In this article, an innovative strategy that can realize transformation among different EAN-13 barcodes is probed and its potential applications are revealed. Unlike the code-39 or Codabar code, the EAN-13 code is of very high density and can encode a large amount of information within a smaller area, although the character set of the EAN-13 code only contains numbers. Therefore, it is possible to encode more information and even dynamic environmental information through the transformation among barcodes. First, according to the EAN-13 encoding rules, the interchangeable feasibility of different barcodes is probed. The interchange among different barcodes is achieved by purposefully tuning the color contrasts, which may be the differences between the specific bars or the contrast between the specific bars and the background of the barcode. Next, with the aid of some chromic materials, the so-called sensitive barcode tag (SBT) is developed and some possible applications are illustrated. Different chromic materials such as thermochromic and pH-sensitive materials have been inserted into the EAN-13 barcode as sensing elements. Under external stimuli, such as temperature rise and pH variation, varied barcodes have been realized. Therefore, through different transformations among EAN-13 barcodes, some external environmental information in our SBT can easily be detected by a conventional barcode scanner.

Compared with the existing barcode technology, our SBT technology is compatible with the current encoding/decoding system and resource-efficient because all transformations are in situ and real time; i.e., all transformations occur on the same barcode tag locally. More than that, in principle, any chromic materials that can be read with an optical barcode scanner can be incorporated into our SBT and act as the sensing elements. As our SBT can provide more information than pure identification, this relevant technology will find numerous applications in intelligent systems. The scope of this barcode technology will be of great value to many IOT fields, such as food safety, drug storage management, and cold chain transportation.

2. Results

2.1. Design Mechanism of EAN-13 Barcode Transformation

In this part, we explain our strategy from the aspect of binary encoding. The physical structure and the coding/decoding rules of the EAN-13 code in detail are shown in Supplementary 1, Supporting Information. In most cases, because 2–7 digits are designed to store the user’s information and are relatively stationary, the transformation skill only involves 8–13 digits. As mentioned previously, only one coding rule needs to be followed for these digits.

To encode or design an EAN-13 barcode, the check digit should be calculated first. The equation for the check digit calculation is

\[
(\Sigma O + \Sigma E) \% 10 = 10 - C
\]  

(1)

Here \(O\) stands for odd data digits, \(E\) for even data digits, and \(C\) for the check digit, respectively (Figure S3, Supporting Information).

Equation (1) can be rewritten into

\[
(C + 3\Sigma O + \Sigma E) \% 10 = 0
\]  

(2)

If the sum, \(M\), is defined as \(M = C + 3\Sigma O + \Sigma E\), \(M\) is an integer multiple of 10. This is a criterion that should be satisfied by all EAN-13 encoding.

If only one digit in the barcode is changed, Equation (2) is no longer satisfied. This kind of EAN-13 barcode is invalid. Therefore, in principle, to achieve the transformation or conversion between barcodes, at least two digits in the barcode should be changed simultaneously.

In addition, if we examine the binary sequences listed in the right half encoding column carefully, as shown in Table S1, Supporting Information, we find that a similarity exists between different sequences in some degree. Table 1 lists these possible binary sequence groups. Through these \(1 \rightarrow 0\) conversions, the original number in barcode turns into a new one. The transformation is reversible. That means through the design of barcode modules, the transformation between different numbers is feasible technically. All possible transformation combinations between two numbers are deduced and shown in Table 2. It can be seen that these combinations are not arbitrary. If \(p(x)\) and \(d(x)\) are defined as two digits’ contributions to \(M\), respectively, based on the aforementioned points, \(\Delta M = p(x) + d(x)\). \(\Delta M\) must be an integer multiple of 10.

Let us discuss the simplest case of transformation between two numbers, i.e., \(\Delta M = 0\).

Two transformation combinations are defined as \((A, B)\) and \((A', B')\). Here, \(A, B, A', \) and \(B'\) stands for the numbers before and after the transformation. Two numbers in one combination should be changed coherently. As shown in Table 2, if the...
influences of $A'$ and $B'$ on the sum $M$ compensate for each other, $\Delta M = 0$ can be guaranteed naturally. Then, the transformation between $(A, B)$ and $(A', B')$ is valid, and vice versa. A similar transformation process is shown in Figure 1. It can be found that relying on the odd or even position choice of two numbers, there are many possible transformation combinations.

