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3D Printed UV−Visible Cuvette Adapter for Low-Cost and Versatile Spectroscopic Experiments

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S Supporting Information

ABSTRACT: Ultraviolet−visible (UV−vis) spectroscopy represents one of the most popular analytical techniques in chemical research labs. A variety of vendors provide instruments that are suited for the analysis of liquid samples at moderate concentrations. However, to accommodate more specialized experiments, expensive accessories are required and often do not fit the specific needs of experimental scientists. In this work, we present a generalized adapter that can be 3D printed and used with existing spectrometers to enable a wide array of experiments to be performed. In the case of liquid samples, we provide a method for dramatically reducing the price of a quartz cuvette with minimal impact on performance. Through simple modification of the design, cuvettes with various path lengths can be prepared. Additionally, we illustrate the ability to turn any sample container into a working cuvette to simplify experimental protocols, prevent contamination risks, and further reduce costs. This strategy also enables gaseous and solid samples to be evaluated easily and reproducibly. Furthermore, we demonstrate how this concept can be extended to interface additional instrumentation with a commercial UV−vis spectrometer. All of the digital designs are provided under a creative commons license to enable other researchers to modify and adapt the designs for their unique experimental requirements.

1. INTRODUCTION

The origins of rapid prototyping lie in the early 1980s with the first development of three-dimensional (3D) printing technologies.[1−3] In more recent years, 3D printing has become increasingly popular in both commercial and retail settings. This popularity is aided by the ease of sharing designs between individuals and the increased availability of 3D printers, particularly fused deposition modeling printers. The availability of free and user-friendly computer-aided design (CAD) programs allows for easy construction or customization of designs. These designs can then be printed, using a variety of specific techniques, to bring the digital design into the physical form. This rapid prototyping technique has found a variety of applications in a wide range of fields owing to the low cost of materials and the unique structures that can be made.

Recently, there has been a rise in scientific tools and software that can be downloaded and modified.[4] Examples of these tools can be found in recent review articles written on this topic.[4,5] These tools include examples of entire instrumentation[6,7] as well as platforms to interface with or enhance the capabilities of existing instrumentation.[8−12]

In this work, we focus on the development of 3D printed structures specifically designed to enhance the capability of commercial ultraviolet−visible (UV−vis) spectrometers. The UV−vis spectrometer is a tool used to evaluate the transmission or absorption of light through a sample. The relevant energies associated with the UV-vis region of the electromagnetic spectrum make this technique particularly powerful for analyzing the energy levels of materials ranging from molecules to semiconducting nanoparticles. Recent publications have demonstrated how spectrometers can be assembled using 3D printed housing and operated using a smartphone.[6,13] However, the relatively low cost of commercial instruments means that most researchers have access to spectrometers that are capable of using a traditional cuvette sample holder. Although standard cuvette sample holders are routinely used to evaluate the absorption of common liquids, there are countless examples of experiments that require different adaptations to be made to evaluate a particular sample under specific conditions.[14−16] This has led many commercial manufacturers to generate a suite of instrumental accessories that are meant to accommodate different experimental conditions. Unfortunately, these accessories are costly and often fall short of the specific needs of new experiments at the cutting edge of science. Previous 3D printed designs are focused on either holding traditional cuvettes in a nontraditional housing[17−19] or are confined to the space of a traditional cuvette.[20−22] Here, we present a universal cuvette adapter to enable a wide range of experiments in an existing

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UV−vis spectrometer, including inexpensive strategies for converting most laboratory sample containers into functional cuvettes. This provides a means to extend the capabilities of most cuvette-based spectrometers at a fraction of the cost of commercial accessories. The CAD described in this work is available under a creative commons license to encourage its use by other researchers and allow for further development.

2. RESULTS AND DISCUSSION

UV−vis spectrometers are one of the most common pieces of major equipment in research laboratories around the world. Information regarding the absorption and transmission of UV−visible light can provide insights into a wide variety of questions. However, the evaluation of different kinds of samples often requires the purchase of expensive accessories that may not be ideal for the specific experiment envisioned by the researcher. Here, we provide a general framework for an accessory adapter that will work in most commercial UV−vis spectrometers and provide examples of the kinds of adaptations that can be made to facilitate different types of experiments at low cost.

