

The EChemPen: A Guiding Hand To Learn Electrochemical Surface Modifications

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The EChemPen: A Guiding Hand To Learn Electrochemical Surface Modifications

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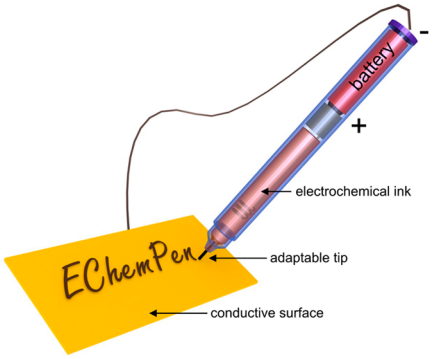
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Supporting Information

ABSTRACT: The Electrochemical Pen (EChemPen) was developed as an attractive tool for learning electrochemistry. The fabrication, principle, and operation of the EChemPen are simple and can be easily performed by students in practical classes. It is based on a regular fountain pen principle, where the electrolytic solution is dispensed at a tip to locally modify a conductive surface by triggering a localized electrochemical reaction. Three simple model reactions were chosen to demonstrate the versatility of the EChemPen for teaching various electrochemical processes. We describe first the reversible writing/erasing of metal letters, then the electrodeposition of a black conducting polymer "ink", and finally the colorful writings that can be generated by titanium anodization and that can be controlled by the applied potential. These entertaining and didactic experiments are adapted for teaching undergraduate students that start to study electrochemistry by means of surface modification reactions.



KEYWORDS: *High School/Introductory Chemistry, First-Year Undergraduate/General, Electrochemistry, Electrolytic/Galvanic Cells/Potentials, Hands-On Learning/Manipulatives, Laboratory Instruction*

INTRODUCTION

Electrodeposition is an electrolytic process that uses electric current to form a coating on a conductive object. It is mainly applied to impart new surface properties to conductive objects,[1−3] but can also be used to visually study electrochemical reactions.[4,5] The most common technique employing the concept of electrodeposition is electroplating, where a metal cation (M^{n+}) is reduced to the corresponding metal (M) at a cathodic electrode following the reaction:

$$M^{n+} + ne^- \rightarrow M \quad (1)$$

Electroplatings are usually performed using two planar electrodes, which are connected to a power supply and are placed in a beaker containing the electrolyte. When the electrical current flows through the cell, the cations are reduced and a newly formed metal layer can be observed on the cathodic electrode surface.[1,2] This is a typical experiment where the students can clearly see the color difference between the immersed and, thus, modified part of the cathode and the rest of the cathode, which remains unchanged.

With the endeavor to employ visually detectable electrochemical reactions for the purpose of writing and erasing, we developed an electrochemical pen (EChemPen). This is a pen-type device which bases on a regular fountain pen principle. The pen comprises a cylindrically shaped insulating shield, which contains the electrolyte and a metal wire wound around a wooden toothpick, as the core of the pen. A conductive surface acts as the second electrode, which can be locally modified by a localized, visual electrochemical reaction ("writing process"). This reaction is triggered as soon as the electrolyte solution is dispensed at the tip, which brings the two electrodes into electrical contact.

In the modern world where students use digital devices such as smartphones, tablets, and stylus to write on a daily basis, the inkless writing mode and the high-end functionality of our EChemPen aroused the students' interest for electrochemistry during a laboratory experiment. From a teacher's point of view, the various electrochemical concepts employed in the EChemPen present a lot of teaching material. Furthermore, these experiments only require cheap chemicals and materials and produce reproducible modifications that can be easily observed with the bare eye due to their strong colors.

To stimulate the students' interest, we propose to realize surface modifications using the EChemPen, as described in the following. The key point is that not only the electrochemical reactions has been studied but also the manufacturing of the

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EChemPen (Figure 1), which has given insights into the mechanisms of electrochemistry. The manufacturing is easy,

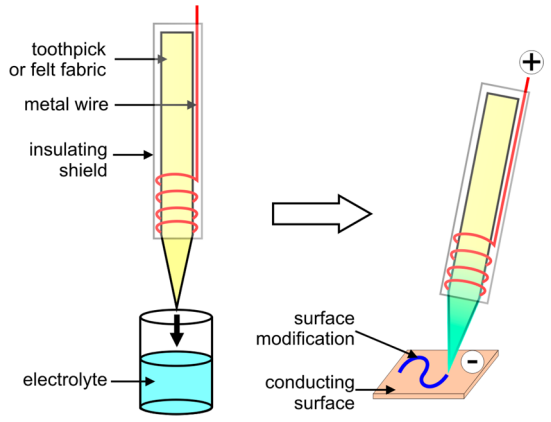


Figure 1. Scheme showing the principle of the EChemPen.

quick, and only requires cheap materials, which promises a wide applicability also in short lessons or in schools with a limited budget. These type of experiments that use household resources are attractive to the students and great fun to teach.[6,7] Commercial electrochemical pen can be found; it is used in industry to study corrosion[8] but mostly to decorate jewelry.[9,10]

MATERIALS

The following equipment and chemicals were used for the different versions of the EChemPen: a power supply (with a potential up to 100 V), button cells, copper wires (1 mm in diameter) coated with an insulating polymer, alligator clips, a metallic spoon, titanium foils, gold surfaces, toothpicks, a heat gun, heat shrinkable tubes, wooden pencils, 1 mL pipet tips, cotton, copper beads, distilled water and aqueous solutions of copper sulfate, sulfuric acid, and pyrrole.

Fabrication and Operation of the EChemPen

We fabricated and tested three versions of the EChemPen (see Figure 2) in order to demonstrate the versatility of the concept and to evaluate the optimal design. The simplest version involves a toothpick and is powered by an external power supply, while the more elaborated one is powered by an integrated battery. The fabrication of these three models is described in the following subsections.

Toothpick-Based EChemPen. The toothpick-based EChemPen (Figure 2 A) uses a regular toothpick as the tip of the pen and a copper wire as the electrode, which is wrapped around the toothpick close to one of its sharp extremities. A direct electrical contact between the copper wire and the electrode surface on which the writing will occur must be avoided in order to prevent an electrical short circuit. The other end of the wire was connected to the power supply. An insulating heat shrink tube was placed around the assembly of toothpick and copper wire in order to avoid any direct contact between the copper wire and the hand of the user. Even if this precaution allows avoiding any hazardous electrical risk, the use of insulating gloves is mandatory during the use of the EChemPen. As shown in Figure 1, the EChemPen was used like a dip pen with the ink as the electrolytic solution that mediates the electrodeposition. As it is often the case in conventional electrochemical experiments, the EChemPen

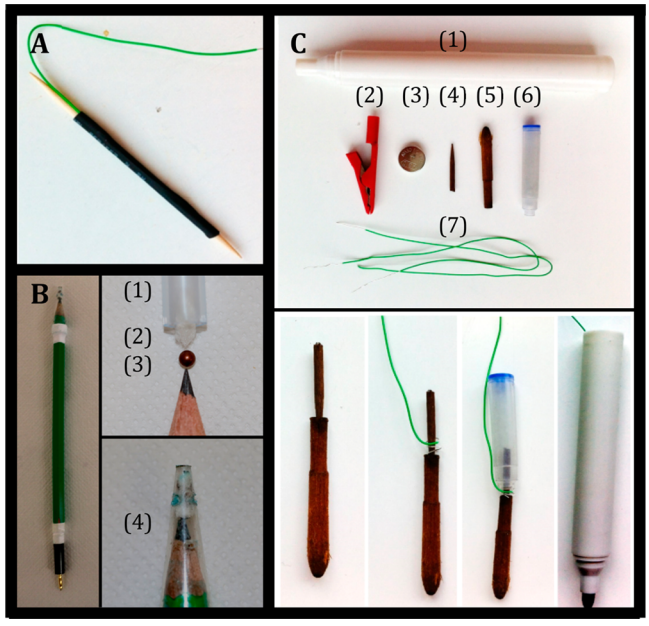


Figure 2. Pictures showing the fabrication of the three versions of the EChemPen. (A) Toothpick-based EChemPen. (B) Pencil-based EChemPen with (1) 1 mL pipet tip; (2) cotton patch; (3) 3 mm copper bead; (4) holes for air draining. (C) Battery-powered EChemPen with (1) pen body; (2) contact clip; (3) batteries; (4) toothpick; (5) felt fabric; (6) ink cartridge; (7) wires.

writing is potentiostatic, i.e., the operator fixes the potential and the current flow is controlled automatically by the power supply. As soon as the EChemPen touches the conductive surface, the electrolyte solution forms a conductive bridge between the copper wire and the conductive surface, which closes the electrical circuit. Therein, the copper wire acts as the anode (or cathode) and the conductive surface acts as the cathode (or anode) and will be modified. During writing, the electrolyte bridge moves with the tip of the EChemPen, and thus, the modified area can be directly controlled by the hand of the operator. The electrolyte must be regularly reloaded to continue writing.

Pencil-Based EChemPen. The wood at both end of a pencil was removed in order to expose the graphite rod. The current will flow through the graphite to reach the end of the pipet tip where the graphite is in contact with the electrolyte. The power supply can either be directly connected to the graphite rod with a crocodile clip or an electrical connector can be interconnected to avoid breaking the fragile graphite rod. As can be seen in Figure 2B, a 1 mL pipet tip was used to form the end of the electroplating pencil. First, the end of the pipet tip was cut to enlarge the opening to 3 mm. A cotton patch was inserted at the end of the tip and a 3 mm copper bead was used as the active electrode material; it was incorporated into the pencil by pushing it on the cotton with the tip of the pencil. This 3 mm metal bead can be replaced by any conductive material that prevents the electrolyte solution getting into direct contact with the pencil lead. Then, the pencil was inserted into the pipet tip and the length of the graphite rod was adjusted to be in electrical contact with the metal bead. Finally, 3 holes were created around the pipet tip, between the metal bead and the end of the pipet to allow draining the air when filling the pencil with electrolyte.

Battery-Powered EChemPen. A battery-powered EChemPen can also be easily fabricated. Even if using a power supply allows controlling the applied potential difference and thus to electrochemically modify the spoon surface, using a battery-powered EChemPen has the convenient benefit of being portable and more attractive to students as a wireless device. The wireless EChemPen is fabricated from a marker pen: the marker was first disassembled and the felt fabric was profusely rinsed to avoid the presence of any chemical. Then, a small toothpick with a wound copper wire was inserted as the writing tip and a cartridge was put over the toothpick as the electrolyte tank (see Figure 2B). Three button cells of 1.5 V were used in a serial configuration, one above the other, to give the desired potential difference (4.5 V). The positive side of the upper battery was connected to the gold surface by using a copper wire taped on its surface and the same procedure was used to connect the negative side of the lowest battery to the tip. This pen works like a real fountain pen where the electrolyte is provided automatically by the cartridge, and thus, it does not require reloading the tip by dipping during the writing process. A metal tip should not be used in order to avoid a short circuit between the tip and the surface.