As an example, the transformation between 6901234123456 and 6901234323436 is shown in Figure 1A. The number changing from 1 to 3, marked in red, increases $M$ by 6, whereas the 5 → 3 change decreases $M$ by 6. Therefore, when 1 → 3 and 5 → 3 change at the same time, 6901234123456 becomes 6901234323436. The relevant barcodes are valid, as shown in Figure 1B. By this way, the transformation of two barcodes is realized through the synergistic reaction between two digits. On the premise of satisfying Equation (2), the interaction can take place between any two digits in the barcode. Figure 1C–F also shows some other examples that can satisfy this kind of transformation.

Of course, upon this foundation, the series transformation of three or four barcodes also can be realized. The relevant examples are demonstrated in Figure 2A–D.

### 2.2. Combining Barcode Transformation with Chromic Materials

It is known that the barcode is featured by the modules and decoded by the corresponding reflected signals that can be read by the scanner. Because the contrast between black and white is the highest in the color system, the barcode is always set as black bars separated by white spaces. Two schemes had been studied to construct the SBT.

In Figure 3A, theoretically, the transformation between any barcode is related to a certain time and space. If the various chromic materials shown in Table S3, Supporting Information, are inserted and act as the modules, the settings of the black bars and the white spaces will be controllable. Then, the corresponding barcode will change with the external stimuli and turn into the new one. Inspired by this fact, we may use the thermochromic materials as sensing materials to sense the ambient temperature. When the temperature varies over their transition threshold, the colors of these materials will change, either reversibly or nonreversibly. At this time the barcode will be regarded as a new one by the scanner (Figure 3A). In this situation, the transformation between two barcodes can be used for switching and alarming. If more and more kinds of functional materials are involved, the barcodes will respond to more than one stimulus and become multifunctional and intelligent.

In Figure 3B, if we examine a barcode carefully, it can be found that in fact two colors exist, i.e., the bar and the background. Therefore, it can be regarded that the scanner read the color contrast between the bars and the background. Because the color contrast is the most important issue for reading correctness, the barcode bars are not limited to the black color. Inspired by the fact, barcodes with different color bars are printed on the pH testing paper. These color bars correspond to the known pH values and are used as the reference indicators. Because the background is sensitive and changes its color with the external stimuli, the color contrast between the background and the color bars will vary. If the color of the background is close to the indicator’s, the contrast between them will be lowered. At this moment the barcode will be regarded as a new one by the scanner (Figure 3B). In this way, more than one color can be inserted into the barcode.

On the whole, we take the barcode transformation as a main methodology and chromic materials as the medium, and we can realize the detection of the external stimuli through these encoded barcodes. Thus, the barcode, as the intelligent sensing element, is a promising environmental sensor.
2.3. Demonstration of the Temperature-Sensitive Barcode Tag (TSBT)

Using Scheme 1, with the aid of thermochromic materials, the series transformation among the barcodes can be realized. Here, the original barcode is defined as 6901234505917.

The transformations between two barcodes was studied first. In this case, only one kind of thermochromic material was involved. Table S4, Supporting Information, shows the corresponding properties of thermochromic materials used. Each material was encoded into the barcode to modified two digits, following the instruction shown in Section 2.2. Fifty TSBT
samples were fabricated and tested. All samples can be successfully identified.

Two other kinds of thermochromic materials with different transition temperature points were encoded into the same barcode. Their colors change from blue or green to white when the temperature rises, respectively. The setup for TSBT temperature testing is shown in Figure 3C. The test results are shown in Figure 4A. The barcode under room temperature is 6901234505917. When the temperature rose to 30 °C, the barcode turned into a new one, 6901234535617. When the temperature continued to increase up to 45 °C, 6901234533637 occurred. When the environmental temperature is lowered from >45 to <30 °C, the barcodes experience series transitions from 6901234533637 to 6901234535617, and returned to 6901234505917 reversibly. Therefore, three barcode transformations can be realized successfully by introduction of two kinds of thermochromic materials. In this way, the barcode is endowed with the function of multiple temperature measurements. The barcode then can discern between or indicate three different temperature ranges, including <30, 30–45 °C, and >45 °C.

To verify the thermal strength of TSBT, i.e., the long-term exposure to high temperatures, we tested the working ability of TSBNs at high temperature. The chosen commercial thermochromic material can bear 220 °C for 10 min. In this experiment, the maximum temperature is 70 °C. The TSBNs were first placed in an oven at 70 °C for 6 h and then cooled to room temperature. Then, the TSBNs were tested within the following three temperature ranges: <30 °C, 30–45 °C, and >45 °C. It was found that all TSBNs can work normally in each temperature range.

To examine the repeatability, one sample was chosen and its performance after 50 temperature cycling tests was evaluated. Repeatability >98% was achieved. This result implies that the temperature switch can be realized by this version. Through the choice of thermochromic material with different transition points, barcode switch can be established.

