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Laboratory Experiment

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Experimenting with a Visible Copper–Aluminum Displacement Reaction in Agar Gel and Observing Copper Crystal Growth Patterns To Engage Student Interest and Inquiry

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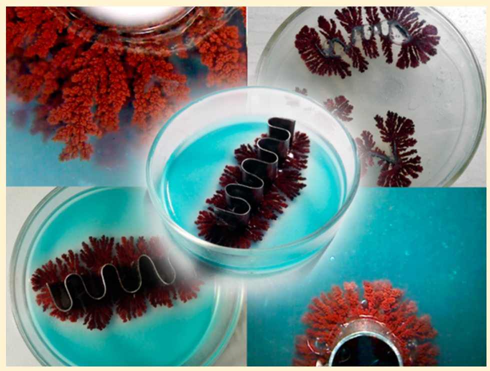
Supporting Information

ABSTRACT: The reaction process of copper–aluminum displacement in agar gel was observed at the microscopic level with a stereomicroscope; pine-like branches of copper crystals growing from aluminum surface into gel at a constant rate were observed. Students were asked to make hypotheses on the pattern formation and design new research approaches to prove their hypotheses. Results of the experiments designed by students well proved the existence of microcells in reaction system, which caused continuous growth of copper branches. The whole experimental teaching process motivated students by stimulating their interest and enthusiasm.



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The copper–aluminum displacement reaction is often used as a classic example of simple redox reaction and illustrates the electrochemical series of metals. In laboratory textbooks, this reaction is used to determine the empirical formula of $CuCl_2$.[1] The kinetic behaviors of the aluminum corrosion process[2] can also be studied through the reaction between Cu^{2+} ions and Al metal. In the experiment, aqueous Cu^{2+} reacts with Al foil. The simplified net ion equation of the reaction is

$$2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu \quad (1)$$

However, the actual reaction process of Cu–Al displacement is more complex.[3−5] Generally, a strongly adhering film of oxide (Al_2O_3) is formed on aluminum surface upon exposure to air, nitric acid, or water. The oxide layer on Al surface renders the Al metal passive but is destroyed by aggressive anions (especially halide ions) in the reaction solution. After the impervious oxide film is removed, the Al metal reacts rapidly with Cu^{2+} ions. When copper sediments deposit on Al sheet, the vigorous releasing of hydrogen bubbles from the aluminum surface can be observed simultaneously because Al metal is of sufficient chemical activity to reduce water, and the pH of copper solutions is usually below 4. This side-reaction disturbs the solution seriously and interrupts the continuous growth of copper crystals. Even the deposition of copper on Al is somehow difficult to observe during the reaction process because the aluminum surface is almost covered with H_2 bubbles. Only after at least one of the reactants is exhausted does the reaction solution become "calm and flat", and then students can observe the change of Al foil and measure the weight of copper sediments. Therefore, it is difficult for students to perceive what is going on during the Cu–Al displacement at the microscopic level. Although the reaction schematics can help students imagine what is happening, some abstract conceptions cannot be understood by macroscopic observation only such as the formation of microcells on metal surfaces during the corrosion process.

It is worthwhile to improve students' learning experience if they can visually observe in detail the interaction between copper ions and aluminum metal, and the growth of copper crystals from the aluminum surface. Therefore, in this experiment, Cu–Al displacement reaction is performed in an agar gel. Agar gel is used as the reaction medium for three reasons: (i) in comparison with the time-consuming preparation of silica or polymer gels, agar gel can be prepared conveniently in a very short time; (ii) agar gel is firm enough to resist the disturbance from H_2 bubbles; thus, copper crystals can grow uninterruptedly in the

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gel; and (iii) agar gel is nearly transparent for observation. As a result, the deposition of copper, the growth pattern of Cu crystals, and the formation of Cu−Al microcells can be observed and verified in slow motion intuitively. The reaction process can be recorded by digital microscope or by students' smartphone cameras. This experiment lasts about 1.5−3 h and helps students understand what is happening in Cu−Al displacement reaction at the microscopic level.

■ EXPERIMENTS

Chemicals

The reagents in analytical reagent grade, for example, $CuSO_4\cdot 5H_2O$, $CuCl_2$, NaCl, aluminum sheet, and dry agar, were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Commercial epoxy resin was used to coat the edges of aluminum strip.

Apparatus

A stereomicroscope equipped with a video dual CCD camera is preferred for this experiment; however, the reaction process can also be recorded with a smartphone camera or even seen with the naked eye.