The most common sample holder used in a spectrometer is the cuvette. A traditional cuvette has outer dimensions of 12.5 × 12.5 × 45 mm, with an interior path length of 10 mm. Cuvettes of this size typically require 2.5−3.5 mL of a liquid sample to acquire an acceptable absorbance spectrum. Cuvettes can be manufactured from a variety of materials such as plastic, glass, and quartz. The choice of material often depends on the required wavelength range of the experiment and the solvent compatibility of the material. Although the wavelength range of glass and quartz is significantly larger than that of plastic, the cost is also 2 or 3 orders of magnitude higher per cuvette. To enable more researchers to utilize these superior materials, we have developed a cuvette adapter that uses either glass or quartz windows on a 3D printed support structure (Figure 1). The adapter requires at least 21 mm of space in the sample compartment of the spectrometer either before or after the commercial cuvette sample holder. After surveying several spectrometer vendors, most research-grade spectrometers have significantly more space in their sample compartment than the required 21 mm. Exceptions include teaching-grade spectrometers and specialized spectrometers (e.g., NanoDrop). The windows of the cuvette can be prepared from either a traditional glass microscope slide cut into three sections or a commercially available planar quartz glass sample (window measurement is 25 mm × 25 mm). This brings the cost of a glass sample holder down to approximately $1 USD and the cost of a quartz sample holder down to approximately $14 USD, including the cost of the 3D printed plastic support (Table S1). Importantly, these adapted sample holders have nearly the same spectral range as the commercially available glass and quartz cuvettes (Figure 1D). The slight differences observed in the UV and near-infrared regions are caused by differences in the glass used in the adapter compared with the glass used in the commercial cuvette.

The major advantage of the 3D printed sample holder is that the digital design of the 3D printed support can be easily modified. As a demonstration of this capability, we have designed a variety of cuvettes with different sample volume requirements and path lengths (Figure 2). As shown in Figure 2A, we have found that changing the sample volume has a negligible effect on the absorbance. In fact, the slight difference between the commercial cuvette and the 3D printed cuvettes

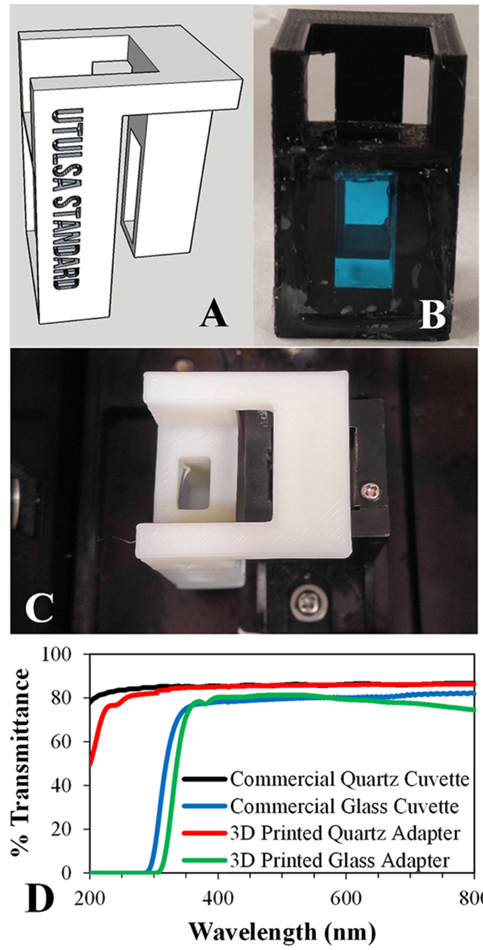

Figure 1. General design and optical performance of a 3D printed cuvette adapter. (A) Two-dimensional image from the CAD of a standard cuvette adapter taken from the side. The portion to the right is placed in the typical cuvette sample holder of a commercial UV−vis spectrometer. (B) Photograph of an assembled 3D printed cuvette adapter containing methylene blue solution. Image taken from the front to show the glass windows that have been added to the adapter using silicone glue. (C) Photograph of a 3D printed cuvette adapter placed in a commercial spectrometer. Adapter printed in natural acrylonitrile butadiene styrene (ABS) for visual contrast. (D) Comparison of the transmittance spectra between commercial cuvettes and 3D printed cuvette adapters prepared with either quartz windows or glass windows.

can be attributed to the slight error in path length caused by the resolution of the 3D printer (Table S2). Although changing the printing speed does not result in a significant source of error, the tolerances of the 3D printer used in this study result in a path length that is extended by an average of 0.46 mm. Accounting for these variances by measuring the printed path length with calipers, the error can be reduced to less than 0.74%. Alternatively, the CAD can be modified to account for the tolerances of the 3D printer. For the 3D printer used in this study, reducing the path length of the digital design from 10 to 9.5 mm reduced the printer error (Figure S1), although this would likely be different for other 3D printers. Intentionally changing the path length follows the predicted behavior of Beer's law when using an aqueous 10 μM sample of methylene blue (Figure 2B). For all of these designs, the cost of each cell only changes according to the price of the plastic required for the 3D printed support, as the window material remains the