All the TSBNs are very stable as temperature sensor changes, almost regardless of whether the color of the bar is black, blue, or green. Color itself does not seem to be the key factor. The effect of contrast seems to be more important. As long as the color contrast between the bar and the background meets the identification requirements, the barcode can be scanned easily. Movie S1, Supporting Information, shows the working process of TSBNs.

To demonstrate historic recording function of TSBN, two irreversible thermochromic materials, with color change temperature of 60 and 80 °C, respectively, were embedded in the same barcode. The whole process for the temperature changing from 29 to 86 °C is shown in Figure S4, Supporting Information. As long as the TSBN has experienced 60–80 °C or >80 °C, the temperature history will be recorded.
matched CMYK for these color pictures dipped in to pH convenient, we chose pH paper with a wide range of color rication process is shown in Section 3. To study the problem fized with the proposed barcode transformation strategy. The fab-

2.4. Demonstration of the pH-Indicative Barcode Tag (PSBT)

TSBTs also have some other potential applications. For exam-
ple, they can be used as temperature bracelets to monitor and record body temperature during the epidemic. Because the bar-
code can be read remotely, the risk of proximity measurement is minimized. TSBTs are also suitable for the cold chain transpor-
tation. For example, they can record the temperature history during vaccine transport.

With Scheme 2, another type of pH-sensitive barcode was real-
ized with the proposed barcode transformation strategy. The fab-
rication process is shown in Section 3. To study the problem conveniently, we chose pH paper with a wide range of color change as the base material of the barcode.

First, with Adobe Illustrator software, we determined the matched CMYK for these color pictures dipped in to pH = 2, pH = 4, pH = 6, and pH = 8. There are (35, 86, 75, 0), (10, 73, 77, 0), (11, 26, 73, 0), and (45, 0, 75, 58). They are denoted as pH (2), pH (4), pH (6), and pH (8) in the context, respectively (Figure S5, Supporting Information). Then two sets of color bars with CMYK values of pH (2) and pH (4) were incorporated into the original barcode 6901234505290. It is known that, in the CMYK color coordinate, the K value, i.e., the black color component, plays an important role on the final contrast.\[^{17,18}\] Therefore, the K values of these two sets of color bars was adjusted to achieve the best contrast. The process of adjusting the K value is shown in Supplementary II, Supporting Information. With the K values of these two sets of color bars defined as \(K_1\) and \(K_2\), we tested the recognition rate of four \((K_1, K_2)\) combinations. They are (45, 35), (45, 40), (50, 40), and (50, 35), respectively. Each time five samples were tested and each sample was scanned ten times under an indoor LED lamp. Figure 3D shows the test process of immersing one sample into one kind of pH solution. The rest of the samples were tested with the same process. Figure 5A–D shows the test results. Here, the number x was used to represent the error barcodes, which cannot be read correctly. When \((K_1, K_2)\) is (50, 40), the PSBT shows three barcodes in different pH solutions. Figure 4B shows the PSBTs immersed in different pH solutions. In the pH = 6 case, because the solution is close to the neutral condition, the color of the pH test paper does not change remarkably; the barcode is still the original barcode 6901234505290. When the PSBT is immersed in the solution with pH = 4, the color of the pH test paper changes obviously. At this time, the background color is close to one of the colors of the preset color bars and the corresponding color bars turn indistinguishable for the scanner, and the barcode changes from 6901234505290 to 6901234565270. When the PSBTs were immersed in a solution with pH = 8, the background color becomes relatively darker. Therefore, the two sets of color bars are merged into background and become indistinguishable. The barcode becomes a new barcode, 6901234563870. When the PSBT was immersed in the solution with pH = 2, the background color changes to red. At the same time, the strong acid environment makes the color of the color bars become relatively darker. Therefore, the two sets of color bars can still be recognized by the scanner and decoded as 6901234505290.

To verify the chemical stability of PSBTs when exposed to low pH, we tested the color change of PSBTs after immersing in a solution of pH = 2 for 1, 2, and 3 min. The test results are shown in Figure S6, Supporting Information. As the immersion time increases, the color of the pH test paper becomes lighter, and the color of the ink does not change remarkably. Therefore, to ensure the chemical stability of PSBTs at low pH and the accuracy
of the scanning results, the PSBTs should be scanned within 1 min.