Procedure

About 2 g of dry agar was added into 100 g of water and heated above 90 °C. After the agar was dissolved thoroughly, an appropriate amount of salts, for example, 11.2 g of $CuSO_4\cdot 5H_2O$/0.9 g of $CuCl_2$ or 12.5 g of $CuSO_4\cdot 5H_2O$/0.6 g of NaCl, was added into the solution while stirring. The solution thus formed was gently poured into several Petri dishes, each with a thickness of about 3−5 mm. The temperature would drop quickly, and the gel would start to set as soon as it got below 45 °C. A 2 wt % agar gel containing 0.5 M Cu^{2+} and 0.1 M Cl^- was suitable for a moderate reaction rate.

The aluminum sheet was shaped into a wave-like strip (see Figure 1). This design caused the releasing of H_2 to occur mainly in the concave areas, which would not disturb the growth of copper crystals on the convex surface along the strip. Other forms of aluminum sheets could also be used, although there might be some difficulties for observation. The edges of aluminum strip were coated with an epoxy resin to prevent reaction on those highly active sites. The aluminum strip was inserted vertically into the gel, and the subsequent reaction could be observed with a digital stereomicroscope or smartphone camera. The procedure is shown schematically in Figure 1; detailed steps are described in the Supporting Information.

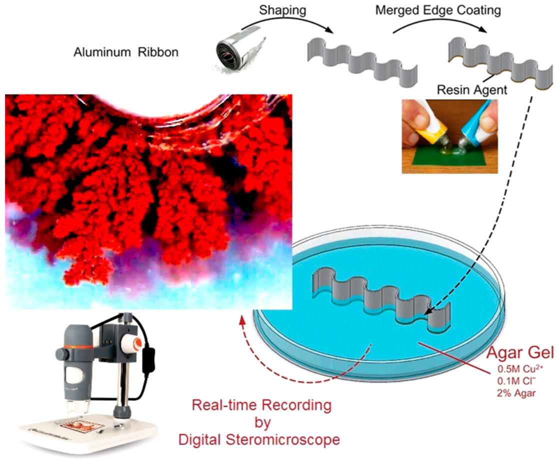

Figure 1. Schematic procedure of Cu−Al displacement reaction in agar gel.

■ HAZARDS

Copper salts, whether in a solid state or in solution, have acute toxicity on oral and dermal tissues and can cause skin and eye irritation. Copper chloride has specific target organ toxicity and may cause respiratory irritation. It is necessary to avoid breathing dust, fumes, mist, vapors, or spray of copper sulfate or copper chloride. Procedures for safe handling include wearing protective gloves, protective clothing, and eye protection and washing hands thoroughly after handling. Recent material safety data sheets (MSDS) should be reviewed. All used chemicals must be collected in labeled waste containers and be disposed of according to local regulations.

■ RESULTS AND PEDAGOGY

The Cu−Al displacement reaction can be observed visually. However, more details of the reaction process can be obtained from the images that are suitably magnified by a digital camera fitted with a stereomicroscope. The continuous growth of copper crystals from the aluminum surface into the surrounding agar gel is shown in Figure 2, which is captured by a stereomicroscope with 100× zoom. It can be seen from the first four images that the color of the gel around the Al strip obviously fades away, which indicates the consumption of Cu^{2+} ions. Copper crystals deposit on the Al surface in 1 min and gradually grow into the gel to form separate copper trees with pine-like branches. The length of copper trees increases to above 15 mm in 50 min. Dynamic growth of copper trees can be viewed in videos (with 10× playback rate) in the Supporting Information.

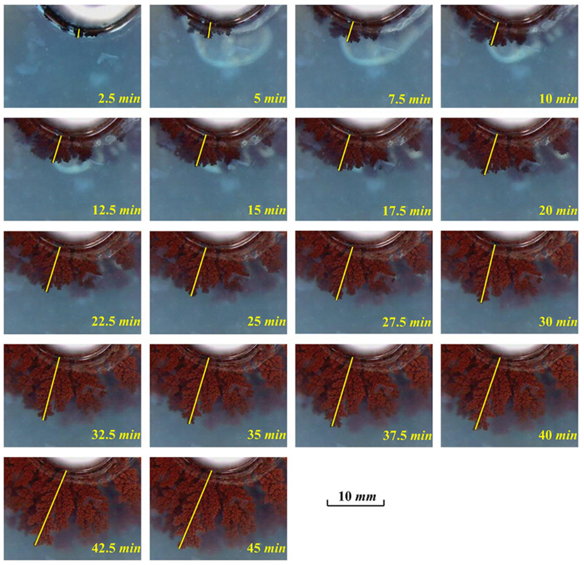

Figure 2. Continuous growth of Cu crystals from Al surface into agar gel. (The yellow line in each image indicates the length of an individual copper crystal branch.)

