Storage of Information Using Periodic Precipitation

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ABSTRACT: In the present work, transparent flexible thin polymer films with silver patterns have been created. The resulting structures made by the printing method represent a new alternative approach for recording, protecting, and transmitting information as well as for nonlinear gradient material formation. An alphabet for process automatization was created, and an automated system for recording and reading information was developed. To protect the information, we suggest the usage of a classic XOR function: the idea of scrambling is to demonstrate the simple and clear example of coding the ITMO University logo, and the code is provided. Additionally, the resulting samples are functional gradient materials with peaks of surface plasmon resonance. In the following, automated peak decoding by UV−vis spectroscopy allows an additional physicochemical method for structure decoding.

INTRODUCTION

In recent times, because of the constant increase in speed and the amount of produced information in our planet increases the interest in developing alternative information storage technologies. Technologies from electronic, optical, and magnetic methods, to low molecular weight molecules, high molecular weight molecules, and biologically derived systems are used to store information.

One of the most popular and used methods of chemical information storing is DNA encoding. The coding technique of DNA-based storage and the one in modern computers differ in their alphabets. Thus, there are bases A, C, T, and G in DNA instead of “1” and “0” in a computer. Four different signals of DNA bases results in a large number of chemical information encoding ways.

Storing information in DNA has some advantages, such as huge data storage density, the stability of the carrier (at low temperatures), the ability to create an error correction mechanism, and the ability to solve some computational problems much faster than on a modern binary computer. However, it does not have the capability to rewrite information, and further clear development is needed. Nowadays, all attempts of experimental chemical information storage and processing are growing areas of infochemistry.

Another way of information coding is encoding the m-SMS molecule, which includes three fluorescent groups (fluorescein, sulforhodamine B, and Nile blue). The main idea is to convert the text to numbers using a public alphanumeric code to obtain a numeric sequence. Moreover, such a method can be considered for further development of chemical computing. These systems are capable of writing any messages by sequentially adding chemical inputs. Reading is accomplished using a hand-held spectrometer.

In the group of Whitesides, the way of chemical encoding based on matching a single pulse of light with an alphanumeric symbol was suggested.

The ignited metals emit light at different wavelengths. It makes possible to discern which metal was burned and to encode the message.

Important is that, notwithstanding very low resolution, the proof of concept of alternative ways is shown. Here, we also focus on proof of concept for our system, and simultaneously, we show a prospective way of UV−vis spectroscopy for decoding the information. The advantages of stimuli-responsive materials are also mentioned.

Rules of coding and decoding are clearly presented. The main disadvantage of such a system is that peaks corresponded to some metals can overlap, so one needs to avoid some sequences. Another procedure is based on a common, small set of molecules (for instance, 32 oligopeptides) to write binary information. It minimizes the time and difficulty of the synthesis of new molecules. This way consists of writing messages in an eight-bit American Standard Code for Information Interchange (ASCII), converting them to an equivalent molecular code and store them in an array plate.

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(four bytes per spot). “Writing” is performed by first translating information into binary. Binary information is converted to oligopeptides immobilized on a self-assembled monolayer, for storage. A MALDI-TOF mass spectrometer analyzes (“reads”) these plates. A program decodes the information in the spectra and generates a bit string that is used to regenerate the original text.

Mankind is confidently moving toward the creation of nanocomputers for various applications: from sensors that can control our metabolism to the creation of powerful fit-hand quantum computers. Minimization is especially important for information technologies. It is demanded to create materials that combine a minimum volume in space and a high recording density. Notwithstanding that the high recording density is needed, the proof of concept in majority cases is done for model systems. Here, we focus on the system where, in the long run, the high recording density is possible and show proof of concept and procedure from automated coding, create the program, and suggest prospects for material science with automatization of formation, writing, and reading. We suggest using functional gradient materials as a new storage medium that in the following can be stimuli-responsive media.

Functional gradient materials are composite or single-phase materials, which change their functional properties uniformly or stepwise in at least one dimension of a particle, film, or bulk sample. The functional gradient materials have found applications in various scientific fields such as the aerospace plane, ceramic engines, optics, nuclear fusion, and medicine. The incredible potential of printing inspires us to engender a new information media based on functional gradient materials.

Here, we present a novel approach with rules of coding and decoding, encrypting the data as well as a prospective way for functional nonlinear materials. Thus, a potential printing way for the flexible film with silver patterns is described. Both coding and a way to provide information security is highlighted together with material science prospects. Future prospects are suggested.