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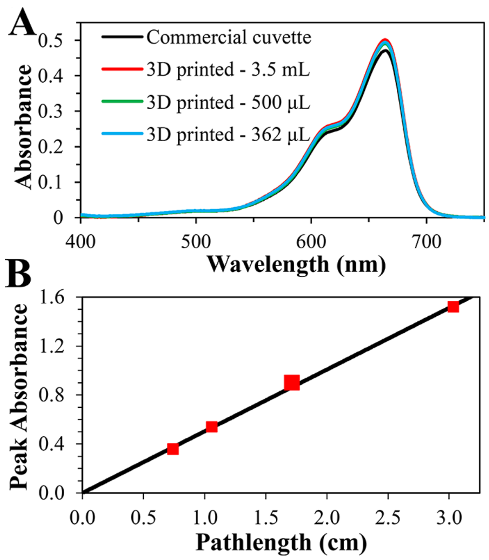

Figure 2. Effect of sample volume and path length on the performance of the UV−vis cuvette adapter. (A) Spectra of 5 μM methylene blue in commercial cuvette and 3D printed cuvette adapters with different sample volumes but all possessing a designed path length of 10 mm. (B) Peak absorbance of 5 μM methylene blue in cuvettes designed with different path lengths. The size of the red square data point represents the error in the absorbance value and measured path length of three different printed cuvette adapters. The path length was determined by measurement with digital calipers. The black line represents the predicted absorbance versus path length according to Beer's law.

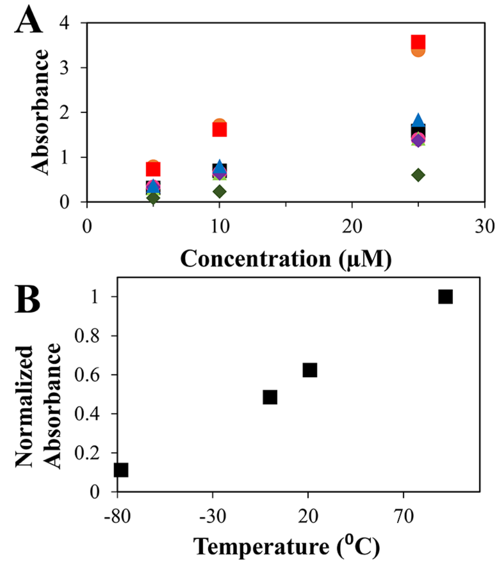

Figure 3. Adapter capabilities for various sample holders. (A) Peak absorbance of methylene blue as a function of concentration for a wide range of liquid sample holders including commercial quartz cuvette (black square), glass test tube (light green triangle), screw cap vial (orange circle), 15 mL centrifuge tube (blue triangle), gas chromatography vial (pink circle), 2 mL microcentrifuge tube (purple diamond), 50 mL centrifuge tube (red square), and an NMR tube (dark green diamond). All absorbance values represent averages from the three measurements. (B) Absorbance of NO_2 at 425 nm as a function of temperature. NO_2 sample was kept in a gas chromatography vial. Measurements represent the average of the three different samples with different orders through the range of temperatures. Data were normalized based on the absorbance of each sample at 92 °C.

same. This is a significant difference compared with commercial extended path length cuvettes, which have significantly higher costs owing to the increase in quartz and glass that must be used. This strategy will allow researchers to easily increase the path length to improve the detection limit (Figure S2) or decrease the path length for concentrated samples, thereby increasing the dynamic range of the spectrometer.

Additionally, there are many liquid samples that researchers would prefer to keep in a different container for simplicity or to prevent contamination from the air or environment. In Figure 3A, we demonstrate the use of a variety of glass vials, centrifuge tubes, and an NMR tube to develop a calibration curve for the concentration of methylene blue. For all of the sample containers tested, the increase in methylene blue concentration resulted in a linear change in the absorbance according to Beer's law. As expected, sample containers that inherently have longer path lengths will have higher absorbance values compared to those with shorter path lengths. These containers are also expected to reach signal saturation earlier than containers with shorter path lengths. Although the nonplanar shape may make the determination of the path length and molar absorptivity more challenging, these unique sample holders may allow researchers to perform more accurate or high-throughput experiments as the transfer of the sample to a traditional cuvette is no longer required. Noteworthy is the fact that these designs do not require any glass or quartz to be applied and do not need to be watertight, which simplifies the experiment, prevents contamination problems, and further reduces the cost. Additionally, by using gas-tight containers, these accessories can enable the evaluation of gaseous samples, as demonstrated by the analysis of NO_2 gas in Figure 3B. Here, the equilibrium between NO_2 and N_2O_4 at different temperatures is demonstrated by simply placing the gas-tight vial filled with NO_2 in different temperature environments and using the appropriate adapter to observe the expected trend.[23−25]