After recording the reaction process, students are required to measure the lengths of copper trees in various screenshots, which are shown as the yellow lines in Figure 2. The length, L, of an individual copper crystal branch versus the reaction time, t, is plotted in Figure 3. By a nonlinear fitting method, the relationship between L and t is given by

$$L = 0.303t + 1.426(1 - e^{-0.387t}) \quad (2)$$

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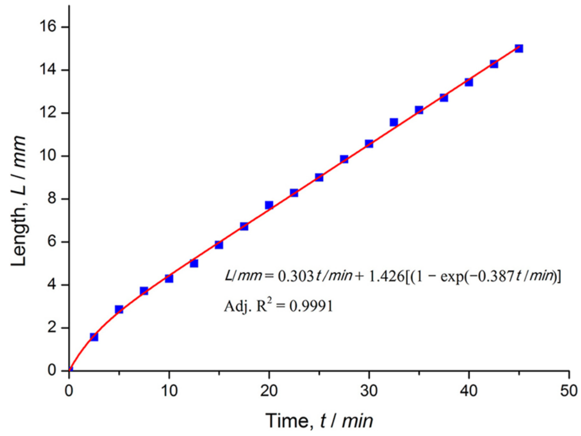

Figure 3. Plot of the length of an individual copper crystal branch with the reaction time.

where the unit of L is mm and min for t. In general, the rate of copper deposition will decrease as the concentration of Cu^{2+} ions drops during the reaction. However, eq 2 shows that the growing rate of copper crystal branches becomes constant after the initial reaction stage, which implies the copper concentration maintains unchanged. This phenomenon puzzles students and arouses their curiosity.

At this point in the laboratory experiment, students are required to have a class discussion on how the copper trees grow. Most of them agree that Cu^{2+} ions must migrate to the aluminum surface and react with Al atoms. The accumulated copper crystals push the copper branches forward into the gel, as a real tree growing from its roots. In this case, aluminum metal seems like soil for the growth of copper trees. However, a few students are against this hypothesis. They propose that copper must deposit directly on the tips of the copper trees, just like leaves growing on a tree in a garden. The students are encouraged to watch the videos carefully to find proof of each of their favorite hypotheses. Some students suggest that if the copper tree grows from its root, the shape of the branch tips would remain unchanged and vice versa. They capture the screenshots of a specific copper tree at various time intervals and overlap these pictures. The result is schematically shown in Figure 4, from which it is obvious that the second hypothesis, namely copper depositing directly on the tips of the copper trees, is correct.

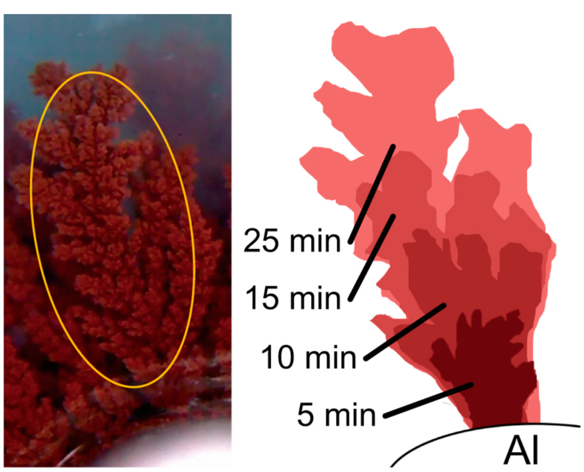

Figure 4. Copper branches and a sketch for the growing stages of a copper branch at various intervals.

This hypothesis can also be used to explain the puzzle from eq 2. As copper ions directly deposit on the growing copper crystal branches, the concentration of Cu^{2+} in the gel around the copper metal will keep almost as constant as its initial concentration. Thus, the growth rate of copper branches remains unchanged for a long time.