■ RESULTS AND DISCUSSION

The material made of agar and silver from silver nitrate was used for the investigation (Figure 1). The gradient structure is formed because of the diffusion of silver nitrate (active substance) into 1 wt % agar gel. During the diffusion of silver ions through agar, Liesegang rings (LRs) are formed. LRs formation is a phenomenon of space-separated precipitation; when due to a combination of supersaturation, nucleation, and diffusion limitation separate bands, rings of precipitation are formed. The resolution during wet-stamping can be enlarged the symbol capacity, we need just to add one more concentration; 0 states for zero concentration (Figure 2b). The alphabets are based on LR phenomena that allow creating a distinguishable pattern. Different positions of silver particles zones and their total amount in the formed pattern make it possible to recognize several different signals. Positioning is controlled by varying the concentration of silver nitrate. This behavior of changing concentration of hot agar solution was added and uniformly distributed over the carrier matrix. In a Petri dish with a diameter of 90 mm, 4 mL of agar. The resulting white salt decomposes under light does not affect the structure. Transmission electron microscopy (TEM) (Figure 1b) images were captured for the confirmation of the particle size. When concentration rises, the dispersion of the particle size is increased.

Alphabets for the transliteration for the writing process is presented in the table in Figure 2a. The alphabets are based on LR phenomena that allow creating a distinguishable pattern. Different positions of silver particles zones and their total amount in the formed pattern make it possible to recognize several different signals. Positioning is controlled by varying the concentration of silver nitrate. This behavior of changing band position with the changing electrolyte concentration is known as Matalon–Packter low. Using this fundamental diffusion regularities is a new way to store and transmit information.

The alphabet was created (Figure 2a–c). Each letter corresponds to a combination of three digits from the set 0, 1, 2, 3, and 4 (Figure 2a). Each digit corresponds to a certain concentration; 0 states for zero concentration (Figure 2b). The choice of the number of symbol coding digits and five different signals let us code $2^5 = 125$ different symbols. This amount is enough to encode 105 basic symbols of the English text. To enlarge the symbol capacity, we need just to add one more concentration that will lead to $2^6 = 216$ different symbols or to use four digits to code, so we get $2^4 = 625$ symbols.

To protect the information, we suggest using a classic XOR function as a special way to coded messages to prevent information leak. Thus, a cipher will be transmitted rather than a message, and only those who have the key will be able to solve it.

The XOR function is a digital logic gate (yes or no type) that gives a true (1 in our case) output when the number of true inputs is odd. Particularly, it gives 0 when two variables are equal and 1 when they differ. For binary notation, if the input is 1, 1 or 0, 0, we get 0, and for 0, 1 or 1, 0, we get 1. It is both an associative and a commutative operation, which means that neither the order nor the grouping of operands affects the results. Thus, applying the formula $B_i = A_i \oplus B_i^{m+1} \oplus B_i^{m+2}$ to the original message, it can always be restored using the
The whole process is called scrambling (Figure 3a–f). Parameters m and n can be changed to generate different keys.

To automate the process of the message reading and decryption, a program was written. This program allows using a scanner as a reading equipment (Figure 4). Thus, reading occurs quickly, and human decoding errors are prevented. Also, the modern scanners because of its high resolution are supposed to be able to read nanoscale (~500 nm and more) features of the films. To eliminate the human factor, to completely automate the process, and to enlarge signal capacity, a robotic printing method is proposed here (Figure 4a). For creating messages using the printing method, replaceable cartridges with silver nitrate solutions of various concentrations are proposed. The cartridges are made of tinted glass or a completely opaque material so that the silver nitrate salt does not decompose. A thin, transparent agar layer is charged to the printer as a substrate. LRs are formed after

To encode the word “ITMO”, we used the following algorithm: (1) according to the table of combinations of different concentrations to symbols: “ITMO” = 131 202 140 142 (Figure 3b); (2) the received message was translated in binary notation, letter by letter, padding it with zeros to seven characters, if necessary: “ITMO” = 0101001 0110100 0101101 0101111 (Figure 3c); (3) the message was scrambled with the given keys (in our case 3 and 5), getting a new sequence 0101101 1011001 1010001 1110110 (Figure 3d); and (4) this sequence was transferred back to the fifth number system, as a result of which we get 140 324 311 433 (Figure 3e). The message is recorded directly into the Petri dish or by robotic printing (Figure 3f). To decode the encoded message, the inverse algorithm is used (Figure 3f–a).
droplets were applied to the surface. Silver nanoparticles (NPs) are formed under irradiation. The dried film is read by a scanner, which decodes it into a finished message using a scrambling formula (Figure 4b).

The formed silver NPs exhibit a phenomenon known as surface plasmon resonance (SPR). The SPR is an optical property that takes place when light interacts with conductive nanoparticles that are smaller than the incident wavelength. This behavior is explained to be the interaction of the silver nanoparticle surface electron cloud with a certain value wavelength light corresponding to the resonance frequency. Silver NPs are especially efficient at absorbing and scattering light. The SPR peak wavelength of such NPs can be tuned from 400 (violet light) to 530 nm (green light) by changing the particle size. UV−vis spectra can be used to increase the resolution for the suggested method, allowing the decoding of the formed structure.