HAZARDS

The students must wear protective glasses, gloves, and a lab coat at all times. They must avoid skin contact with solids and solutions and dispose of the solutions as instructed by their teacher. They must wash their hands before leaving the laboratory. To avoid electric risk they must wear gloves.

ELECTROPLATING OF COPPER

As a first example, we describe the local electroplating of copper onto a surface of stainless steel, in this case a spoon. This experiment is shown in Figure 3 and in video 1 (provided in Supporting Information). Here, the pencil-based EChemPen, filled with a solution of copper sulfate (0.5 M), was used. The copper spoon was connected to the power supply with a crocodile clip. The electrodeposition of copper will occur at the surface according to the following reaction:



Figure 3. Writing/erasing of copper letters on a spoon, for more information, check video 1 in Supporting Information. (A) writing with copper; (B) full text; (C) copper erasing.

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \quad (2)$$

To perform this reduction reaction, the surface has to act as a cathode and, thus, needs to be connected to the negative pole of the power supply. The EChemPen was connected to the positive pole and acted as an anode where the counter reaction, the oxidation of the copper bead (that was located inside the tip), occurred:

$$Cu^0 \rightarrow Cu^{2+} + 2e^- \quad (3)$$

A potential of 20 V was applied, which led to the local deposition of metal copper at the surface of the spoon where the tip of the EChemPen is located. This phenomenon was used for writing the word "NSYSA", as shown in Figure 3. This is a classical electrochemistry experiment where the negative electrode is the cathode and the positive electrode is the anode. The current flows through the electrolyte solution, which brings the tip into electrical contact with the surface.

After writing with metal copper, we showed that the copper writing can be easily erased just by inverting the polarity of the EChemPen. When the surface of the spoon is connected to the positive pole of the power supply, it becomes an anode, which triggers the dissolution of the copper according to reaction 3. On the contrary, the copper bead becomes a cathode and the previously dissolved copper ions have been deposited on the bead following reaction 2. This simple phenomenon can be used to erase the copper writing, as it can be seen in Figure 3 and video 1. Now that we have shown that the EChemPen can be used for writing on the negative pole by the cathodic reduction of a metal salt, we will show in the following that it can also be used for the anodic electrodeposition of a conducting polymer.

ELECTRODEPOSITION OF A CONDUCTING POLYMER

Electrodeposited conducting polymers (the main examples being polypyrrole, polyaniline, polythiophene, and poly(3,4-ethylenedioxythiophene)) are materials of strong interest in the domains of sensors,[11] actuators[12] and electrochromic devices.[13] As shown in Figure 4A, the electrodeposition of polypyrrole (PPy) proceeds through the oxidation of pyrrole. This generates a radical cation, which reacts with another radical cation to form oligomers. The solubility of the polymer decreases with its length and PPy ultimately precipitates at the surface.[14,15] The EChemPen is used here to generate this conducting polymer locally on gold. The gold surfaces can be

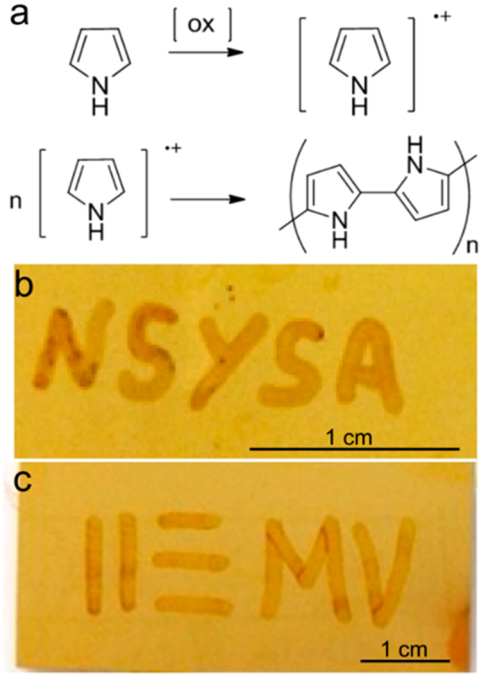


Figure 4. (A) Mechanism of electropolymerization. Electrodeposition of polypyrrole (B) using the EChemPen (toothpick configuration). (C) using the portable EChemPen.

used several times after cleaning with a tissue soaked with ethanol in order to remove the electrodeposited polymer. Nevertheless, the polymer can be formed at any other conductive surface that can undergo at least 1.5 V/NHE[16] without being damaged (i.e., platinum or carbon), which corresponds to the potential required for the oxidation of pyrrole to polypyrrole.

The experiments shown in Figure 4B were performed by using the simple toothpick configuration connected to a power supply, while the electropolymerization shown in Figure 4C was performed with the battery-powered portable configuration. The electropolymerization occurs at the gold anode, and the reduction of water (reaction 4) occurs as counter reaction at the copper-wire cathode.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (4)$$

Figure 4B shows the result of the electropolymerization using the toothpick configuration. A potential of 4 V was applied to write the word "NSYSA". The symbols shown in Figure 3C were written with the portable configuration using three button cells of 1.5 V each, which corresponds to a potential difference of 4.5 V in this case. These experiments show the simplicity of the two EChemPen configurations and that this concept can be used for the straightforward writing employing the electropolymerization of PPy. In the following, we introduce a last experiment that can be performed by students with the EChemPen.

ANODIZATION OF TITANIUM

Anodization is an electrochemical process where an oxide layer is formed on a metal surface. The anodization of titanium is an electrochemical technique of first interest, and since it is applied in various industrial processes, it is also of strong interest in current scientific research.[17,18] Furthermore, applying anodization to the EChemPen enables us to visualize the effect of the potential difference applied during the electrochemical experiment. Indeed, the applied potential controls the thickness of the created titanium oxide layer, which is linked to the color of the anodized area. Thus, the color of the formed titanium oxide layer can be directly controlled by the applied potential.[19,20]

In these experiments, titanium was locally anodized for the creation of a colored writing. An acid solution (H_2SO_4 at 0.5 M) was used as electrolyte without any soluble precursor, which suppresses the competing deposition reaction. The acid solution only serves as electrolyte and ensures sufficient ionic conduction between the pen and the surface. The titanium itself was oxidized to titanium oxide according to the following reaction:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (5)$$

The anodization of titanium is a process that is used in the production of jewelry to obtain surfaces with different colors.[8] With the use of the toothpick-based EChemPen, the five different potentials 20, 30, 40, 50, and 60 V were applied using the power supply. As shown in Figure 5, these potentials gave titanium layers of the colors brown, purple, blue, light blue, and yellow, respectively.

The anodization of titanium generates a thin film of TiO_2. The thickness of this film is typically in the order of tens to hundreds of nanometers and depends on the applied potential. In these nanoscale films, light that reflects from both the top and the bottom surface of the TiO_2 film can constructively or destructively interfere to produce different colors.

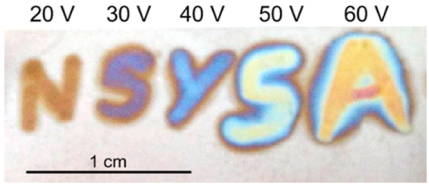


Figure 5. Titanium oxidation using the EChemPen.

STUDENT RESULTS

The toothpick EChemPen was used by the students to perform copper deposition on metallic spoon. The students completed the experiment in 1 h. They found difficult the step where the copper wire is put around the toothpick because the wire should not be too long to avoid direct contact with the surface, but it still needs to be close to the end of the toothpick. Some of them were surprised by the bubbles that appear during the writing process. The bubbles came from water reduction. If the writing is too long, the EChemPen will stop working if it is not refilled. Others students were afraid by the increase in the temperature at the end of the toothpick, and possibly on the spoon (because of the Joule effect) that could appear if the writing is too long. When writing with the copper solution, the letters may not appear like usual nice orange-red color of metallic copper but darker. It is because copper oxide can also be formed. As a general impression, the students found the experiment funny and interesting. Thanks to this experiment, concepts such as oxidation and reduction reaction that seemed difficult to assimilate previously became easy to learn. They understood the role played by the anode, cathode, and the polarity of the electrodes in different electrochemical reactions.

CONCLUSION

In summary, we presented the EChemPen, a simple device that can be built by students to write electrochemically. The three proposed laboratory experiments based on the electroplating of copper, the electropolymerization of pyrrole, and the anodization of titanium introduce electrochemistry to students in a new attractive way. Students can manufacture their EChemPen themselves and compare their results. The experiments produce results that are directly visualized and that can be tuned by changing simple parameters such as the polarity and the potential value. We believe that the EChemPen presents an educationally very stimulating mean for teaching students different concepts of electrochemical reactions. Furthermore, these experiments are very well suitable for a surface modification course, including analytical chemistry or instrumental analysis, and could also be adapted for classroom demonstrations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00149.

Instructor notes (PDF, DOCX)
Student handouts (PDF, DOCX)
Screenshots of video (PDF)
Video showing the use of the EChemPen to write on a spoon (AVI)

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Notes

The authors declare no competing financial interest.

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Instructor notes

We recommend to use the electrochemical pen as a supplementary exercise to complete a classic experiment when electroplating is studied.

This experiment can be made by two students in one hour.

On Figure 1 we detailed the fabrication of the electrochemical pen using the tooth pick. The copper wire is wind around the tooth pick then a heat shrinkable tube (or a scotch tape) is used to fix the copper wire to the tooth pick and to avoid direct contact between the experimenter and the tooth pick to prevent counters shock.

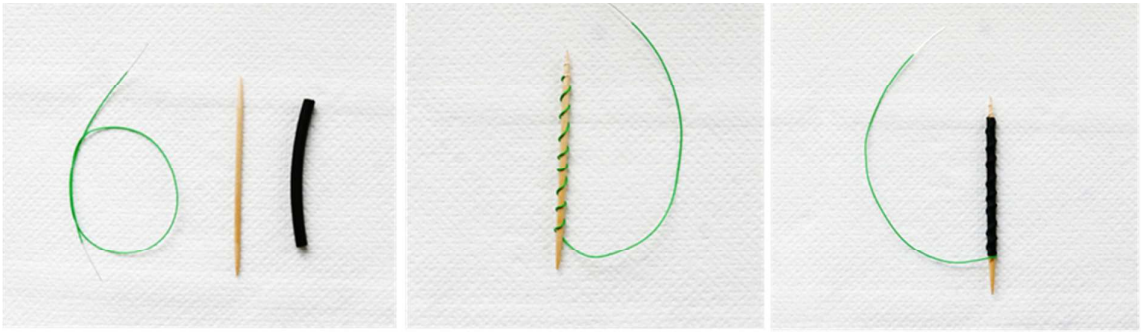


Figure 1 : The three components used to manufacture the electrochemical pen. The copper wire, the tooth pick and the heat shrinkable tube.

