SUPPLEMENTARY INFORMATION

Multiplexing Steganography Based on Laser-Induced Breakdown Spectroscopy Coupled with Machine Learning

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Experimental section

Reagents and fabrication of LIBS inks

$CuSO_4$ was purchased from Chengdu Kelong Chemicals Co., Ltd. (Chengdu, China). $AgNO_3$ was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. (Guangzhou, China).

Different concentrations of LIBS ink were prepared by mixing different amounts of metal salts into commercial ink. In this study, low-concentration LIBS inks were prepared by dissolving 0.1 g $AgNO_3$ and $CuSO_4$ powders in 5 mL of regular ink respectively; the high-concentration LIBS inks were prepared by dissolving 0.3 g $AgNO_3$ and $CuSO_4$ powders in 5 mL of regular ink respectively.

Experimental setup

The Nd:YAG laser (Innolas, Germany) was used for producing radiation pulses at 1064 nm and a 10 Hz repetition rate with pulse energy adjustable from 1.5 mJ to 100 mJ. Czerny-Turner multi-spectrometer (Avantes, Netherlands) was applied to collect the emission light. The digital delay generator (Stanford Research Systems, DG535) was used to send pulse signals to simultaneously trigger the following devices.

The LIBS instruments for stego-text imaging have been described in our previous study.[1] In brief, the LIBS setup mainly comprises four parts:

(1) Plasma excitation device. A Q-switched Nd: YAG laser is used to generate laser pulses. The laser beam is focused on the sample to excite the plasma through the well-designed optical path. After the generation of plasma, the radiation signal is detected by the photodetector and simultaneously triggered by the digital delayer.

(2) Displacement device. The electric XYZ stage is directly triggered by pulse signals from the digital delayer with a 2.0 μs delay time. As the displacement table moves, the laser generates plasma at different positions on the sample surface according to the set matrix.

(3) Signal-collecting device. The spectrometer is synchronously triggered to run with the same delay. The plasma signals were collected by an optical fiber at a 45° angle relative to the laser spot and then transmitted to the four-channel spectrometer, which is equipped with four linear compact charge-coupled devices (CCDs) with 2048 pixels for spectral acquisition. The collected spectra covered the range of 179–900 nm with a resolution of 0.15 nm.

(4) Positioning and imaging device. For the positioning device, a confocal green laser (532 nm) passes through the optical path and reaches the sample to directly indicate the focus position of the laser. For the imaging device, the CCD camera achieves the real-time imaging of the analysis area with a lighting system composed of LED lights. The clear image on the monitor shows that the laser is focused on the right position.

LIBS analysis

The imaging for the stego-text was performed on the LIBS setup. The laser (λ = 1064 nm) was fired at a repetition rate of 10 Hz. The laser energy is set to 25 mJ with optimization (Fig. S1). The stego-text sample was fixed on the XYZ stage and moved pixel by pixel (100 μm apart) to scan the entire sample area. The size of the matrix was set according to the actual size of the stego-text to ensure full coverage. With the default laser repetition rate, the analysis time per unit of area for a typical sample was 16 min/cm^2. For a single letter or number, A total of 4900 spectra were collected within 8 minutes for imaging. A specific emission line was selected for Ag and Cu. After baseline correction, elemental spatial distribution images were obtained by calculating the normalized peak area of selected lines, including the range of 327.5 nm to 328.5 nm for the peak of Ag Ⅰ 328.06 nm, and the range from 324 nm to 325 nm for the peak of Cu Ⅰ 324.75 nm. The information of stego-text was visualized by elemental distribution images with a false-color scale. Orange and cyan colors corresponded to Cu or Ag element ink, respectively. By increasing the minimum value of the color scale, only the areas with high concentrations of Cu or Ag ink were seen in the images.