To study the influence of the bar width on the recognition rate, the bars with different width values ranging from 0.43 to 0.33 mm and 0.53 mm were studied. The \((K_1, K_2)\) is fixed at (50, 40). Figure 5E shows the scan results. The recognition results for the bar width of 0.53 and 0.43 mm are almost the same. But for the bar width 0.33 mm, only 6901234563870 is read out, indicating that the barcode turns indistinguishable. Therefore, it is concluded that 0.43 mm is the minimum width that can be set for the bar. Once the bar width is greater than this value, the width of the bar has little effect on the final scan result. Figure S7, Supporting Information, shows the PSBTs with the bar width of 0.33 and 0.53 mm. Figure S8, Supporting Information, shows their microscope images.

We also studied the influence of light on the final recognition rate. Figure 5F shows the scan results under an indoor LED lamp and in a closed box installed with a LED. The results show that the light does not have much effect on the scan results. Movie S2, Supporting Information, shows the working process of PSBTs under indoor LED lights.

In PSBTs, we use a scanner to read the pH value instead of the traditional colorimetric method. This will have great value in batch recording. In principle, the barcode recognition rate can be improved through using more sophisticated sensing materials (with good optical resolution, linearity or sensitivity, etc.).

In terms of fabrication, the screen printing and the inkjet printing technologies are very simple and low-cost for mass production, which display superiority over complicated processing technologies. In terms of application, barcode-like sensors are a new type of monitoring device. They do not require the construction of a circuit system, which makes their production cost low. In addition, they can quickly read and record information locally and remotely, which makes them useful in many fields.

3. Conclusion

We proposed a barcode transformation theory suitable for the EAN-13 code coding rules, and the developed SBTs that can perceive external environmental information with the aid of some sensitive materials. The barcode transformation can be realized by changing the color of either the bar or the background. Our SBTs are compatible with the current decoding systems and can be read by a scanner. Except for the conventional identification, the SBT barcode sensors can act as an instant detection device. More importantly, some other commercial test papers, such as urine test paper, heavy metal test paper, and microbial test paper, can be embedded in our barcode transformation theory. This is also the goal of our next research.

4. Experimental Section

Materials: Thermochromic powder was purchased from Shenzhen Symphony Color Technology Co., Ltd., Shenzhen, China, and cyclohexanone and polyvinyl chloride (PVC) screen printing inks were purchased from Zhongshan Zhongyi Ink Coating Co., Ltd, Zhongshan, China. pH test paper was purchased from Shanghai Sanaisi Reagent Co., Ltd, Shanghai, China.

Fabrication of TSBTs: First, the computer software Adobe Illustrator was used to draw the barcode. The barcode with a bar width of 0.43 mm. The short bar height is 15.71 mm, while the long bar height is 18.71 mm. A cross-shaped alignment mark was designed in the top right-hand corner of the barcode to guarantee the alignment accuracy. Then, the original barcode was printed onto A4 paper (Figure S9A, Supporting Information). Next, the thermochromic powders were mixed with
cyclohexanone and PVC in a ratio of 4:1:10 and incorporated into the barcode as the sensitive bars by screen printing.

Fabrication of PSBTs: pH test paper was used as the substrate. First, four kinds of pH standard solutions with pH = 2, pH = 4, pH = 6, and pH = 8 were prepared, respectively. pH testing papers were dipped individually into these solutions and their corresponding color pictures were recorded by the camera under an indoor LED lamp. With Adobe Illustrator software, the matched CMYK values of these color pictures were determined. Second, through adjusting the printer setting, the color bars according to the previously mentioned CMYK values were inserted into the barcode. Next, the barcodes with preset color columns were printed on the pH test paper with the color printer (Figure S9B, Supporting Information). Then a transparent waterproof layer was coated on the pH test paper with the color printer (Figure S9B, Supporting Information). Finally, the established PSBTs were observed through a microscope (BD-61T) was used to capture images and videos of the PSBTs and TSBTs. The computer software Adobe Illustrator cc 2018 was used to extract the CMYK value of the photo. A mobile phone (iPhone 6s Plus) installed with a scanning software named “PowerBarcode” was also used to scan the barcode.

Characterization: A color printer (L4168 EPSON) was used to print barcodes on A4 paper and pH test paper. A microscope (BD-61T) was used to observe the magnified surface morphology of the various barcodes. A Canon 750D camera was used to capture images and videos of the PSBTs and TSBTs. The computer software Adobe Illustrator cc 2018 was used to extract the CMYK value of the photo. A mobile phone (iPhone 6s Plus) installed with a scanning software named “PowerBarcode” was also used to scan the barcode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

barcode transformation, EAN-13 code, pH-sensitive barcode, thermochromic materials

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