Because two electrolytic solutions are used to write, the students need to build two pens in order to avoid contamination of the second solution by the first one.

Bubbles and increasing of temperature can happen during writing. The bubbles are H_2 and O_2 produced by water reduction and oxidation respectively. When writing with the copper solution the letter may not appear like usual nice orange-red color of metallic copper but darker. It is because copper oxide can also be formed. Indeed, water electrosplitting reactions also induce local pH changes in the solution. But to simplify the problem, and the equations for the Cu^{2+} reduction teachers should speak only about metallic copper. The oxidation reaction is water oxidation and also oxidation of the copper wire.

To remove the writing using the electrochemical pen you just need to inverse the polarity. Indeed if now the spoon is connected to the positive borne oxidation reaction will happen on the spoon by consequence Cu and Zn can be oxidized in Cu^{2+} and Zn^{2+} respectively.

On Figure 2 we described the fabrication of the battery-powered electrochemical pen. The batteries (LR44) are put one above the other inside the corps on the pen. A scotch tape is used to fix the copper wires on the first and on the last battery.

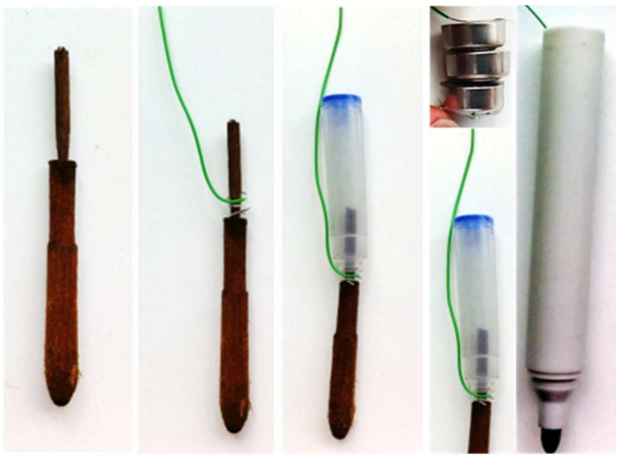


Figure 2 : Battery-powered electrochemical pen

The Titanium foil used was purchased from Alfa-Aesar, the thickness was 250 µm. Before used titanium was rinsed successively in ethanol, acetone and distilled water.

Introduction to electrochemical reaction with the electrochemical Pen

Safety Considerations:

Wear protective glasses, gloves and a lab coat at all times. Avoid skin contact with solids and solutions. Dispose of the solutions as instructed by your teacher. Wash your hands before leaving the laboratory.

To avoid electric risk never work without gloves.

Introduction:

Chemical reactions where electrons are transferred from one reactant to another are called redox reactions or oxido-reduction reactions. A redox reaction can be decomposed in two half-reaction, the oxidation and the reduction. During the oxidation a species will lose one or more electrons whereas during the reduction a species will gain one or more electrons. Electrochemistry allows driving non spontaneous redox reactions using electricity.

An example of reduction reaction is the formation of a metal from the corresponding ions.

$M^{z+} + ze^- \rightarrow M$

An example of oxidation reaction is the dissolution of a metal

$M \rightarrow M^{z+} + ze^-$

Purpose:

You will write your initials, on the metallic object provides by your teacher (spoon, key…) by using the method of electroplating. Each initial should be made of a different metal. At the end of the experiment you must find a method to remove your initial using electrochemistry.

Materials and Equipment:

-toothpick

-copper wires

-Copper sulfate

-Zinc sulfate

-9 V battery (or power supply)

-50 mL beaker

-insulated wire leads with crocodile clips at both ends

-insulated copper wire

-wire stripper

-Heat shrinkable tubes (not essential) can be replace by a simple scotch tap

-Heat Gun (not essential)

Procedure:

1. Manufacturing of the electrochemical pen.

Cut 30 cm of the insulated copper wire. At both ends remove 1 cm of the insulated layer, roll up the copper wire around the tooth pick by letting 0.5 cm between the end of the copper wire and the end of the tooth pick. During the experiment the copper wire must not touch the surface of the spoon. Put a heat shrinkable tubes around the tooth pick and the copper wire and use the heat gun to stick together the tooth pick and the copper wire, see figure 1 for the final electrochemical pen. Prepare two electrochemical pens, one for each solution.

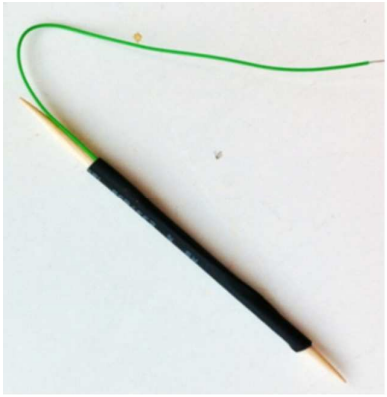


Figure 1 : Toothpick-based electrochemical pen

2. Electrolytic solution preparation.

Prepare 20 mL of 0.5 M $CuSO_4$ and 20 mL of 0.5 M $ZnSO_4$ into two 50 mL beakers with distilled water.

3. Local electroplating

Use the wire with the crocodile clip to connect the negative side of the battery (or power supply) to the spoon, and another wire to connect the positive one to the electrochemical pen.

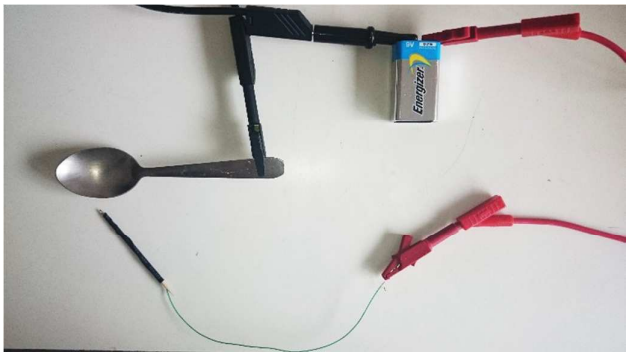


Figure 2 : spoon and electrochemical pen connected to a battery.

Immersed the toothpick in the desired solution, then write slowly on the spoon. A thin film of solution must connect the end of the toothpick to the end of the copper wire. Refill the solution as needed.

4. Propose a method to remove your writing.

Questions and Conclusions.

1. During metal deposition, which electrode (the spoon or the electrochemical pen) is the cathode? Explain your answer.

2. Write the half-reaction that occurs at the cathode? Is it an oxidation or a reduction?

3. Write the half-reaction that occurs at the anode? Is it an oxidation or a reduction? (Oxygen is produced)

4. Explain why is it possible to remove your writing?

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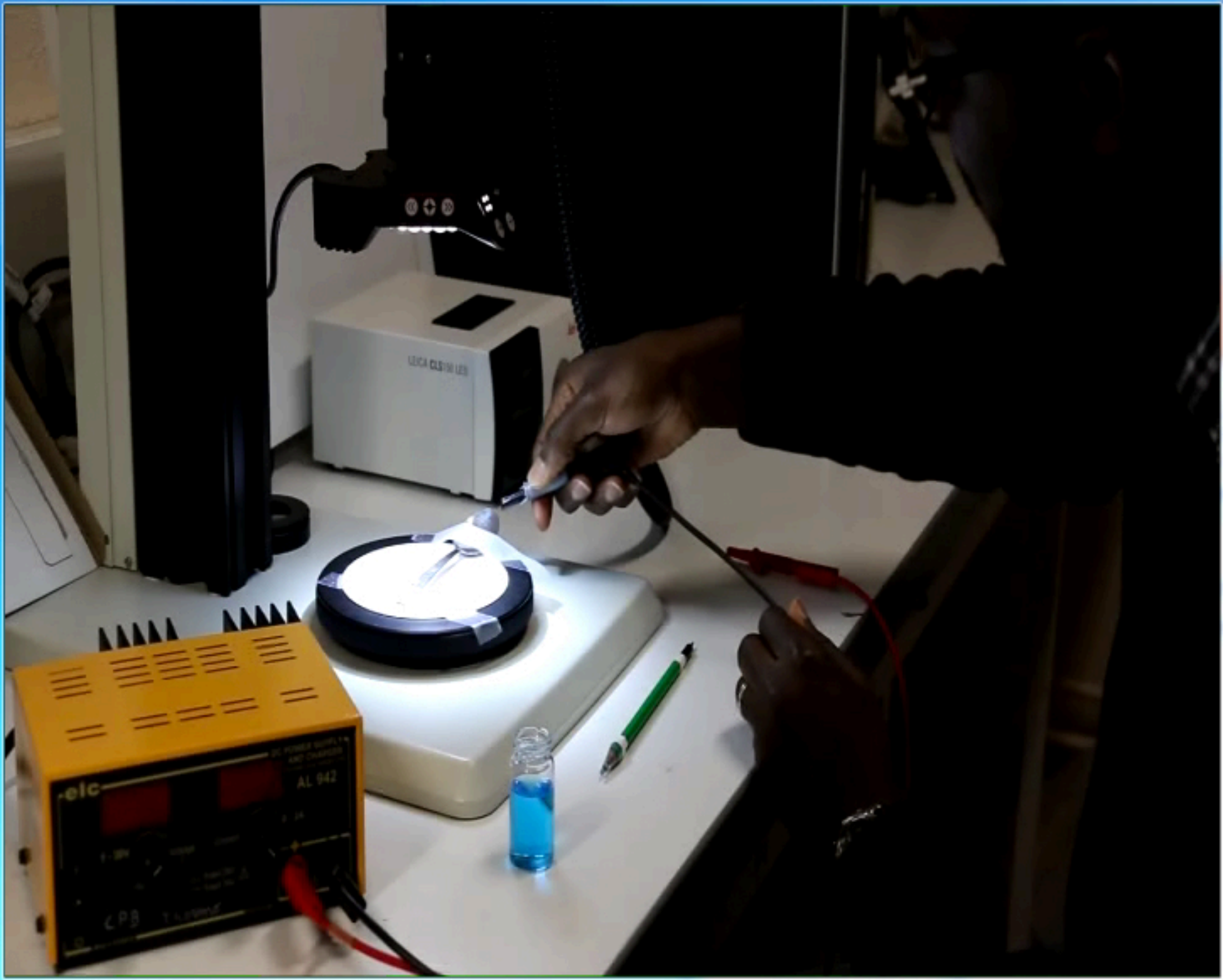
EChemPen