Further development will lead to the formation of diffraction patterns upon light transmission. Using controlled patterning by means of Liesegang phenomena, we possibly will manage to create a diffraction grid. Thus, we will be able (i) to read both intensity and the position of light and (ii) to use lasers to read less than 300 nm size features, and therefore, the storage density will increase.

One could think of more insights into programming by controlling the concentration of silver nanoparticles or by, for example, direct synthesis or precipitation of existing ones. Some additional material can be compared with the polymer with silver NPs: NP redistribution controlling into polyelectrolyte multilayers by temperature. AgNPs in situ formation on the elliptical vaterite beads and its potential effect on surface-enhanced Raman scattering. This behavior is explained to be the interaction of the silver nanoparticle surface electron cloud with a certain value wavelength light corresponding to the resonance frequency. The SPR peak width indicates particle uniformity. The resulting plasmon resonance peaks (plot on the left).

Moreover, it is possible to use gradient polymeric coatings or tunable wettability to help in controlling the deposition of gradients and further increase the resolution for information coding.

With a change in the concentration of the active substance, the characteristic peak of SPR also changes. Various shapes provide us with different SPR plots, as shown in Figure 5a.

Dried films were easily removed from the Petri dish. Such material distinguished for its flexibility, lightness and with the silver NPs contained in it, has a high optical density (Figure Sb). As stated above, with a change in the concentration of the active substance, the characteristic peak of SPR also changes. Therefore, a new alternative method of encoding and protecting information is proposed (Figure 5a). Plots with SPR peaks were obtained for describing the system (Figure 5a). As can be seen, the peaks correspond to the wavelengths from 445 to 519 nm, which is common for silver nanoparticles. Depending on the conditions of the reaction, the sizes of nanoparticles can vary and can aggregate in different ways; because of this, the characteristic wavelength and peak width also shift. Therefore, a method for encoding and decrypting a message by creating characteristic peaks is also provided. In this case, the Agilent Cary 60 UV−vis spectrophotometer becomes the reader. For such a method, we are supposed to create special nozzles for the spectrophotometer, with the help of which it becomes possible to read messages of very small sizes and without mistakes.

The film with nanoparticles can be stable upon most presumable environmental conditions, including stability up to 250 °C. We have heated our samples up to 200 °C and maintain and did not observe visible changes neither in agar degradation nor in silver particle positions. The film can be bent many times. The films are highly flexible and robust. The formed structure is also stable under irradiation (405 nm, 5 mW/cm² for 24 h). The material is stable under wet conditions, and after soaking in water, it retains the pattern.

CONCLUSIONS

In conclusion, we developed a printed, flexible film with silver patterns: the functional gradient materials. We created a new alphabet for coding information in the structure of the film. Each silver pattern contains silver NPs that exhibit the phenomenon of SPR. The program for automated information coding and scrambling is presented. The simple structure imaging can be used for decoding patterns using the scanner as the reading equipment. In addition, by decoding the patterned structure, the SPR peak wavelength of the formed silver nanoparticles—which can be tuned from 400 nm (violet light) to 530 nm (green light) by changing the particle size—can be decoded by UV−vis spectrophotometry. Because of the possibility of creating nanostructures based on the obtained gradient material, microsensor sources of information transfer can be developed in the future.

METHODS

Chemicals. Agar (A1296, powder, CAS number: 9002-18-0) and silver nitrate (Nitric acid silver(I) salt, molecular weight: 169.87, CAS number: 7761-88-8) were purchased from Sigma-Aldrich. Pure water from Millipore Elix (18 MΩ−
cm$^2$/cm) was used to prepare the necessary solutions for the experiment.

**Instruments.** UV–VIS Spectrophotometry. UV–vis spectrophotometry was used to characterize the optical properties of the thin films. Measurements were carried out using a two-beam scanning spectrophotometer with a high resolution spectrophotometer UV-1800 (Shimadzu, Japan). Spectra were recorded in a range of 200–800 cm$^{-1}$ at a medium scan rate.

**Transmission Electron Microscopy.** Before measurements, the samples were mounted on a 3 mm copper grid with a carbon film and fixed in a grid holder. The morphology of the samples was studied using the Hitachi transmission electron microscope. Images were acquired in the bright-field mode at 100 kV accelerating voltage.\(^{58}\)

**Other Equipment.** The scanner Canon CanoScan 9000F Mark II is used as the reading medium.

**Experimental Thin-Film Fabrication.** For creating an experimental model, 1% AgA1296 solution was used as the carrier matrix. In a Petri dish with a diameter of 90 mm, 4 mL of hot agar solution was added and uniformly distributed over the surface. The matrix was completely gelled and ready for use within 1–3 min. After that, silver solutions with various concentrations were applied dropwise with a drop volume of 3.36 μL to the surface. The diffusion reaction proceeds from 2 to 5 h under irradiation of the visible spectrum.

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The authors declare no competing financial interest.

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