There are also many instances when the sample of interest is a solid rather than a liquid or gas. In these cases, commercial accessories can be challenging to use depending on the area of interest relative to optical viewing window of the sample holder. Here, a 40 mM methylene blue solution was prepared in isopropanol and spin-coated onto a microscope slide patterned with scotch tape. As shown in Figure 4A, the adapter can be easily modified to accommodate the samples of different shapes and location with effectively no change in the spectrum. As this design does not require the addition of glass or quartz, the minimal cost of the 3D printed object enables the use of custom sample holders for individual samples if necessary. The ability to edit the CAD can also allow researchers to systematically change the sample angle relative to the beam path for experiments requiring increased absorbance or unique analysis (Figure 4B).

In Figure 5, we demonstrate how this universal cuvette adapter can be used to interface additional analytical methods to perform spectroelectrochemical analysis of the classical blue bottle experiment.[26,27] The general design of this unique accessory allows for the placement of three electrodes, the capability of the holding electrolyte, and the addition of a gas (Figure S3). The results demonstrate how dissolved gases affect the electrolyte solution. Spectroscopic and electrochemical analyses are performed simultaneously to determine the effect of the oxidation state on the optical properties. Most

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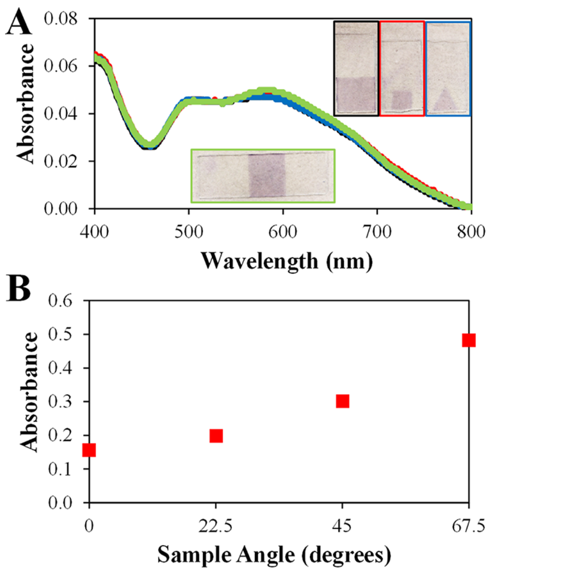

Figure 4. Analysis of methylene blue films on the surface of glass microscope slides. (A) Absorbance spectrum of films covering a large region (black), covering a limited square portion (red), covering a triangular shaped region (blue), and the center portion (green) of a microscope slide. Photographs of the samples analyzed are included as insets. (B) Absorbance of the film at 500 nm as a function of sample angle. Theoretically, the path length increases as 1/cos(angle).

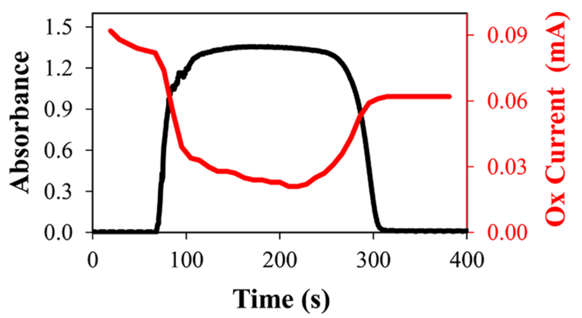

Figure 5. Spectroelectrochemical analysis of the blue bottle experiment. Absorbance at 664 nm (black curve) and oxidative current (red curve) were taken as a function of time. Oxidative current was determined from cyclic voltammograms taken throughout the experiment. Compressed air was bubbled into the electrolyte solution at 65 s. Bubbling was stopped at 220 s.

importantly, this experiment provides a proof-of-concept for the interfacing of multiple instruments through the use of a simple 3D printed accessory that costs less than \$2 USD to prepare.