"Writing with copper on metal"

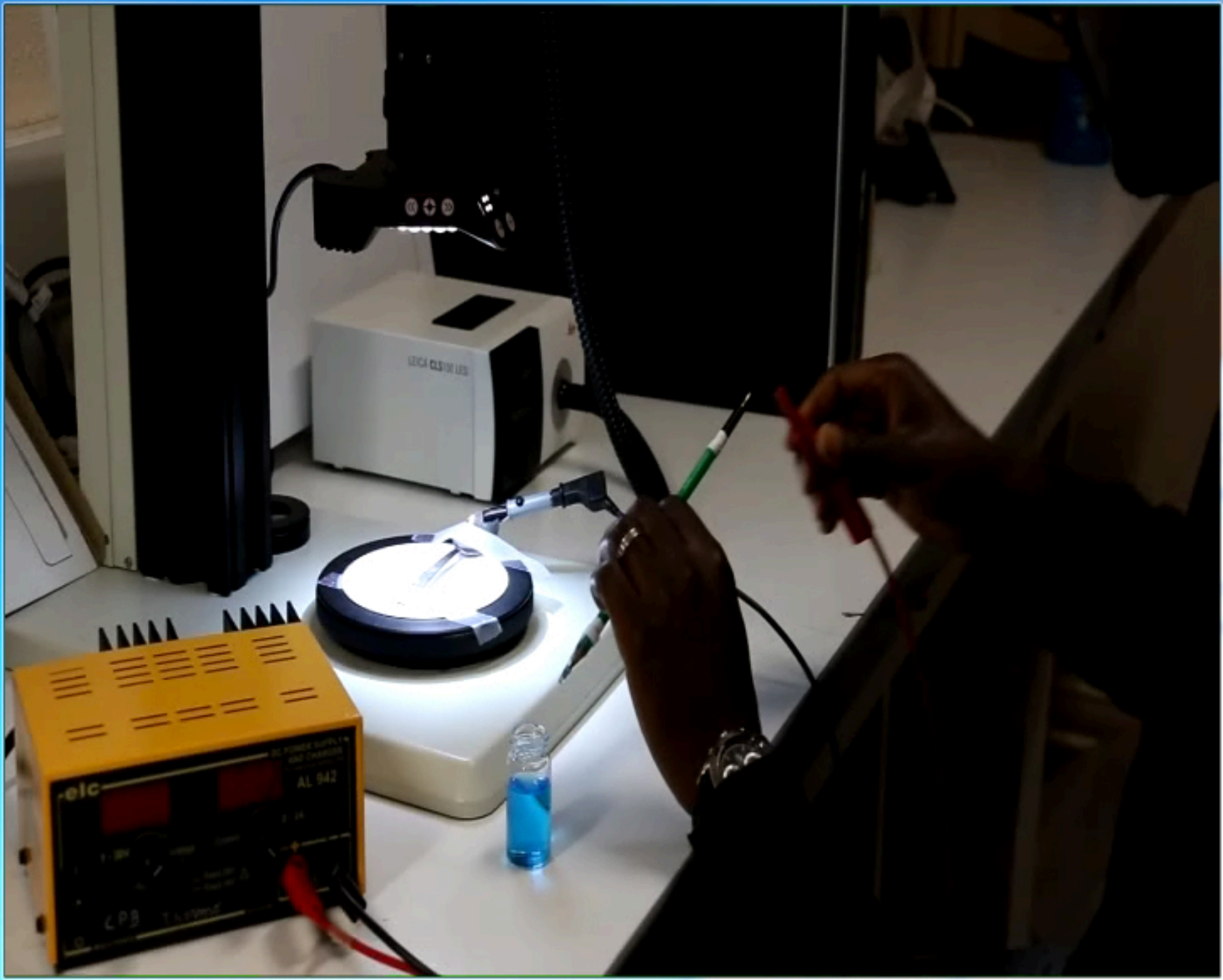
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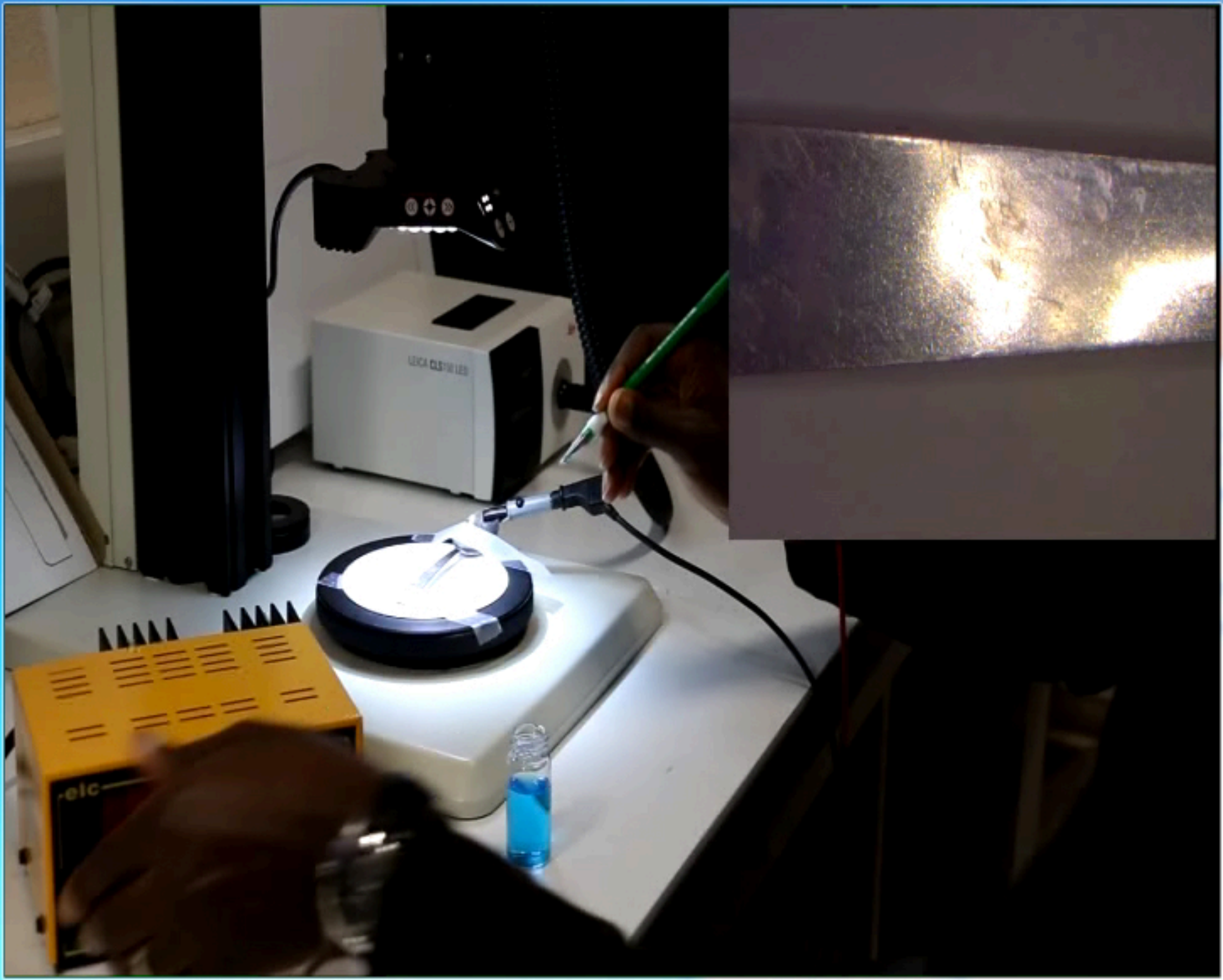
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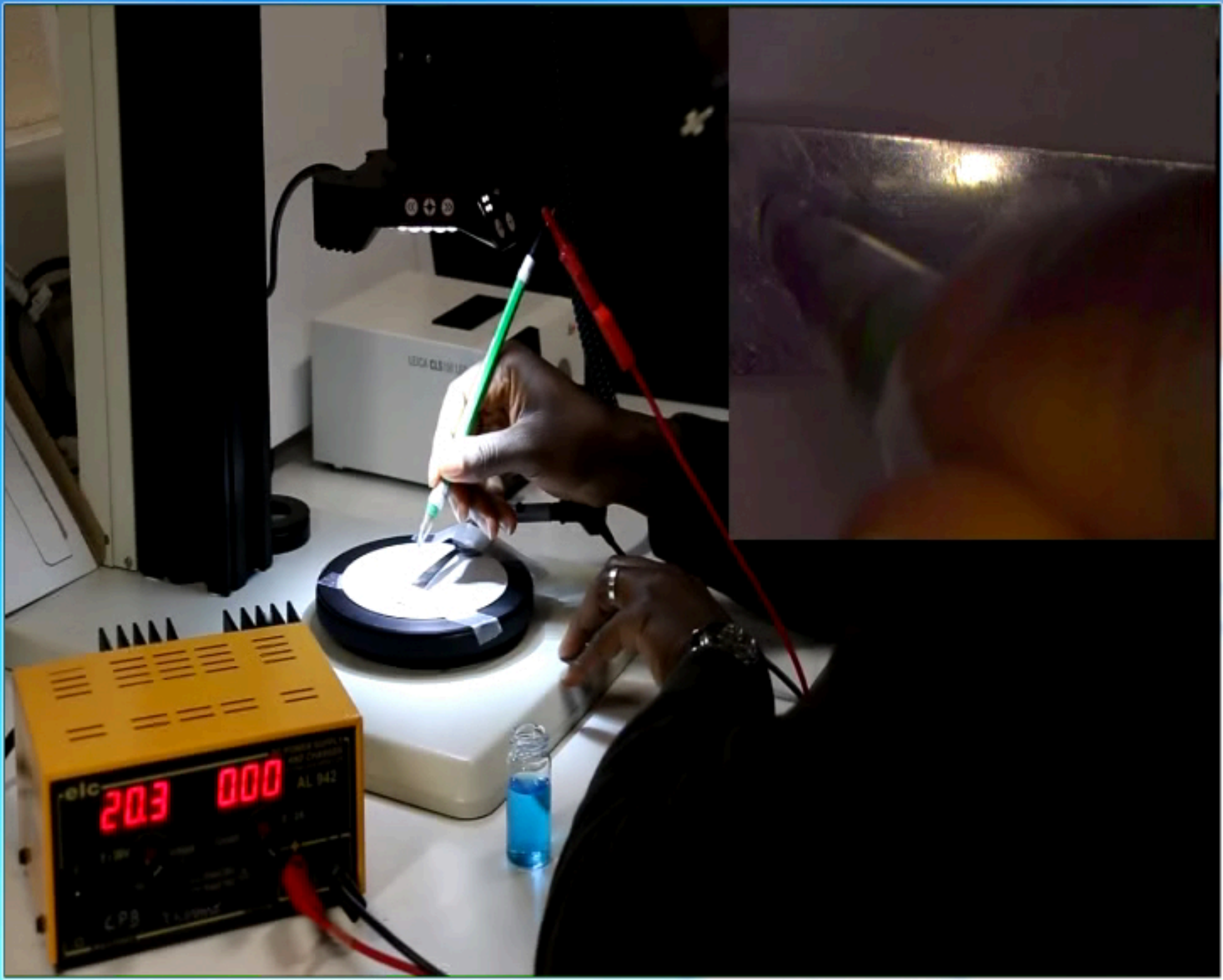
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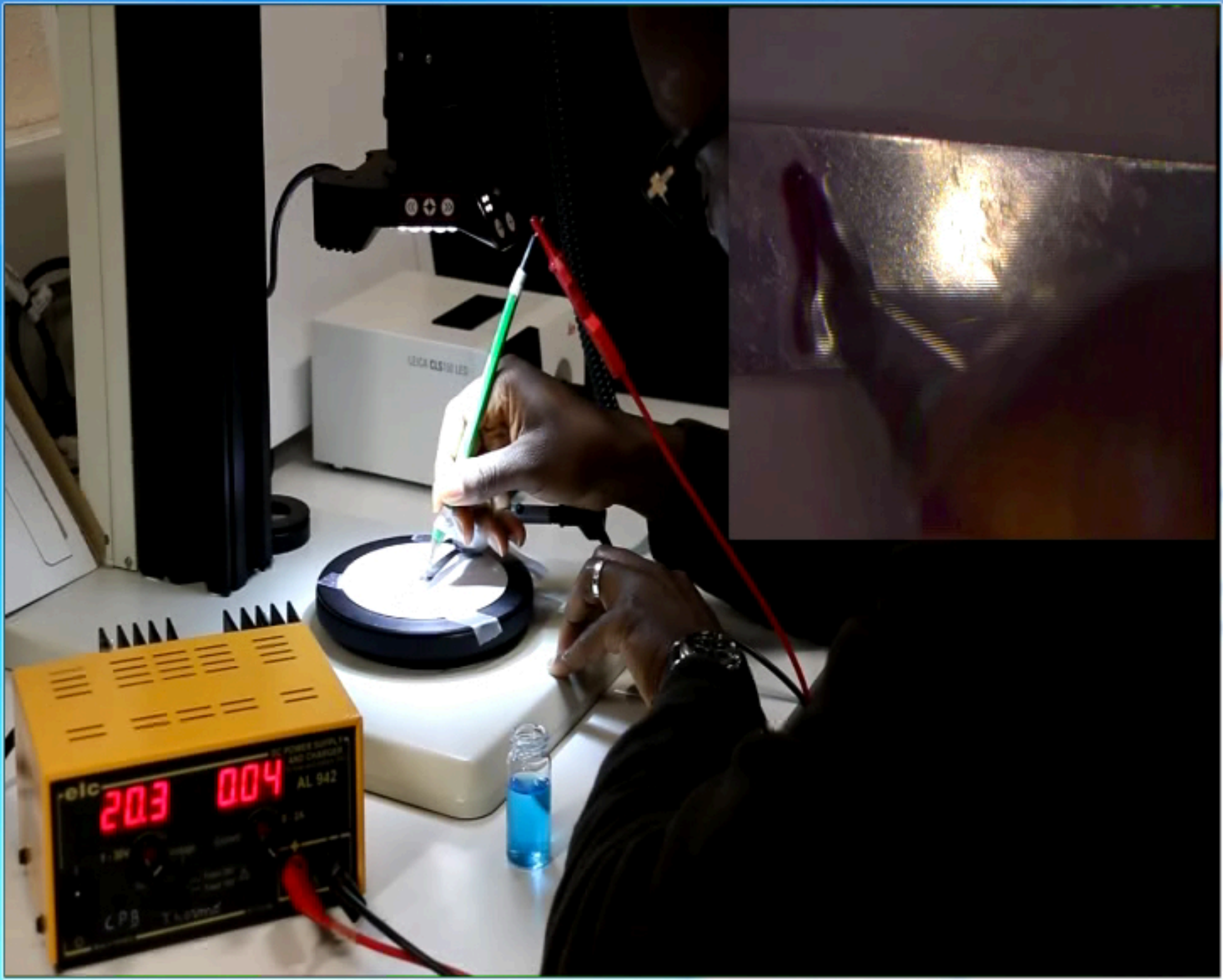

