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Teaching Experiment in Science

DISTANCE LEARNING: HOMEMADE COLLOIDAL SILVER

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Abstract. To continue the experimental education of Chemical Engineering students during the SARS-Covid 19 pandemic, our school opted for assembling laboratory kits for each one of them and sending them by courier service to their homes. This arose much interest and was particularly successful in an Electrochemistry and Corrosion elective course, because up to 25 experiments were performed in each of the Fall 2020 and Spring 2021 semesters. By having their kits at home, students were also able to design experiments on their own. One such experiment –the preparation of a colloidal silver solution– only required readily available kit materials and some other home and kitchen items to produce an easily observable Ag colloidal solution. Lower classes (e.g., General Chemistry, High School Chemistry) should be able to reproduce this experiment as well. The entire procedure can be completed in 1 h.

Keywords: silver nanoparticles; electrochemical oxidation; capping agents; glucose

Introduction

Silver nanoparticles (AgNPs) are rather useful in the fields of catalysis, polymer additives, optics, thermal and electrical conductivity enhancement, microelectronics, chemical detection, medicine, drug delivery, pigments, photonics, imaging, labelling, water treatment, and other applications. They are also used in microorganism sensing and deactivation as they inhibit growth, metabolic, and cellular processes of microbial communities (Zhou, Rees & Compton 2011; Singaravelan & Alwar 2015; Dang et al. 2022). Due to such a variety of applications, sizable amounts of AgNPs are released every year into global water systems, and the risk they pose needs further clarification (Zhou, Rees & Compton 2011).

AgNPs´ bottom-up and top-down physical, biological, and chemical preparation methods are quite varied, including laser ablation, arc discharge, gamma or electron irradiation, microwave processing, radiolytic reduction, submerged arc discharge, evaporation-condensation, thermal decomposition, biological synthesis, chemical reduction, microemulsion formation, electrochemical and photochemical techniques, and the like. Green synthetic pathways (i.e., with no chemical residues) are gaining importance. Reviews on the subject are available (Iravani et al. 2014; Singaravelan & Alwar 2015).

Capping agents (e.g., polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), polyamidoamines (PAMAM), gluconic acid, citrates, succinates, thiols, alcohols, and chitosans) are needed for stabilizing and protecting the AgNPs to prevent their clustering (Yin et al., 2003; Zhang et al., 2008; Iravani et al., 2014; Tseng et al., 2018). The generated particle sizes are rather diverse and can be maintained within specified requirements by a judicious use of such agents, together with a selection of the nature of the reducing agent employed for the Ag(I) → Ag(0) transition, and its concentration adjustment. Typical chemical reducing agents include $NaBH_4$, trisodium citrate, dimethylformamide (DMF) (Chauhan, Mehto & Kumar 2019), ascorbates, polysaccharides, glycols, aldehydes, hydrazine, H_2 (Panacek et al. 2006; Iravani et al. 2014), glucose, Na_2SO_3, KBH_4 (Tavakoli et al. 2014), NaH_2PO_2 (Creixell-Echeagaray et al. 2011), etc. Solvents utilized include pyridine, DMF, water (Nasretdinova et al. 2015; Chauhan, Mehto & Kumar 2019), ethanol (Starowicz, Stypuła & Banaś 2006), and ethylene glycol (Creixell-Echeagaray et al. 2011), among others.

The generation of Ag(0) particles is followed by their agglomeration into oligomeric clusters that lead to metallic colloidal Ag particles (Iravani et al. 2014). AgNPs characterization methods include ultraviolet-visible spectroscopy (UV–Vis), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and diffuse reflectance spectroscopy (DRS) techniques, among others. For a home observation, it is fortunate that AgNPs show characteristic colors (observable by the naked eye) originating from light absorption and scattering due to a specific plasmon resonance that depends on their size (Singaravelan & Alwar 2015), which makes their initial characterization very simple. This resonance is the frequency at which the Ag-conduction band electrons oscillate in response to the alternating electric field of an incident radiation (Chauhan, Mehto & Kumar 2019). In the present case, a yellow-brownish solution with an absorbance peak reported in the vicinity of 400 nm (that corresponds to particle sizes ~10-40 nm) (Solomon et al. 2007; Tseng et al. 2018) is obtained by applying an external electric potential to an electrochemical cell using a commonly available Ag object (e.g., a ring, earring, etc.) as anode, and reducing the Ag(I) thus generated to Ag(0).

Experimental and Results

Due to its simplicity, flexibility, and low cost, the electrochemical route for AgNP preparation is perhaps the most popular method, both in the anodic and cathodic modes. In the first case, an Ag(0) anode produces Ag(I) to be later reduced in a homogeneous fashion; in the second case, Ag(I) is reduced to Ag(0) at the cathode surface (Singaravelan & Alwar 2015). The electrochemical methods can be utilized either potentiostatically or galvanostatically (Starowicz, Stypuła & Banaś 2006). A third electrochemical route involves both steps, i.e., oxidative dissolution and reductive deposition (Rodríguez-Sánchez, Blanco & López-Quintela 2000; Starowicz, Stypuła & Banaś 2006; Kuntyi et al. 2019). A fourth electrochemical approach involves Ag(0) anodic oxidation with a chemical reduction in the bulk solution effected by an electrochemically produced mediator (Nasretdinova et al. 2015). A technical difficulty may arise in the second and third cases because the freshly synthesized AgNP can flocculate in the vicinity of the cathode; this has been solved by using a rapidly rotating cathode to transfer them to the bulk solution (Ma et al., 2004) or else by stabilizing the newly formed silver clusters (Yin et al. 2003). The fourth case involves a more complicated system due to the use of a mediator.

