



SCIREA Journal of Materials

<http://www.scirea.org/journal/Materials>

March 20, 2019

Volume 4, Issue 1, February 2019

An Innovative Self-Weld Framework of Microscale Copper Phthalocyanine

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Abstract

Microscale frameworks were obtained by copper phthalocyanine-sulfuric acid blends in our proposal. In the frameworks, crystals and unoccupied space are at an equivalent-size level. During dehydration, wires spontaneously weld at their contacts to construct a framework. Dehydrated and post-annealed frameworks have morphological equivalence by the applied imaging equipment. Under incident X- and IR- rays, these α -dominated frameworks have a response of β crystallites. The identification of a new X-ray-crystallographic event in α - β transition is elusive from our obtainable information. We suggest this unidentified state tends to the responsibility of our process. Observing the self-weld and flexibility indicates the high-feasibility of a free standing framework. Our proposed process and frameworks urge for the fundamental understanding in the sulfuric recrystallization of phthalocyanine. Optimizing our process, characterizing properties of frameworks, and understanding in the formation of each phase are in progress.

Keywords: phthalocyanine, framework, polymorphism, sulfuric recrystallization, organic electrode material, porous semiconductor

1. Introduction

A framework is one alternative to achieve a porous bulk in state-of-the-art electrode [1, 2] and substrate [3-8] materials. We believe a metal-phthalocyanine [9-31] framework provides electrical carriers and flexibility as well. Polymeric and semiconductive frameworks diversify the existing small-scale-pored materials [32], such as metallic foam [33-35]. The subsequent hierarchicalization upon these metal-phthalocyanine frameworks is attainable. To realize their structural hierarchy in applications, developing a facile process of metal-phthalocyanine frameworks is demanded. Here, wet-chemically constructing copper phthalocyanine frameworks in microscale is reported by us. Crystal-structural and morphological features of the frameworks were characterized. Our approach fundamentally differs to the well-patented phthalocyanine manufacture via acidic solvents [20, 36-39].

2. Materials and Methods

2.1 Sulfuric Recrystallization of Copper Phthalocyanine

Sulfuric blends consisted of powdery copper phthalocyanine (Pigment 15, TCI) and sulfuric acid ($\geq 51\%$, MACRON FINE CHEMICAL). The dissolution time of green-yellowish blends (Concentration = 0.005 g/ml) was one hour. A blend (Volume = 2 ml) was dropped on a petri-dish (Glass, PYREX) in 1 hour for precipitation of sulfates. To collect blue copper phthalocyanine, sulfates were centrifugalized after rinsing in RO-water. Dilute sulfuric waste was neutralized by an aqueous solution of sodium hydroxide (1.25 M). The neutralized mixture was dried and its sediments were recycled.

2.2 Construction of Frameworks

To coat a framework, the slurry (acicular copper phthalocyanine and RO-water) was dropped on a substrate. Two substrates were adopted: rigid (plain micro slides, VWR) and flexible (premium inkjet transparency film, HP). The framework-coated substrates were dehydrated at 25 °C for 8

hours before further treatments. The post-annealed frameworks on glass slides were obtained at 150 °C for 1 hour. The framework on the transparency film was bended for imaging. One droplet of slurry on a glass slide was naturally dried to observe the self-weld.

2.3 Characterization

Crystal-structural characteristics of raw and recrystallized copper phthalocyanine were recorded by X-ray diffractometer (Cu K α , BRUKER) and Fourier transform infrared spectroscopy (attenuated total reflectance, THERMO FISHER SCIENTIFIC). Micro-structural features and the bended framework were imaged by optical microscopy (ZEISS and NIKON).

3. Results and Discussion

Under optical-microscopic imaging, the architecture of solids by drop-coating is in a blue framework (**Fig. 1**). Microscale solid rods are randomly stacked with unoccupied space in an equivalent size-level. A morphological difference in two frameworks (**Fig. 1a & 1b**) is not observable by our applied imaging method. The crystalline characteristics of framework-coated glass substrates are in α -dominated phase of copper phthalocyanine (**Fig. 2**). To identify foreign peaks to α phase, the precursory copper phthalocyanine powders were tested under the same condition. The hired powdery form is β -predominant with few unidentifiable peaks in the 2 θ -larger-than-20° range. The precursor indexes that β phase's (-211) and (-213) planes exist in our sulfuric recrystallized frameworks. The X-ray-diffractive information of the post-annealed framework majorly approximates to the as-dehydrated one. Only an oddball peak (2 θ near 12.5°) disappears after annealing.