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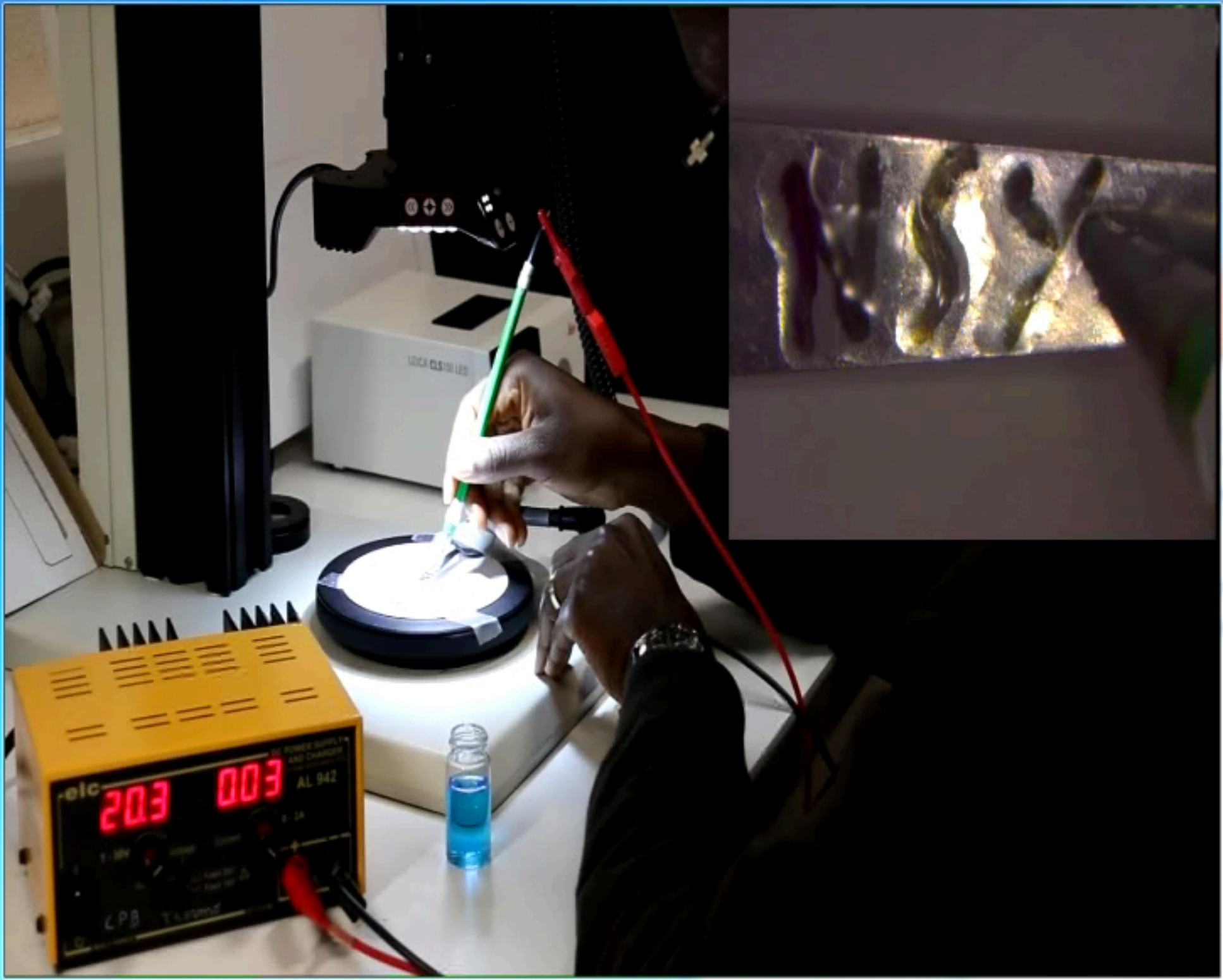

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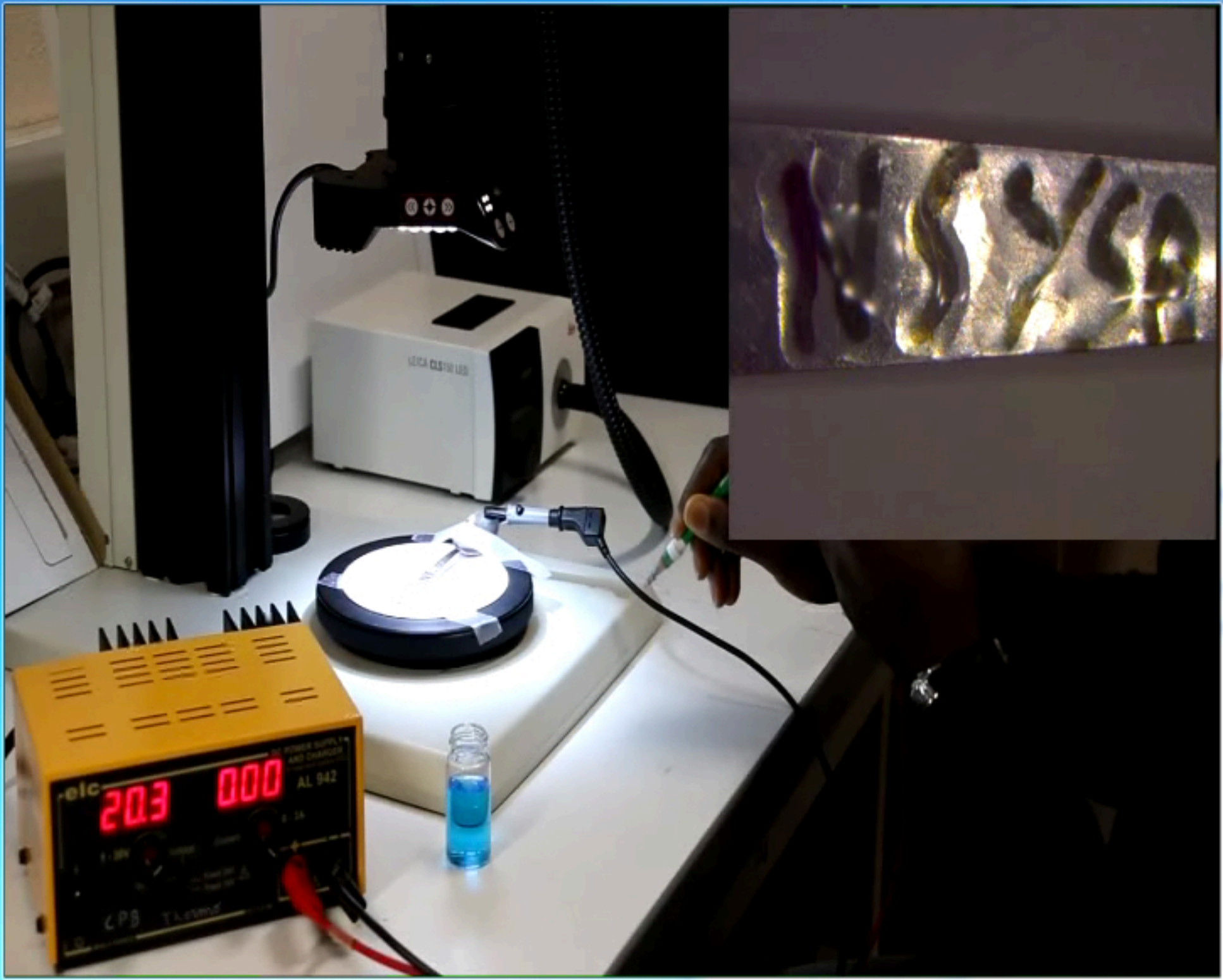

