

The Synthesis of Functional Nanostructures Using the Ink Jet Method

Scott Williams and Aaron Bodell; School of Print Media; Rochester Institute of Technology; Rochester, New York, USA.

Abstract

Polymethine dyes are unique organic colorants with an inherent ability to associate in structured aggregates. These aggregates exhibit electronic behavior that can be leveraged in device manufacture. Research results will be presented that furthers the goal of using the ink jet technique as a method of producing a highly uniform and predictable aggregate structure capable of charge separation functionality.

Introduction

The printing industry is enjoying a rebirth with the growing need to produce smaller electronic devices. Gravure, flexography and digital printing methods, such as ink jet printing, have been used to produce high quality electronic devices and sensors on a production scale [1]. Printed radio frequency identification (RFID) circuits, for example, have been identified as the 21st century version of the packaging barcode [2]. Active devices, however, are going to require power. Therefore, the RIT Print Science Laboratory focuses on using the printing method as a means to produce efficient power sources for emerging nano-devices.

Photovoltaic devices would be the power source of choice given their portability and renewable attributes. The generalized design of a photovoltaic cell is illustrated in Figure 1.

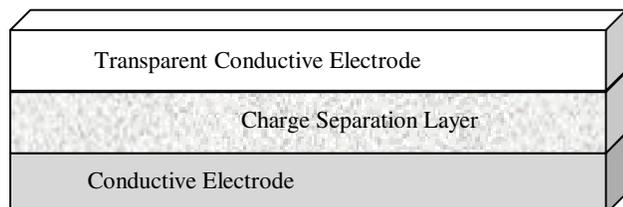


Figure 1. Photovoltaic Device

Dye-sensitized solar cells, such as the Graetzel cell, have been demonstrated, but often suffer from low conversion efficiency [3]. Alternative dye-based designs would involve the fabrication of a charge separation layer using the inherent electronic properties of the dye material rather than relying on electrochemical processes. We choose to fabricate a charge separation layer leveraging the delocalized π electronic character of the polymethine dye (PMD) aggregates.

PMD aggregate properties have been extensively studied and reported in the literature [4,5]. These aggregates have also been used as the charge separation layer in photovoltaic devices [6,7] with limited success. We believe that one reason, for the limited efficiencies, results from the fabrication method. In most cases, dye aggregates are precipitated onto a TiO_2 electrode surface using bulk phase dye solutions. This would result in an inhomogeneous

aggregate distribution of varied structure and electronic character. Our approach is to control the synthesis, and therefore the structure of the PMD aggregate, using a two-step ink jet method. In this method, an aggregate of uniform size and structure can be crystallized via the addition of an aggregate promoter.

Experimental Approach

The optimum dye and promoter concentration will be determined using a two-nozzel ink jet printer developed in our laboratory (see Figure 2).

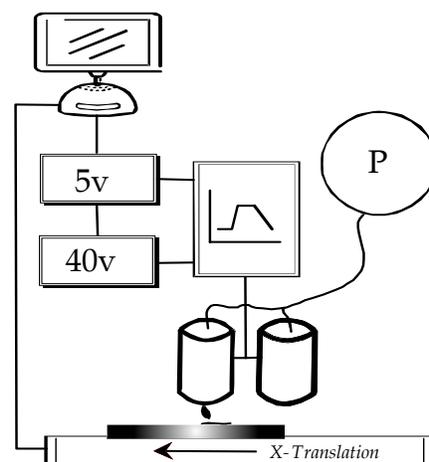


Figure 2. Two-nozzel Ink Jet Printer

This printer is designed using two high speed solenoid valves capable of sub-microliter dispensing by controlling both head pressure (P, compressed nitrogen gas) and electronic actuation waveform (electronic timing circuit). By adjusting these parameters, we can modulate both the spatial and temporal dependence of aggregate formation with dye concentration.