Optimization

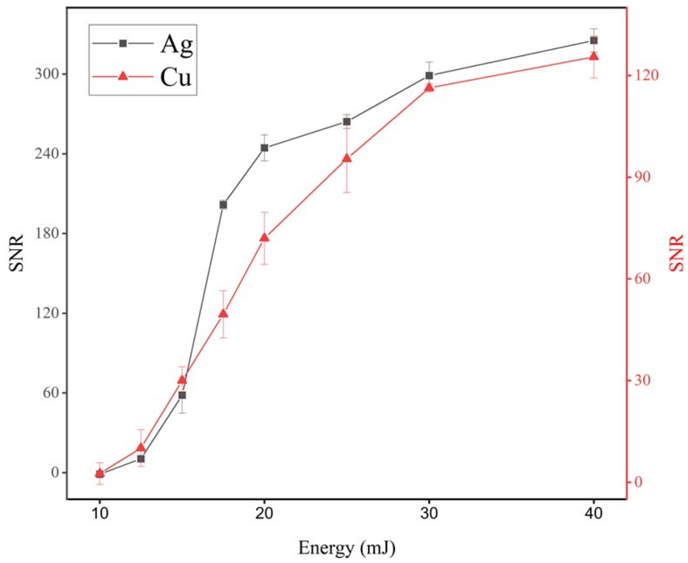

Fig S1 Optimization of LIBS analysis energy

Evaluation of the stability

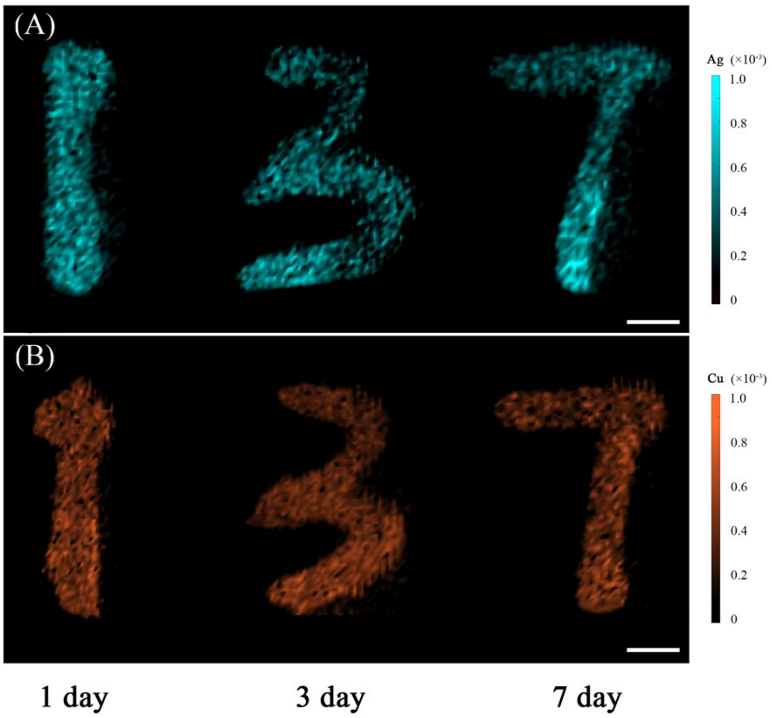

Figure S2 Evaluation of the stability of this steganography. (A) Three numbers of "1, 3, 7" written in Cu ink; (B) Three numbers of "1, 3, 7" written in Ag ink

Evaluation of the stability

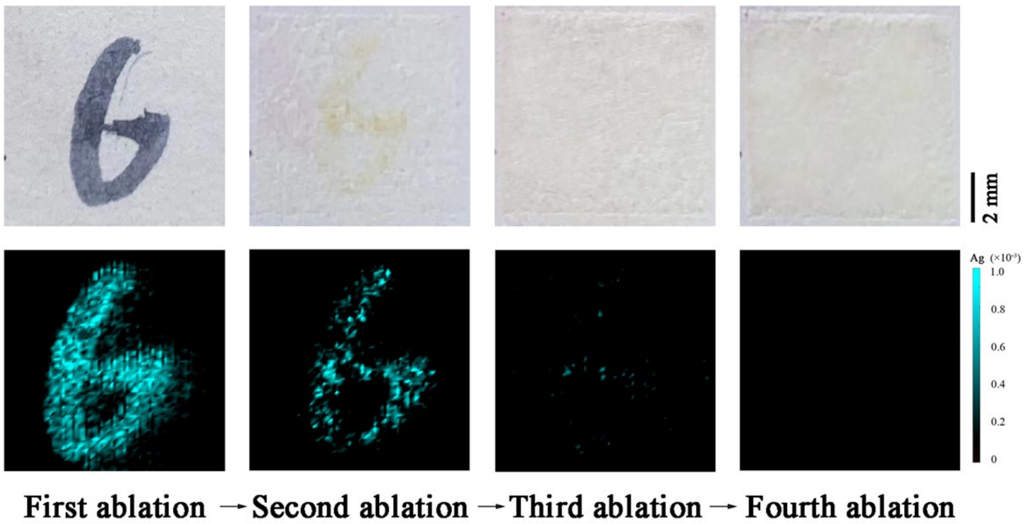

Figure S3 Repeated ablation of steganographic text written in low-concentration Ag ink.

Reference

1.Q. Lin, S. Wang, Y. Duan and V. V. Tuchin, Journal of Biophotonics, 2021, e202000479.

Conflicts of interest

There are no conflicts to declare.