Porous-wall Hollow Glass Microspheres for Security Printing Applications

***Forest Thompson*[1]*, George Wicks*[2]*, Grant Crawford*[1]**
[1]*South Dakota School of Mines and Technology; Rapid City, SD,* [2]*Applied Research Center; Aiken, SC*

Abstract

Porous-wall hollow glass microspheres are a one-of-the-kind material with many potential uses in security technology. This work focuses on the development of security inks containing porous-wall hollow glass microspheres, whereby the microspheres serve as storage vessels for a variety of functional materials. This preliminary work comprises two feasibility studies. One study resulted in the successful aerosol jet deposition of hollow glass microspheres onto a substrate. The other study resulted in the loading of porous-wall hollow glass microspheres with gold nanoparticles. Both studies demonstrate the feasibility of developing and delivering a security ink utilizing porous-wall hollow glass microspheres that are loaded with functional materials. The results encourage the continuation of research to achieve this goal.

Introduction

In recent years, the production of counterfeit goods has grown into a world-wide issue that is detrimental to both the world economy [1] and the well-being of consumers, impacting a variety of products (e.g. pharmaceuticals [2] and auto parts [3]). Counterfeiting technology has developed in recent years, often resulting in negation of existing security features used for product authentication. As a result, there is a need for novel, functional materials to be incorporated into the next generation of security-end products. Porous-wall hollow glass microspheres (PW-HGMs) are one of these materials. These glass microspheres typically have diameters that range from 10 microns to 100 microns and wall thicknesses of 1-2 microns [4]. Figure 1 shows a scanning electron microscope (SEM) image of multiple PW-HGMs. The most unique feature of PW-HGMs is their interconnected wall porosity (see Figure 2) that is generated and controlled after producing phase separation during the manufacturing process [4]. The 10-3000 Å pores enable the hollow spheres to be loaded with solids, liquids, and gases for use in a wide range of applications including renewable energy, medical imaging, and drug delivery [4-6].

The objective of this research was to initiate the development of a security ink that contains PW-HGMs loaded with one or more functional materials (e.g. materials with unique optical, electrical, magnetic, thermal, or chemical properties). Such a novel PW-HGM-based security ink could be used to fabricate next-generation security devices with direct write printing technology. Encapsulating various payloads within PW-HGMs would allow for an efficient deposition process that utilizes the same printing parameters for a variety of functional materials. Thus, a variety of functional security inks may be developed and deployed within a single technology envelope. Additionally, the encapsulation of functional materials within thin glass walls can be exploited to create security features for use in anti-tamper applications.

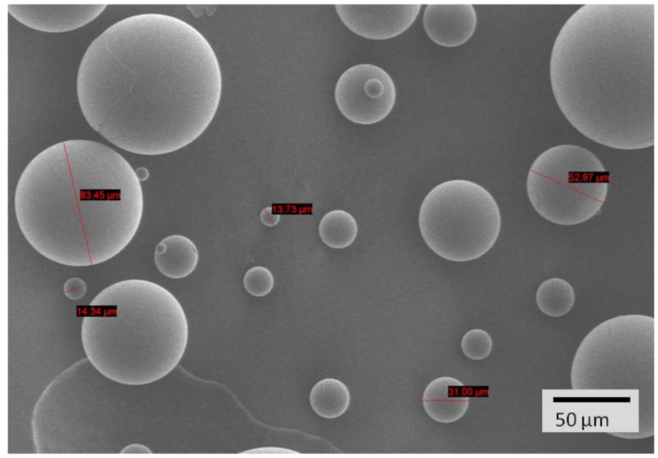

Figure 1. SEM image showing multiple PW-HGMs.

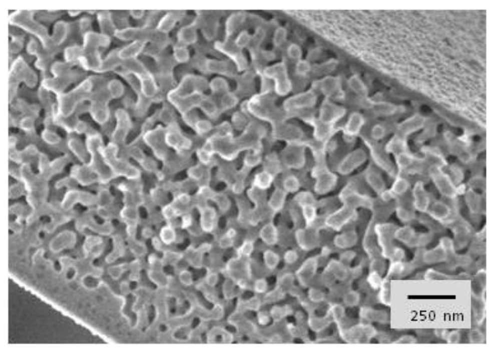

Figure 2. SEM image revealing the wall cross-section of a PW-HGM. The dark gaps between the wormlike glass features are the interconnected pores (about 50-100 nm in diameter in this case) through which PW-HGMs can be loaded with a variety of materials.