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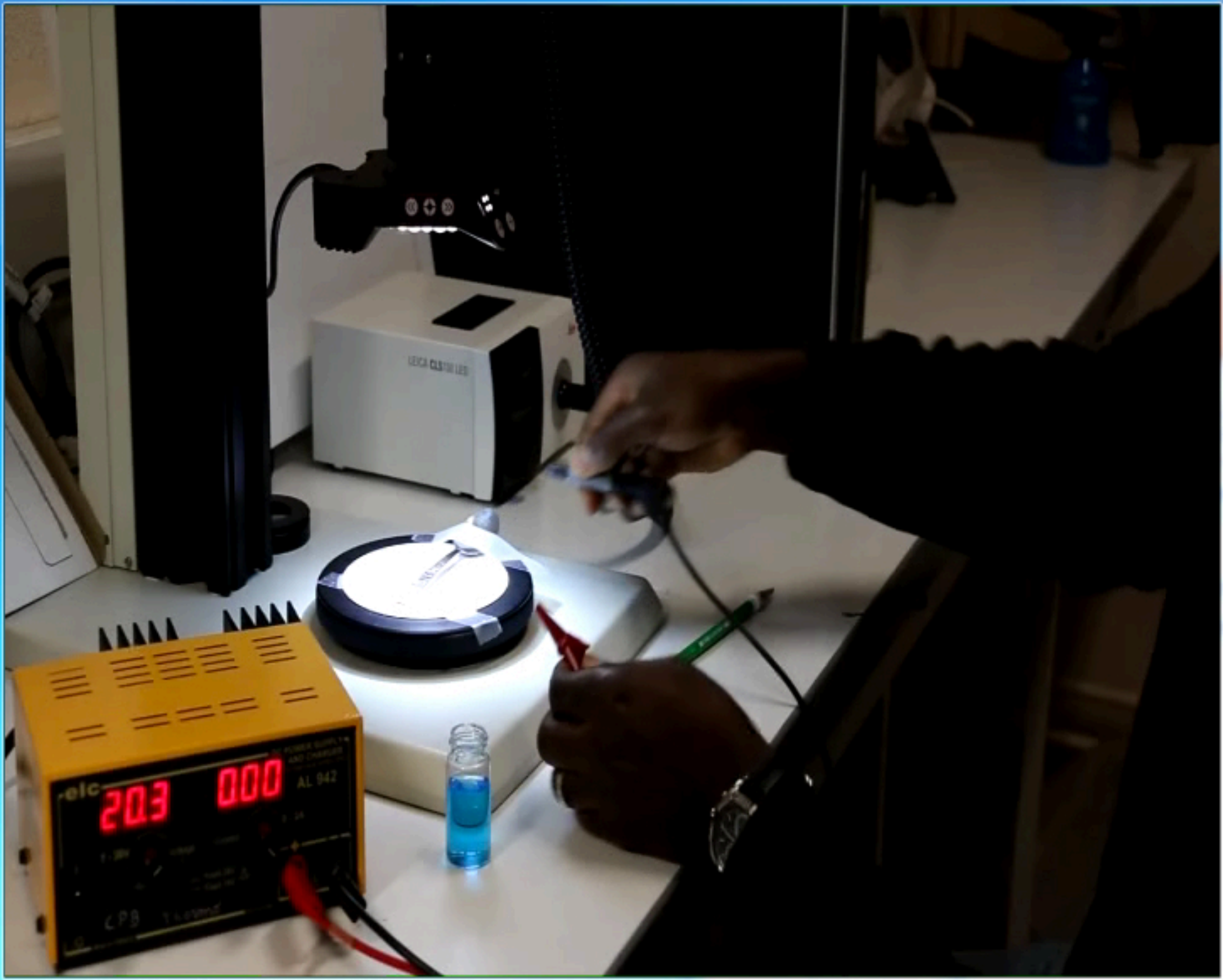

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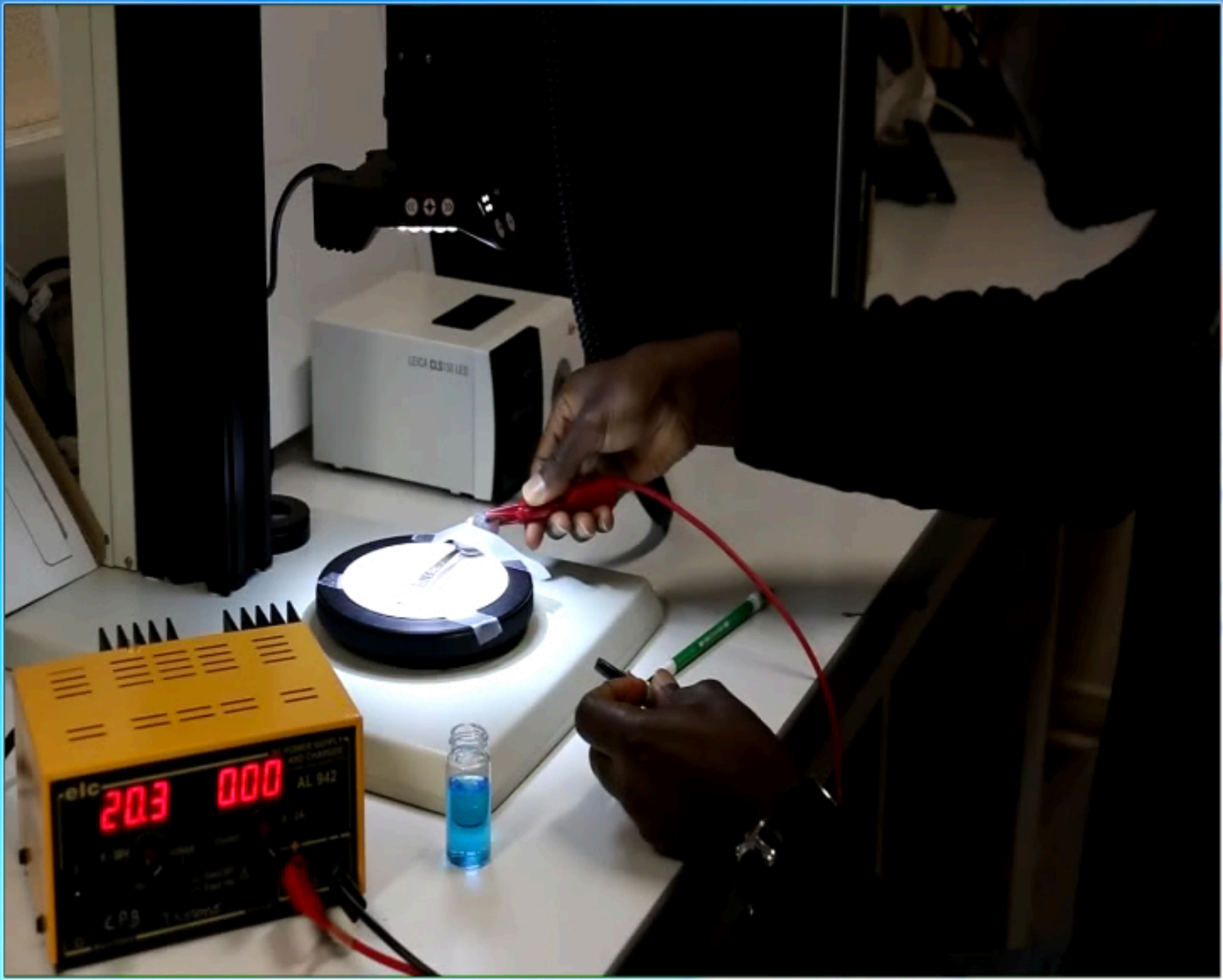