3. CONCLUSIONS

Here, we have developed a general design for a 3D printed adapter for a traditional UV−vis spectrometer, which can be used to replace expensive cuvettes with inexpensive alternatives while maintaining the same functionality. Through simple modification of the digital design, we have demonstrated the ability to change the sample volume or path length, hold various sample containers, analyze gaseous or solid samples, and interface the spectrometer with additional equipment. We believe that these designs will make UV−vis spectroscopy more affordable and more versatile for researchers working in a wide range of fields. From a practical perspective, we note that the printing of a standard adapter typically takes about 1.5 h and that the assembly of this adapter can take up to 2 h including the adhesion time for the addition of glass or quartz windows (Supporting Video). We recommend the use of black filaments, as UV−vis cuvette adapters prepared with other colors may impact the resulting spectrum. Although most cuvettes used in this work were printed with an infill of 100% to ensure water tightness, experiments performed with 3D printed cuvette adapters with infill values as low as 10% were found to be watertight for over 2 weeks. Additionally, not all 3D printed thermoplastics are compatible with all solvents. ABS, for example, will dissolve in acetone. Using polylactic acid (PLA), however, will enable the use of acetone but may not be compatible with other solvents. Thus, the choice of a 3D printing filament may impact the possible experimental conditions. Alternatively, using an adapter capable of holding a suitable sample container (such as those demonstrated in Figure 3) avoids potential solvent compatibility issues entirely and also prevents contamination between different samples.

All of the digital designs developed in this work are available free of charge under a creative commons license and can be found on the digital sharing site Thingiverse (https://www.thingiverse.com/LeBlanc-Research-Group/designs). We sincerely hope that researchers use and modify this general accessory to suit the needs of their unique experiments. For research groups without easy access to 3D printers, there are a variety of companies that will perform 3D printing and ship the custom part for a minimal fee (e.g., https://www.shapeways.com/). As these designs can be digitally shared and printed at low cost, we anticipate that more complex UV−vis experiments will be developed, with designs that can be subsequently shared for increased reproducibility. More broadly, this work demonstrates the ability to use 3D printing to enhance the capabilities of common instrumentation. Extending this concept to other instruments is of ongoing interest to our research group and the scientific community in general.

4. EXPERIMENTAL SECTION

All 3D printed objects were designed with SketchUp Make 2017 available free from Google (http://www.sketchup.com/). Designs were sliced using Cura for LulzBot (https://www.lulzbot.com/cura), a free software that is based on the more universal Cura software from Ultimaker (https://ultimaker.com/en/products/cura-software). All cuvettes were printed on a LulzBot Mini printer using black PLA filament made and sold by MatterHackers. Specific printing parameters can be found in the Supporting Information. All CAD and .stl files described in this work are freely available under a creative commons license (https://www.thingiverse.com/LeBlanc-Research-Group/designs). **Cuvettes**: Fisherbrand Semi-Micro Quartz Cuvette (cat no. 14-958-125) and Fisherbrand Glass Cuvette (cat no. 14-385-910B) were used for comparison with the 3D printed cuvettes. To construct the 3D printed cuvette, either quartz slides purchased from Technical Glass Products Inc. (25 mm × 25 mm × 1 mm) or Pearl Brand glass microscopes slides (75 mm × 25 mm × 1 mm) were used. The glass microscope slides were cut to 25 mm × 25 mm size using a Ted Pella Diamond Scriber (cat no. 54463). Quartz and glass slides were secured using Loctite Clear Silicone Glue.

4.1. Chemicals. NO_2 gas was generated by adding approximately 2 cm of copper wire to 10 mL of concentrated (68−70%) Fisher Chemical Trace Metal Grade nitric acid (UN2031). Solutions of methylene blue were made using ACROS methylene blue (CAS# 61-73-4). Spectroelectrochem-

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ical experiments were performed using 25 μM methylene blue, 0.475 M Fisher Scientific potassium hydroxide (CAS# 1310-58-3), and 0.185 M ACROS D(+)-glucose (CAS# 50-99-7) as the electrolyte, a 1″ × 1″ ITO-coated PET working electrode, a Ag/AgCl reference electrode, and a platinum mesh counter electrode.

4.2. Instrumentation. All spectra were collected using a Shimadzu UV-1800 UV–vis spectrometer. The potentiostat used for the spectroelectrochemical experiment was a Biologic SAS SP-300.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01310.

Detailed printing parameters, cost breakdown of the 3D printed adapter, the 3D printed adapters designed in this work, and additional details regarding the experiments (PDF)

Assembly of a 3D printed cuvette with glass windows (AVI)

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Author Contributions

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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