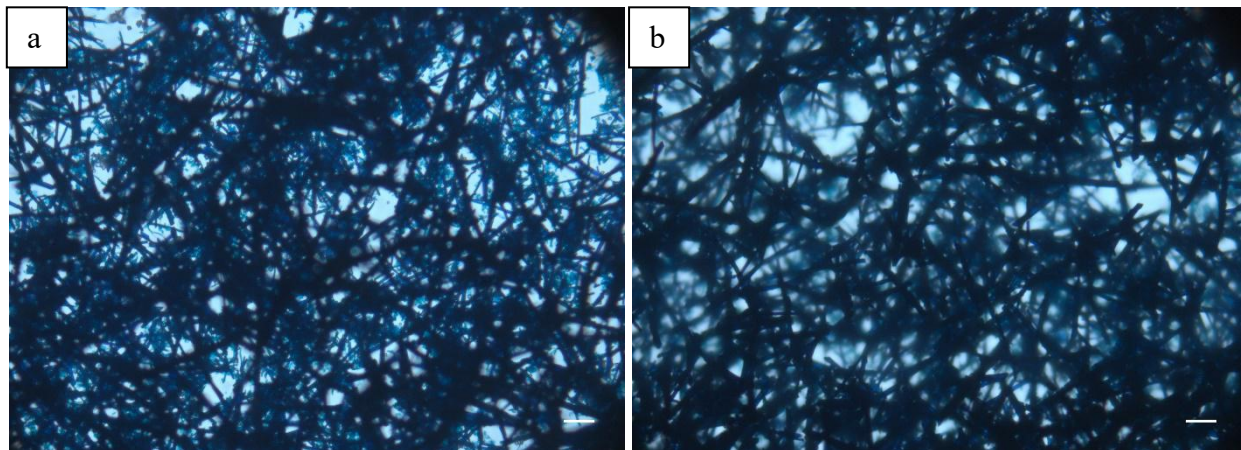


Fig 1. Optical-microscopic plain images of recrystallized frameworks. a. The as-deposited framework. b. The post-annealed framework. The scale bar is 50 μm . A glass slide is used for the substrate of a framework.