We have selected two dye candidates in our initial survey phase of this project. 4,5,4',5'-Dibenzo-3,3'-diethyl-9-methylthiacarbocyanine bromide (DTCB) and 1,1'-Diethyl-2,2'-carbocyanine chloride (DCC) were chosen for their propensity to form J and H type aggregates in the presence of a promoter. DTCB was prepared at a $250\mu\text{M}$ concentration in distilled water. The DTCB aggregate promoter was sodium chloride prepared at a $23\mu\text{M}$ stock concentration. DCC was prepared at a 10mM concentration in ethanol. The DCC aggregate promoter was 0.2M sodium dodecyl sulfate (SDS) in distilled water.

Solution spectral measurements were obtained using a Cary 100 Spectrophotometer configured with a 1nm bandpass. Reflective spectral measurements were obtained using an Edmund Scientific bifurcated fiber optic collection system integrated onto a

BRC111A CCD array spectrometer. The effective spectral resolution of this system is one nanometer.

Results

DTCB J-aggregate formation, in the presence of increasing NaCl concentration, has been well documented in the literature. Figure 3A illustrates the spectral differences between the monomer and J-aggregate form of DTCB. We found, however, that there was a significant temporal dependence on aggregate formation that may be linked to the solvation rate of reactant species.

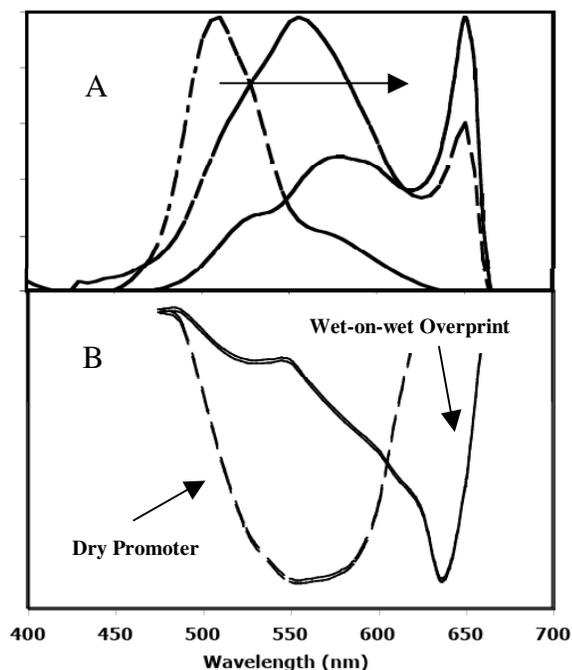


Figure 3. 250mM DTCB in water with (A) increasing concentration of NaCl promoter added dropwise into three milliliters of dye solution, and (B) reflective transmission measurements of a printed dot in the order promoter followed by dye solution. The dry promoter curve corresponds to allowing a one hour time delay between overprinting sequence to allow for sufficient drying.

We first printed the DTCB solution onto an office grade uncoated bond stock. The reflectance spectrum of the dried dye mark, in the absence of promoter, was consistent with DTCB in the monomer form. We followed by overprinting the DTCB dye with the NaCl promoter by introducing a time-delay between the two marks. Figure 3B illustrates that only the monomer species was present when we allowed the promoter mark time to dry before overprinting with DTCB. By overprinting wet-on-wet, or directly (less than a one second delay) overprinting each mark, J-aggregate formation appeared (Figure 3B).

H-aggregate formation was achieved using DCC dye with an SDS promoter. As with DTCB, H-aggregate formation occurred when two components were overprinted wet-on-wet with little intermittent time delay. Figure 4 shows a light micrograph, at 480x magnification, of the surfactant-promoted aggregate. The

approximate aggregate size was measured, in this experiment, to be 600 x 50 μ m.



Figure 4. DCC H-aggregate in the presence of SDS.