If copper ions do not migrate onto the aluminum metal, then how does the displacement reaction occur? At this stage, the teacher gives the students a hint on the possibility of the formation of microcells between copper and aluminum, which contains two half-cell reactions. The anode reaction is

$$2Al \rightarrow 2Al^{3+} + 6e^{-} \quad (3)$$

It occurs on the aluminum surface and relates to the dissolution of aluminum substance. The corresponding cathode reaction is

$$3Cu^{2+} + 6e^{-} \rightarrow 3Cu \quad (4)$$

It occurs on the tips of the copper and relates to the growth of the copper branches. These two electrodes interconnect into a microcell via the slowly formed copper branch. Therefore, a copper branch serves as a wire, that is, a conductor through which electrons flow from aluminum to the copper branch tips.

This suggestion from the teacher is quite helpful to students, especially those in high school. After discussing the concepts of electrochemistry, students are expected to design new experiments to validate the hypothesis of microcells. Some students design a simple experiment, as shown in Figure 5, panel A.

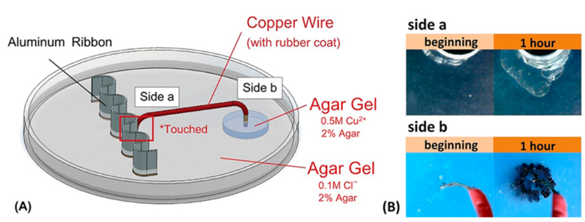

Figure 5. Experiment designed to validate the hypothesis of the microcells. (A) Schematic diagram of the experiment. (B) Reaction process as seen with the stereomicroscope.

Agar gel containing only 0.1 M Cl^{-} is prepared, and the aluminum strip is inserted. A little piece of gel far from the aluminum strip is modified with 0.5 M Cu^{2+}, and this piece of gel is connected to the aluminum strip with a copper wire coated with rubber. The results are shown in Figure 5, panel B. No copper branch growth on the aluminum surface is observed (Figure 5B, side a), only some bubbles are released, which indicates water reduction on the Al surface. On the other end of the wire, copper branches grow continuously over an hour (Figure 5B, side b). This experiment proves that a copper branch can be replaced by a copper wire, and microcells do occur in such a system.

However, some other students question the validity of this experiment because it just "creates" a microcell of Cu−Al electrodes with $CuSO_4$ and NaCl as electrolytes. It cannot conceivably prove the existence of the microcells in the original Cu−Al displacement system. A modified experiment is then suggested by the students, as shown schematically in Figure 6, panel A. The reaction system is the same as that in Figure 1, and the two ends of a copper wire are inserted into the gel. The wire is just in front of the aluminum strip; the wire and strip are not in contact with each other. It can be seen in Figure 6, panel B that when copper branches growth on the aluminum metal

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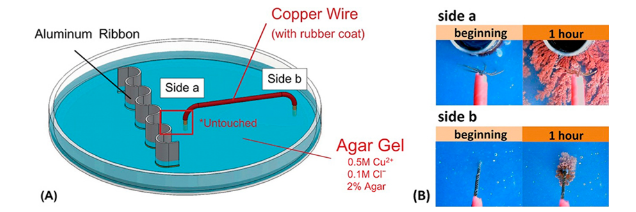

Figure 6. Modified experiment designed to validate the hypothesis of the microcells. (A) Schematic diagram of the experiment. (B) Reaction process as seen with the stereomicroscope.

becomes long enough to contact the wire (Figure 6B, side a), the other side of the wire (Figure 6B, side b) generates similar copper branches. The results verify that copper branches act as conductors. Thus, aluminum (the anode) dissolves while copper metal deposits on the copper branches (the cathode), and microcells do exist in the Cu−Al displacement reaction system.

■ CONCLUSIONS

Reactions in gels are a common way to make a process visual.[6−10] Slowing down the reaction rate in agar gel gives students the opportunity to observe a reaction process in detail. By using this method, the students not only accomplish a reaction experiment based on a specific chemical equation, but also they encounter the concepts of crystal growth and microcells through dramatic images of real-time change and visible crystal growth. Since neither teachers nor students are clear about what may happen in a reaction in gel under a microscopic view, scientific curiosity draws the entire class together. This hands-on experiment can be handled easily and safely by undergraduates in general chemistry laboratory courses as well as high school students in introductory chemistry courses. Students are expected to integrate the knowledge that they have acquired to analyze the experiment phenomena and design new research approaches to prove hypotheses. According to students' feedback, a chance to practically design an experimental proof by themselves is truly a valuable experience.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00207.

Overview of the experiment arrangement and pedagogy; handout for students; hazards and disposal information; selected images of Cu−Al displacement reaction (PDF, DOCX)

Two videos (ZIP)

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Notes

The authors declare no competing financial interest.

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