As first steps in developing a security ink incorporating functionally loaded PW-HGMs, two feasibility studies were performed. One study sought to show that glass microspheres could survive a printing process using an aerosol jet deposition system. The second study focused on demonstrating the feasibility of loading PW-HGMs with metallic nanoparticles through the wall porosity.

Aerosol Jet Deposition of Glass Microspheres

Objective

Before working directly with the limited quantities of the unique PW-HGMs available for this research, inks containing solid-wall hollow glass microspheres were developed. The chemical, mechanical, and rheological properties of the ink, suitable for the specific direct write technology utilized for the printing process, had to be identified. Additionally, parameters involved in the printing process needed to be optimized to ensure successful deposition of the microspheres onto a substrate.

Materials and Methods

An ink consisting of 5.0 wt% polyvinylpyrrolidone (PVP) and 0.2 wt% 3M™ iM30K Glass Bubbles (average diameter of 18 μm [7]) in ethylene glycol was developed for aerosol jet deposition by a Sono-tek ExactaCoat SC system. The loading of the ink with both the glass microspheres and the PVP, which was used for adhesion of the microspheres to the substrate following printing, was restricted by the printing system's rheological limitations, which were experimentally determined. Ethylene glycol's viscous nature helped to slow the hollow glass microspheres' tendency to float to the surface of the ink. Sufficient dispersion of the microspheres in the ink was maintained to allow for generation of an aerosol spray.

The ink containing the iM30K Glass Bubbles was printed onto glass and paper substrates. Printing parameters such as volumetric infusion rate and line spacing were experimentally optimized to eliminate overspray of the ink and infusion line blockage caused by microsphere buildup.

Results and Discussion

The iM30K Glass Bubbles were successfully deposited onto glass and paper substrates. Figure 3 shows SEM micrographs of iM30K Glass Bubbles with PVP printed onto copy paper using an aerosol jet deposition system. From inspection of Figure 3, it is clear that the microspheres remain intact after printing with limited signs of microsphere fracture. Also, it is interesting to note that the microspheres appear aligned with the paper fibers, potentially caused by evaporative assembly. Figure 4 shows the same ink printed on a glass substrate. The image was captured near the edge of the printed area and depicts part of a ring of microspheres which is believed to have formed during drying due to the coffee ring effect [8]. From inspection of Figure 4, cracks which formed during the drying process are present in the film. These results demonstrated that, with the proper ink characteristics and printing parameters, hollow glass microspheres can be printed using an aerosol jet deposition system.

Future work must be done to further optimize the printing of glass microspheres. As shown in Figure 3, there is a non-uniform coverage of the paper substrate after printing. Thus, improved coverage of substrates with glass microspheres should be sought. Additionally, the coffee ring effect, which occurred after printing on glass substrates (Figure 4), need to be minimized in future work, perhaps through the use of binary solvents [9].

The process used to develop the ink that resulted in the successful aerosol jet deposition of these solid-wall hollow glass microspheres will be extended in the future to the development of inks containing PW-HGMs. It should be noted, however, that the iM30K Glass Bubbles used in this feasibility study are both relatively small and very strong. PW-HGMs, on the other hand, will be weaker due to the induced wall porosity. This means that techniques used to strengthen PW-HGMs, such as coatings, will also need to be explored in future research.

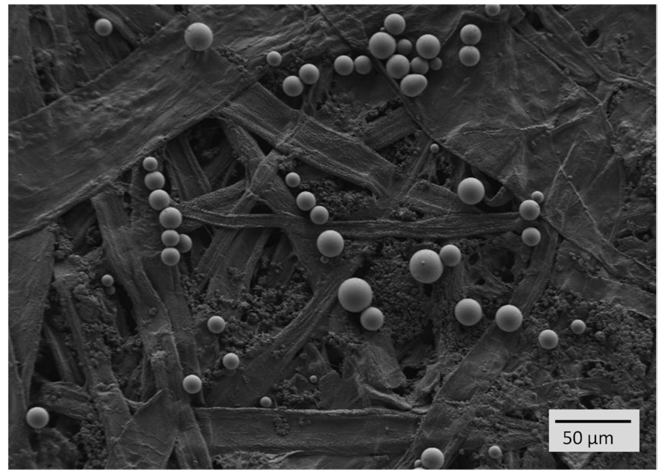

Figure 3. SEM image showing aerosol jet deposition of iM30K Glass Bubbles with PVP onto copy paper.