Conclusion

According the Fisk's second law of diffusion, the rate of crystal growth is directly proportional to collision, incorporated into a diffusion coefficient, volume and dye concentration terms. Solution phase crystallization of nanoparticles, in bulk or macroscopic volumes, is typically achieved by favoring collision over the diffusion processes through stop-flow type mixing procedures. There still exists, however, a distribution of microenvironments, within any macroscopic volume region, that will result in a corresponding distribution of crystal structures. Our ink jet printing approach is to minimize the volume parameter, which is often the rate-limiting term, by conducting the experiment in sub-microliter volumes further minimized by rapid solvent evaporation rates on the order of the crystallization rate. Since we can control the concentration term, we are left with designing crystal structures based on the time-dependent processes that control crystallization. The ink jet method also provides a mechanism for accurate placement of an aggregate at a pre-determined location on an electrode surface.

Our early experimental results indicated that there appears to be a significant influence of the solvation rate on aggregate formation. At sub-microliter reaction volumes printed onto an absorptive paper support, we can control the promoter concentration by using an overprint time delay. If there is minimal time delay, wet-on-wet overprinting, the crystallization reaction proceeded to a stage whereby aggregates with larger than desired dimensions (Figure 4) were obtained. Likewise, when the time delay supported drying before the placement of the subsequent dye drop, no aggregates were detected. This result suggests that the aggregate formation rate would be much faster than the solvation and diffusion rate. Future experiments will be designed to accurately adjust the overprint time delay to control the crystal morphology.

In order for an aggregate to function as an effective charge separation medium, the crystal structure must be devoid of defects. A single crystal defect, in the aggregate, can quench electron transfer processes necessary for photovoltaic function. Bulk phase preparation methods would result in a distribution of structures of varying efficiency. The low conversion efficiencies may result

from a limited number of aggregates with the optimal structure to support the charge separation process. Our approach is to first learn how to homogenize and control the structure of these aggregates; and then, study the conversion efficiency as a function of size and composition.

The Print Science Laboratory at RIT is also engaged in research to investigate how the printing processes may be leveraged to make the other elements of the photovoltaic device, as well as, RFID technology development. For example, gravure and flexographic proofing resources are being directed to the formulation and manufacture of the conductive electrode elements illustrated in Figure 1. The objective is to obtain an efficient and fully printable photovoltaic cell that can be scaled according to the overall device requirements.

References

- [1] Jennifer Rigney, International Conference on Digital Printing Technologies (IS&T NIP 20, Salt Lake City, UT, 2004) pg. 274.
- [2] L.E. Frenzel, "Tag It!", *Electronic Design*, 53:10, 43 (2005).
- [3] Kohjiro Hara and Hironori Arakawa, *Handbook of Photovoltaic Science and Engineering* (Wiley (2003)), pg. 663.
- [4] Tadaaki Tani, *Photographic Sensitivity: Theory and Mechanisms*, (Oxford (1995)), pg. 111.
- [5] Freek J.M. Hoeben, et. al., "About Supramolecular Assemblies of π -Conjugated Systems", *Chem. Rev.*, 105, 1491-1546 (2005).
- [6] David Adams, et.al., "Charge Transfer on the Nanoscale: Current Status", *J. Phys. Chem. B*, 107, 6668-6697 (2003).
- [7] Kazuhiro Sayama, et.al., "Photochemical Properties of J Aggregates of Benzothiazole Merocyanine Dyes on a Nanostructured TiO₂ Film", *J. Phys. Chem. B*, 106, 1363-1371 (2002).

Author Biography

Scott Williams received his B.S. in Biochemistry from Purdue University (1984), and his Ph.D. in Physical Chemistry from Montana State University (1989). Since then, he has held academic positions at the RIT School of Photography and the Chemistry Department at the South Dakota School of Mines and Technology. He currently teaches materials and process related courses in the RIT School of Print Media. He conducts research in the area of ink and paper coating chemistry.

Aaron Bodell is a senior undergraduate student in the School of Print Media.