Therefore, the simplest approach is the first one. In the present experiment we follow it by using a common Ag object (e.g., a silver earring or a ring) as the anode to generate Ag(I) which is then reduced by glucose in the aqueous phase to yield AgNPs. To do this, place ~40 mL of water in a 50-mL beaker. Add a spatula-tip of Na_2CO_3 to produce an electrolytic solution. With the aid of alligator clips, connect the positive pole of an AC-to-DC adjustable voltage power adapter (e.g., Steren model ELI-035) to a resistor (e.g., 10 kohm). A useful, nominal voltage setting of 3 V gives a true voltage of ~7.2 V; the resistor is used to decrease the current that reaches the cell (in this case from 300 to 0.72 mA) and avoid the formation of Ag_2O. Connect the other end of the resistor to the Ag piece (anode) through an alligator clip. Connect a Cu wire (e.g., 10 cm long, 22 AWG caliber) through another alligator clip to the negative pole (cathode) of the power source. See Figure 1.

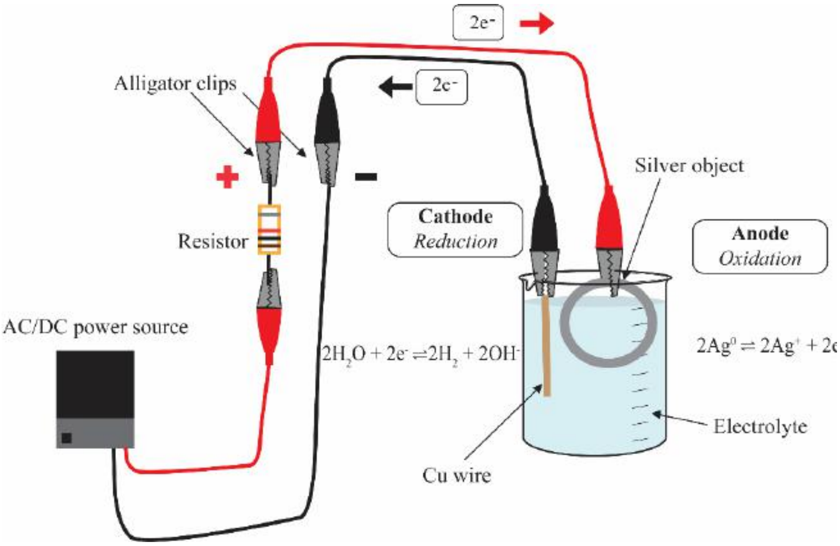

Figure 1. Experimental setup

When the setup is ready, immerse the anode and cathode into the solution avoiding contact of the alligator clips with it. Then, connect the adapter to a regular home electricity outlet (i.e., 120 V). While the reaction is in progress, prepare a glucose solution in a 10-mL beaker by dissolving ~4 mL of pancake syrup (e.g., Karo brand) as reducing and capping agent in ~4 mL of water. Once the desired electrolysis reaction time has elapsed (e.g., ~15 min), unplug the power adapter from the outlet source, remove the electrodes from the solution, and add to it a couple of drops of the glucose solution to initiate the reduction of Ag(I) to Ag(0). If desired, a faster reduction can be achieved by heating the solution (to ~70 – 80 °C). Use a suitable background for a good contrast to observe the yellow plasmon coloration. See Figure 2.

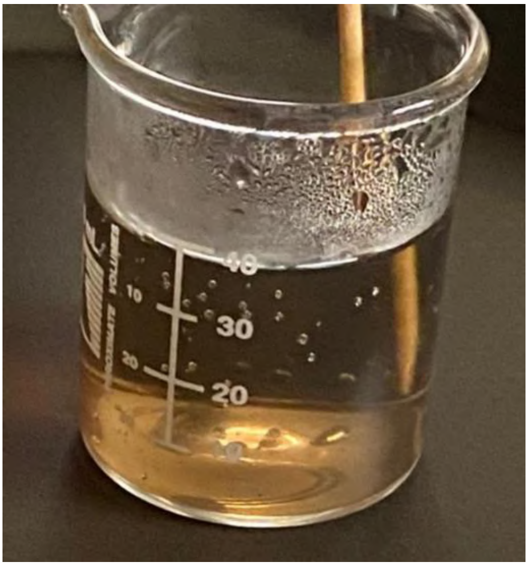

Figure 2. Colloidal Ag generated

Discussion

The reactions in the electrochemical cell are as follows:

Oxidation:

$2Ag(s) \rightarrow 2Ag^{+}(aq) + 2e^{-}$ $\quad E^{0} = 0.799\ V \quad$ (1)

Reduction:

$2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$ $\quad E^{0} = -0.83\ V \quad$ (2)

The reactions during the chemical reduction are:

Ag(I) reduction by glucose:
$2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$ (3)

Glucose oxidation by Ag(I):
This reaction in a basic medium involves a complicated mechanism that can produce peroxide, carbon dioxide/carbonate, carbonyl, or carboxylate species. Details are outside of the scope of the present work, and a simplified scheme involving two possible routes has been proposed (Pulit and Banach, 2013).

$C_6H_{12}O_6(aq) + 2Ag^{+}(aq) + 3OH^{-}(aq) \rightarrow C_6H_9O_6{}^{-}(aq) + 2Ag(s) + 3H_2O(l$ (4a)

$2C_6H_{12}O_6(aq) + 2Ag^{+}(aq) + 2OH^{-}(aq) \rightarrow 2C_6H_{10}O_7(aq) + 2Ag(s) + 3H_2(g)$ (4b)

Hazards

Colloidal silver is generally considered as non-toxic. Discard according to local regulations. The power adapter is a source of direct electrical current. Although the risk is small, it must be used with great care to avoid an electrical shock.

Conclusions

A simple, homemade experiment to produce silver nanoparticles is developed with easily available materials and reagents in a 1-h lab period.

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