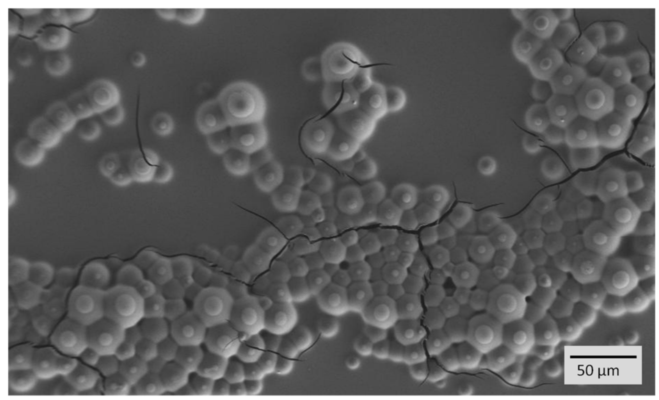

Figure 4. SEM image showing aerosol jet deposition of iM30K Glass Bubbles with PVP onto a glass slide.

Loading of PW-HGMs with Nanoparticles

Objective

As mentioned in the introduction, PW-HGMs have been loaded with a wide range of materials for a variety of applications. Limited research, however, has been conducted on loading PW-HGMs with metallic nanoparticles with properties applicable to security printing, such as unique optical, electrical, magnetic, thermal, or chemical properties. Loading PW-HGMs with gold nanoparticles was attempted simply to demonstrate proof of concept for the loading of PW-HGMs with functional nanoparticles.

Materials and Methods

PW-HGMs, with an average diameter of about 27 microns, were soaked in an approximately 18 nanomolar citrate-capped gold nanoparticle aqueous dispersion. Pressure and heat were used to impregnate the PW-HGMs with the 12-15 nm spherical gold particles. Multiple loading cycles were performed and, after each cycle, the PW-HGMs were washed and dried to gradually build up the amount of gold on the interior of the microspheres.

The loaded PW-HGMs were then cracked open and characterized using field emission SEM and energy dispersive X-ray spectroscopy.

Results and Discussion

Gold nanoparticles were found on the wall interior and inside the wall porosity of a PW-HGM that had been cracked open for characterization. Figure 5 shows an SEM image of the interior surface of a PW-HGM after completion of the loading process. Note, this sphere was deliberately fractured to inspect the internal surface. Clearly, gold nanoparticles (light regions), present in both clusters and as individual particles, were found uniformly distributed on the interior microsphere surface. From inspection of the inset in Figure 5, the wall porosity (dark circles) can also be observed. The individual spherical nanoparticles are indeed about 12-15 nm in diameter and the pore openings in this particular area are roughly 12-20 nm in diameter. Figure 6 shows an SEM image revealing the wall cross-section of a PW-HGM after completion of the loading process and the deliberate fracture of the sphere. From inspection of Figure 6, and comparison with Figure 2 (unloaded sphere wall cross-section), the wall cross-section contains a significant coverage of gold nanoparticles (light regions). Also, the pores in this area are about 50-90 nm at their widest points. The presence of gold nanoparticles on the interior wall surface and within the microsphere's internal wall porosity strongly suggests that nanoparticles traveled through the porosity and loaded the glass microsphere. The PW-HGM had undergone five separate loading cycles, all of which utilized both pressure and elevated temperatures, and soaking times ranging from 30 minutes to 2 hours.

The discovery of gold nanoparticles on the interior wall surface and within the wall porosity of a PW-HGM demonstrated that the loading of PW-HGMs with metallic nanoparticles is indeed feasible. These results suggest that methods can potentially be developed to load PW-HGMs with nanoparticles that are functionalized for security printing applications.

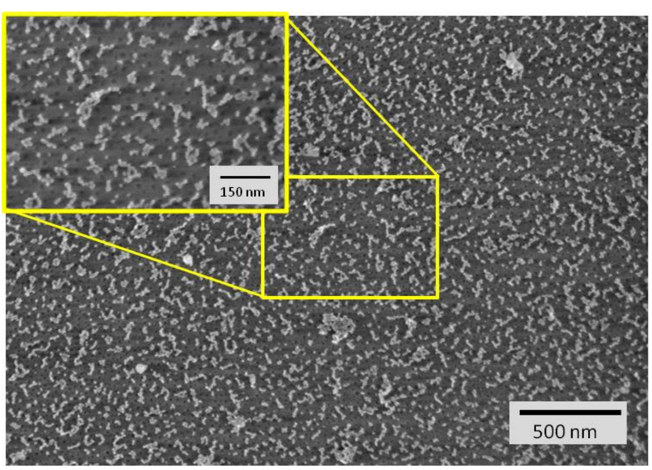

Figure 5. SEM image of the interior wall surface of a PW-HGM after loading the sphere with gold nanoparticles. The inset depicts a higher resolution image where the gold nanoparticles (light regions) and wall porosity (dark circular openings) are clearly visible.