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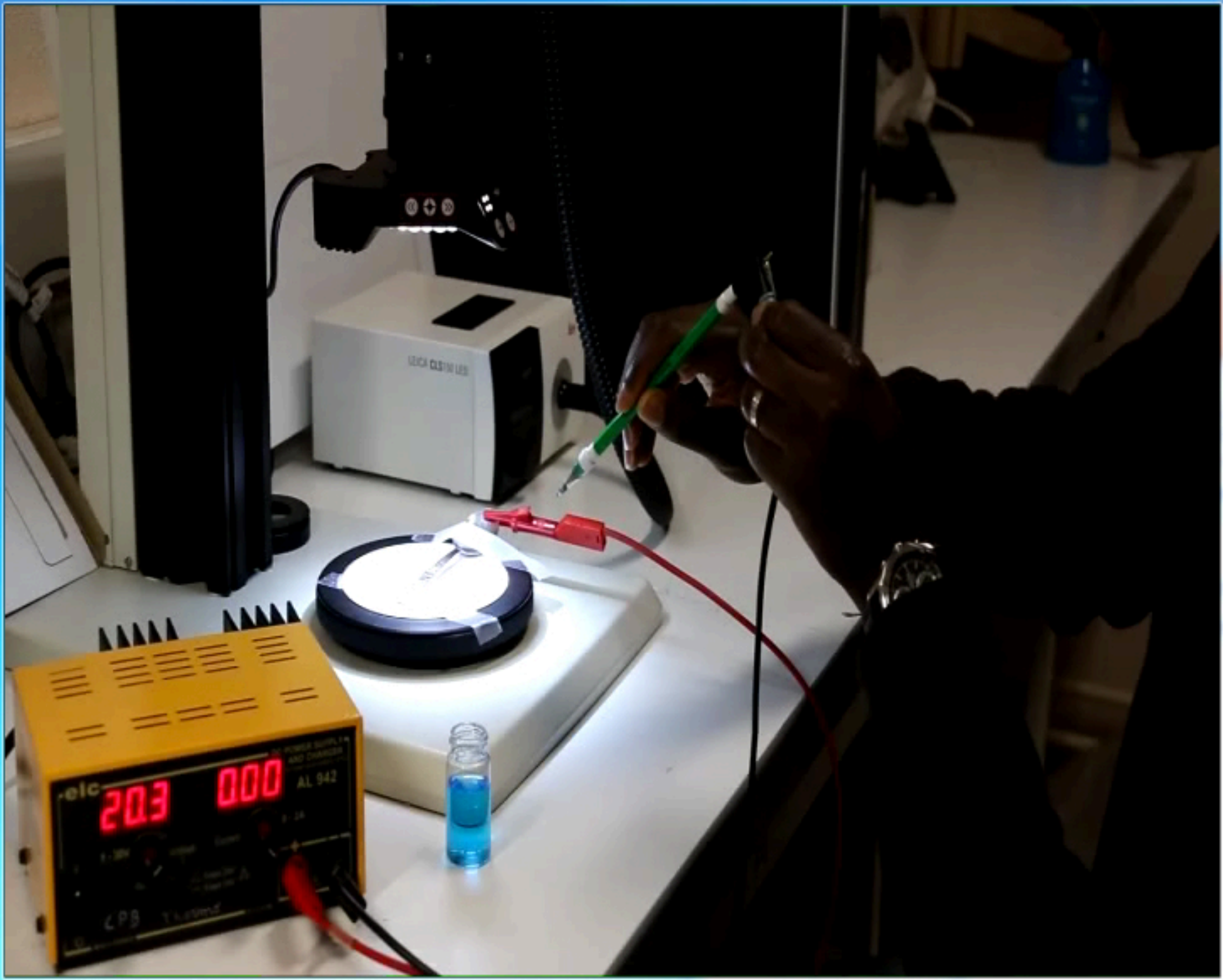

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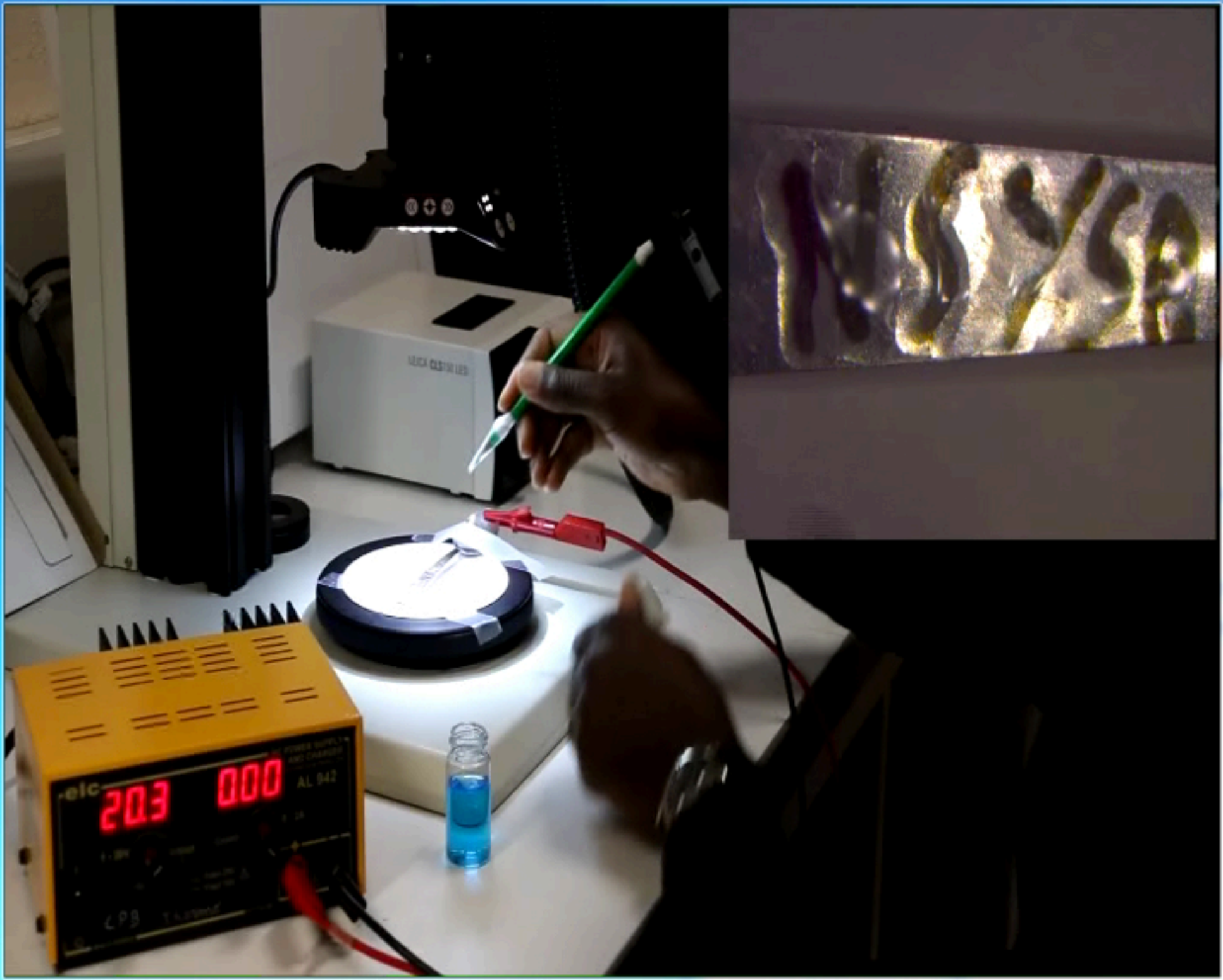

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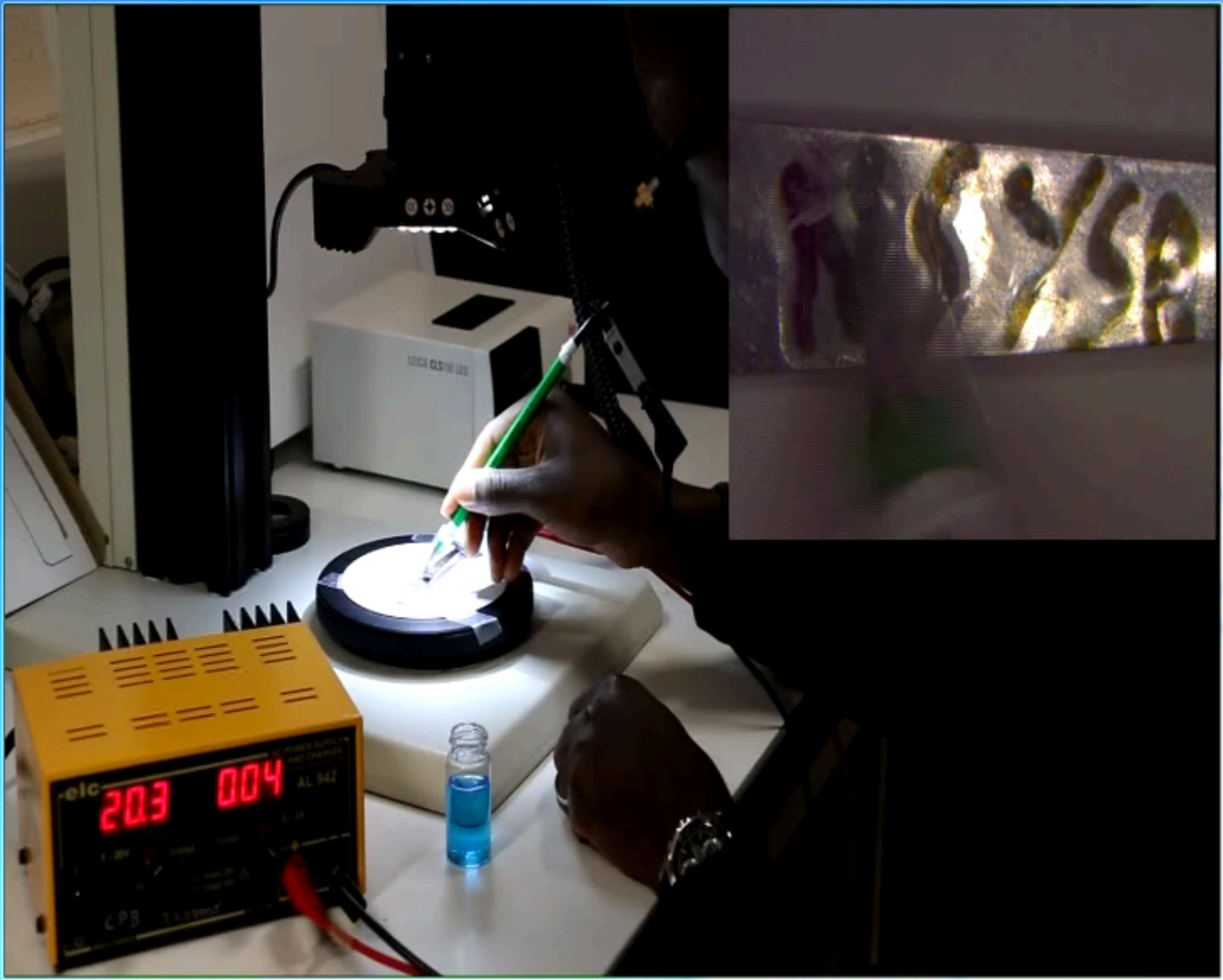