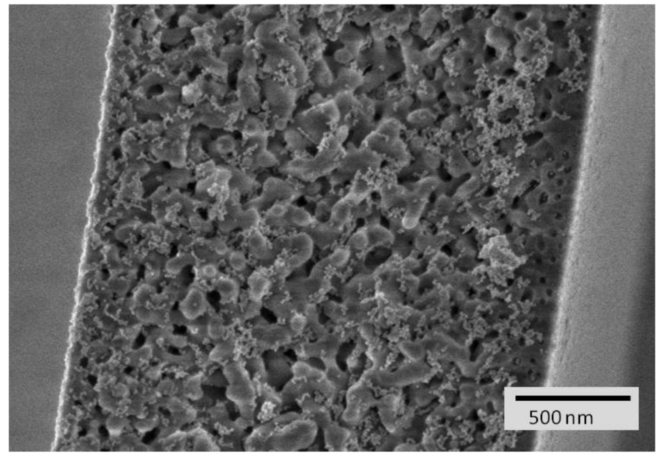

Figure 6. SEM image showing the PW-HGM wall cross-section after loading the sphere with gold nanoparticles. Gold nanoparticles are present as light-colored spheres and clustered spheres in this image.

Conclusions

These feasibility studies have demonstrated the ability to print solid-wall glass microspheres, albeit small and very strong microspheres, with an aerosol jet deposition system and the ability to load PW-HGMs with gold nanoparticles. Based on these encouraging results, further research on incorporating PW-HGMs into security inks seems worthwhile. Steps will be taken towards loading PW-HGMs with a variety of functional materials, including metallic nanoparticles, and then developing an ink that contains these loaded PW-HGMs for use in aerosol jet deposition systems. Such a novel ink would have many applications in new generations of security features.

References

[1] International Chamber of Commerce, "Global Impacts Study," http://www.iccwbo.org/Advocacy-Codes-and-Rules/BASCAP/BASCAP-Research/Economic-impact/Global-Impacts-Study/, accessed April 2015.

[2] T.K. Mackey and B.A. Liang, "The Global Counterfeit Drug Trade: Patient Safety and Public Health Risks", Journal of Pharmaceutical Sciences, vol. 100, no. 11, pp. 4571-4579, 2011.

[3] Motorindia, "How to Combat Widespread Auto Parts Counterfeiting", http://www.motorindiaonline.in/aftermarket/how-to-combat-widespread-auto-parts-counterfeiting/, accessed April 2015.

[4] G. G. Wicks, "Nanostructures and 'Nanonothingness' in Unique Glass Microspheres", International Journal of Applied Glass Science, vol. 5, no. 2, pp. 100–104, 2013.

[5] R. Mohtadi, K. Tange, T. Matsunaga, G. Wicks, K. Heung and R. Schumacher, "A New Way for Storing Reactive Complex Hydrides on Board of Automobiles", Materials Innovations in an Emerging Hydrogen Economy, Ceramic Transactions, eds., G. G. Wicks and J. Simon, vol. 202, pp. 91-96, Hoboken NJ: John Wiley & Sons, Inc., 2009.

[6] S. Li, L. Nguyen, H. Xiong, M. Wang, T. C.-C. Hu, J. She, S. M. Serkiz, G. G. Wicks and W. S. Dynan, “Porous-Wall Hollow Glass Microspheres as Novel Potential Nanocarriers for Biomedical Applications”, Nanomedicine, vol. 6, pp 127–136, 2010.

[7] 3M Energy and Advanced Materials Division, “3M Glass Bubbles: iM30K”, http://multimedia.3m.com/mws/media/625127O/3m-glass-bubbles-im30k.pdf, accessed July 2015.

[8] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel and T. A. Witten, “Contact Line Deposits in an Evaporating Drop”, Physical Review E, vol. 62, no. 1, pp. 756 – 765, 2000.

[9] J. Park and J. Moon, “Control of Colloidal Particle Deposit Patterns within Picoliter Droplets Ejected by Ink-Jet Printing”, Langmuir, vol. 22, no. 8, pp. 3506 – 3513, 2006.

Author Biography

Forest Thompson received his BA in physics from Colorado College (2014) and is currently working on thesis research for his MS in materials engineering and science at the South Dakota School of Mines and Technology. His work focuses on security ink development for the Center for Security Printing and Anti-Counterfeiting Technology.