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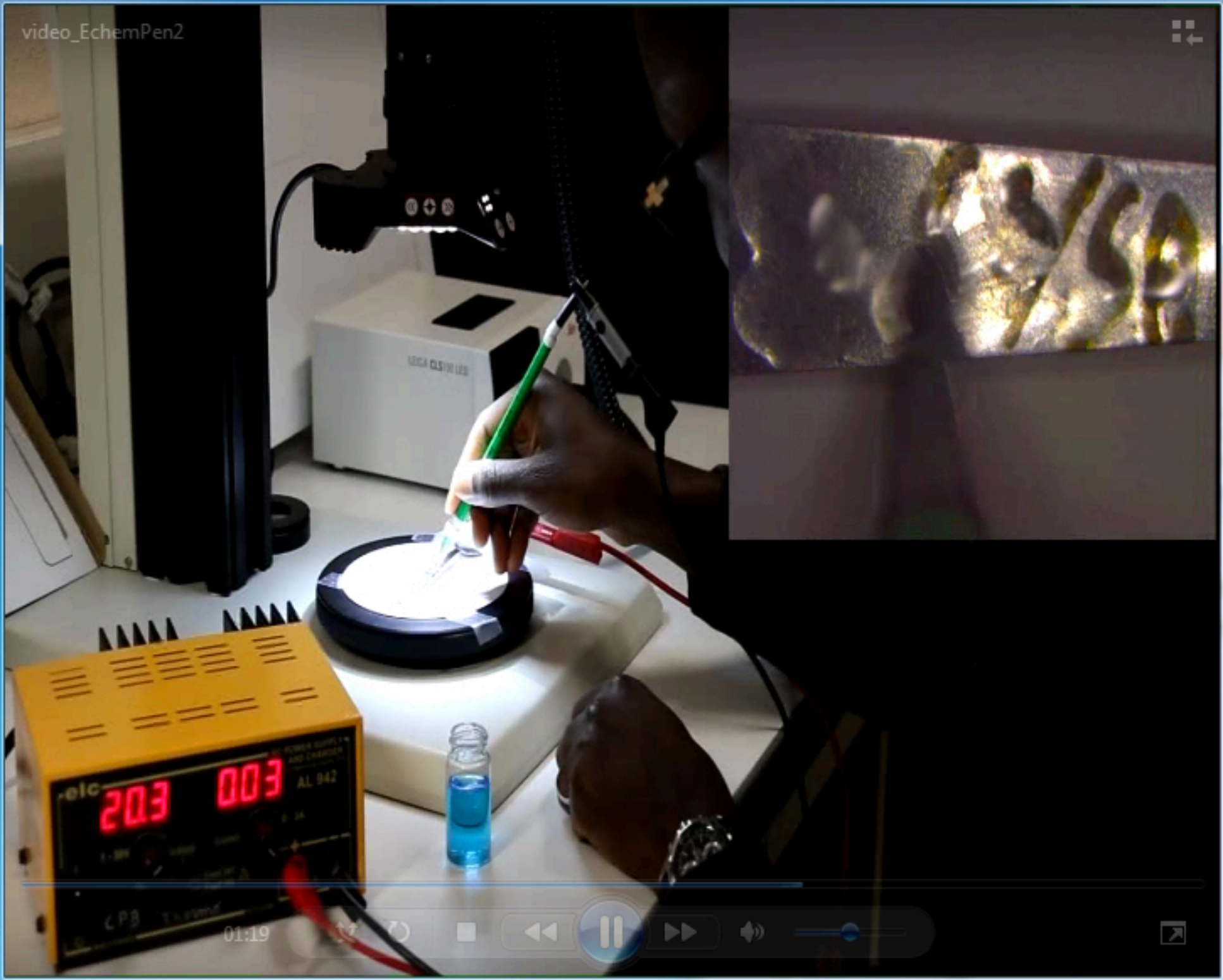

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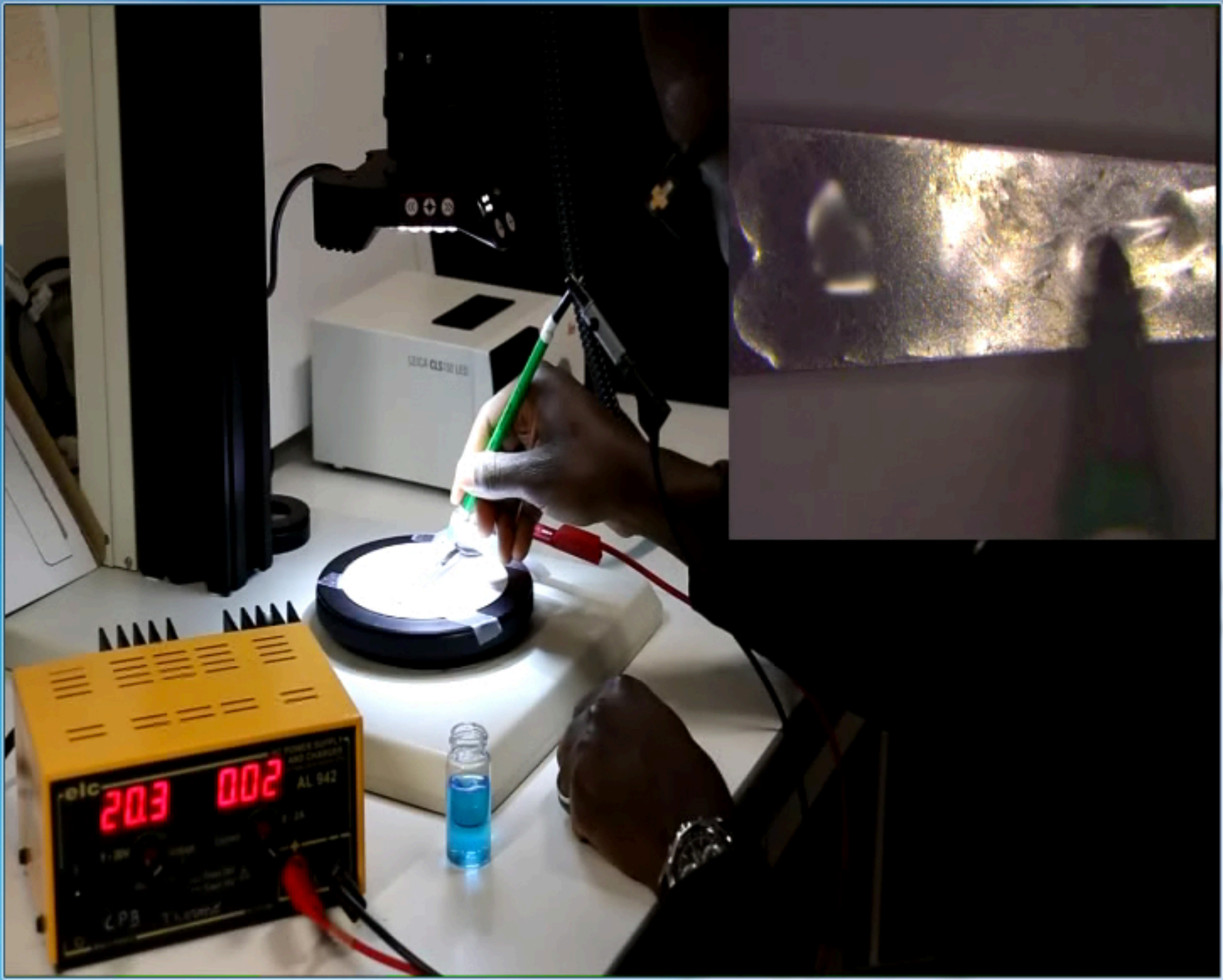

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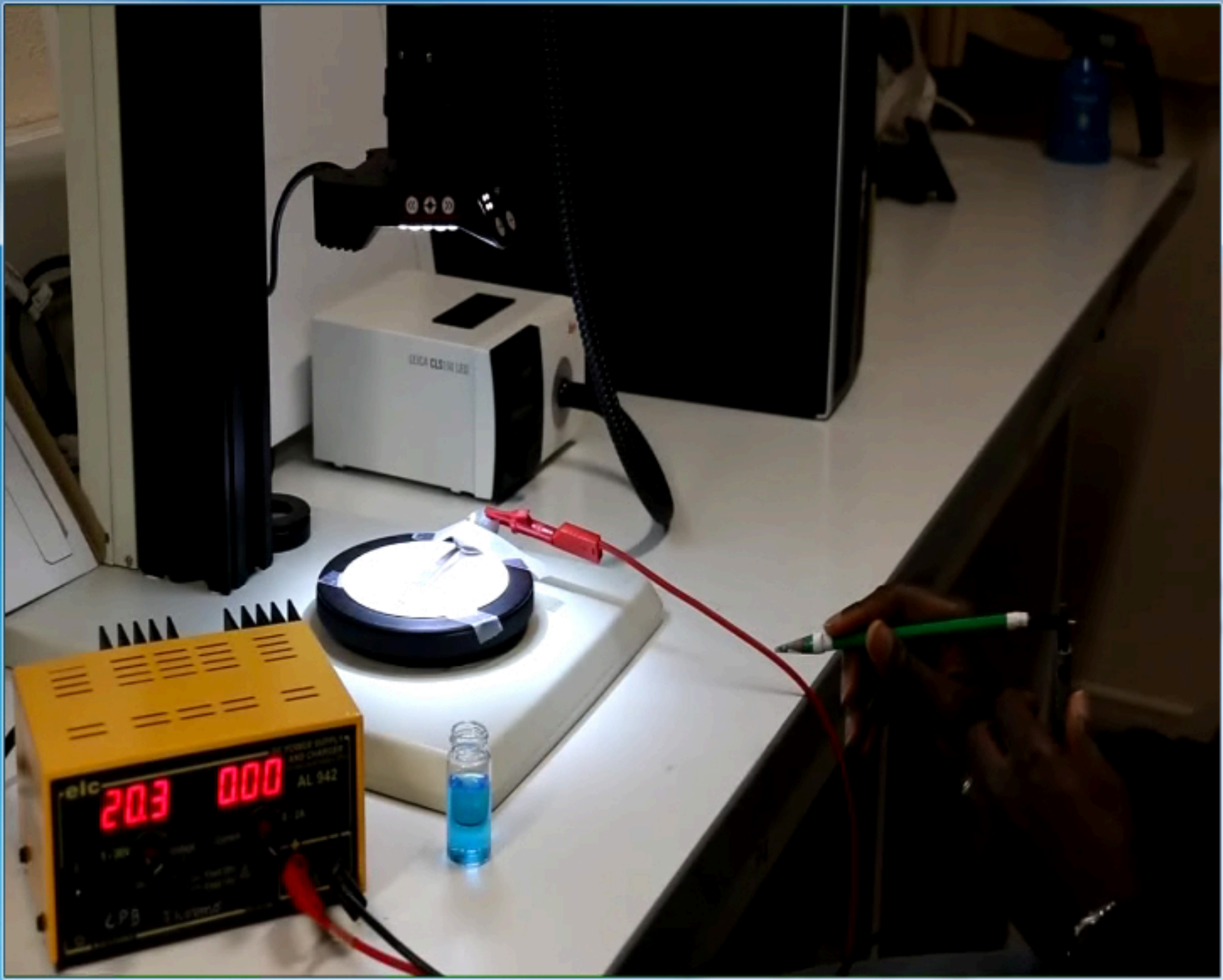

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