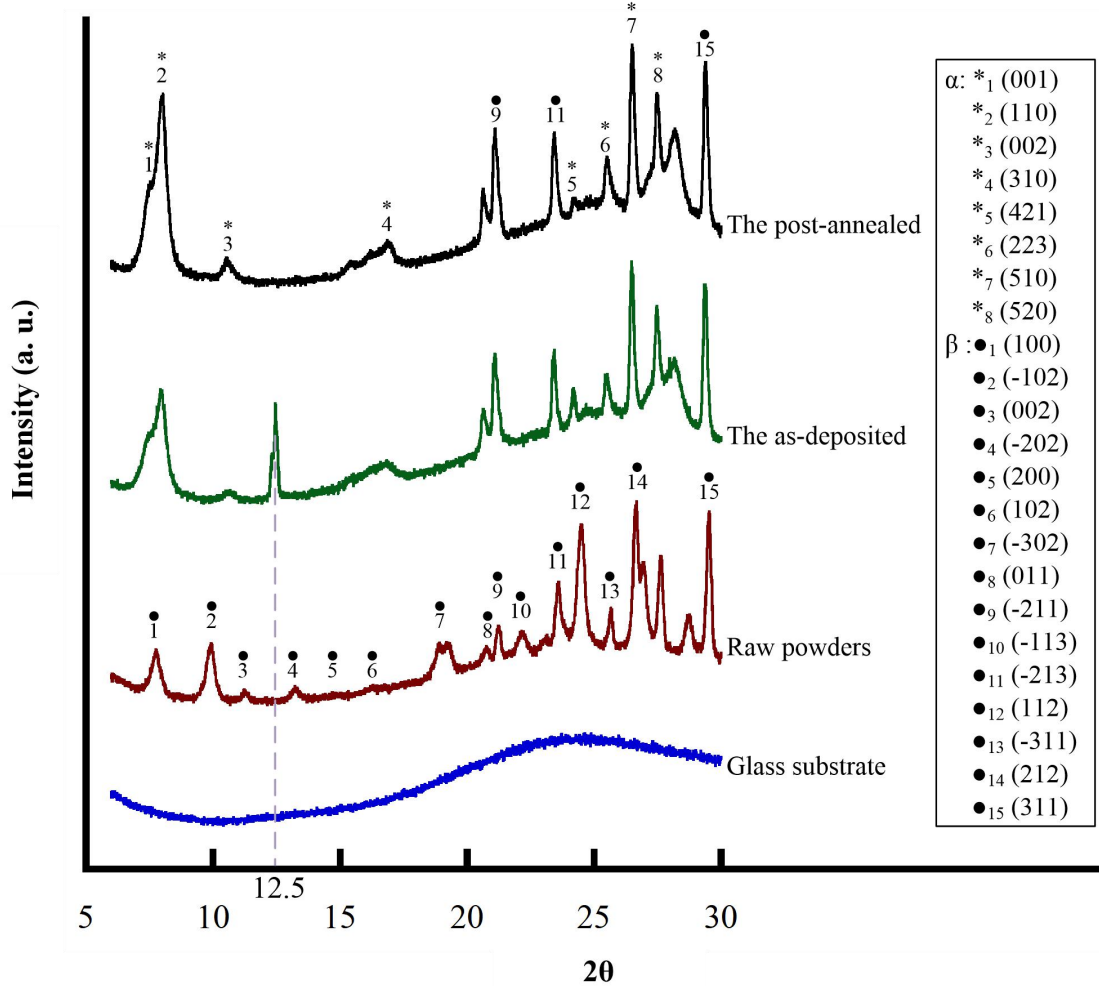


Fig 2. X-ray diffractive crystal-structural characteristics of raw powders and recrystallized frameworks of copper phthalocyanine. A glass slide is used for the substrate of copper phthalocyanine.

We describe this peak as an oddball since where this peak is shows its abnormality. This peak has its identity beyond the documented polymorphism of copper phthalocyanine. For copper phthalocyanine, phase transformation between α and β with specific stimulation has been reported. β -transformational events in a solvate of α -polymorph were recorded, discussed [17, 23, 27], and mentioned [20, 30]. Thermal input converted α -crystals into the more stable β one [9, 30]. Polymorphic behavior from α to β reversed under acidic and mechanical loading [17, 30].

When water diluted a low-sulfuric-concentration blend ($< 60\%$), β -remains were found in a precipitated α -product [20]. Besides α - β polymorphism, the γ - or ε -recrystallization was relative [30] to α phase as well. However, we believe this oddball belongs to transitional peak in the α - β phase transformation or α -related polymorphs. Our point of view is supported by the publishing reports. Primarily, a small change in parameters [30] of sulfuric process varies the crystal-structure of copper phthalocyanine. Further, employing approximately-51% sulfuric acid without purposeful dilution indicates the possibility of α - β -coexistence. Simultaneously, our framework's dubious peak locates in the 2θ -region of α - β -transitional pattern [23, 27]. Intuitively, this peak doesn't result from the possible preferred orientation in our dry slurry. More likely, we consider the employed sulfuric recrystallization brings about this peak in α -modified copper phthalocyanine. Under our hypothesis, the thermal load certainly removes the oddball representing a relatively unstable state. To understand this peak and how β -phase subsists in α -modified rods, further investigation is demanded.

The subsistence of β phase in the α -copper-phthalocyanine frameworks was double confirmed by FTIR (**Fig. 3**). Raw powders of copper phthalocyanine are β -featured: 729, 780, 956, 983, 1101 and 1174 (cm^{-1}). In contrast, both frameworks have α -fingerprints at 720, 770, 864, 870, 940 and 1190 with 956 and 983 (cm^{-1}) of β -signals. IR-responsive decomposition is at 636 or 1068 (cm^{-1}) in the post-annealed framework. Inputting thermal energy relaxes the deformation assigned to C-C out-of-plane [15, 31] and C-H in-plane [31] at respective bands. However, a basis-rearrangement-elicited change in IR-responses of copper phthalocyanine was believed around 726 and 1334 (cm^{-1}) [9, 29, 31]. The disappearance of the diffractive anomaly is still hard-to-treat since polymorphic bands shift or decompose insignificantly after annealing.

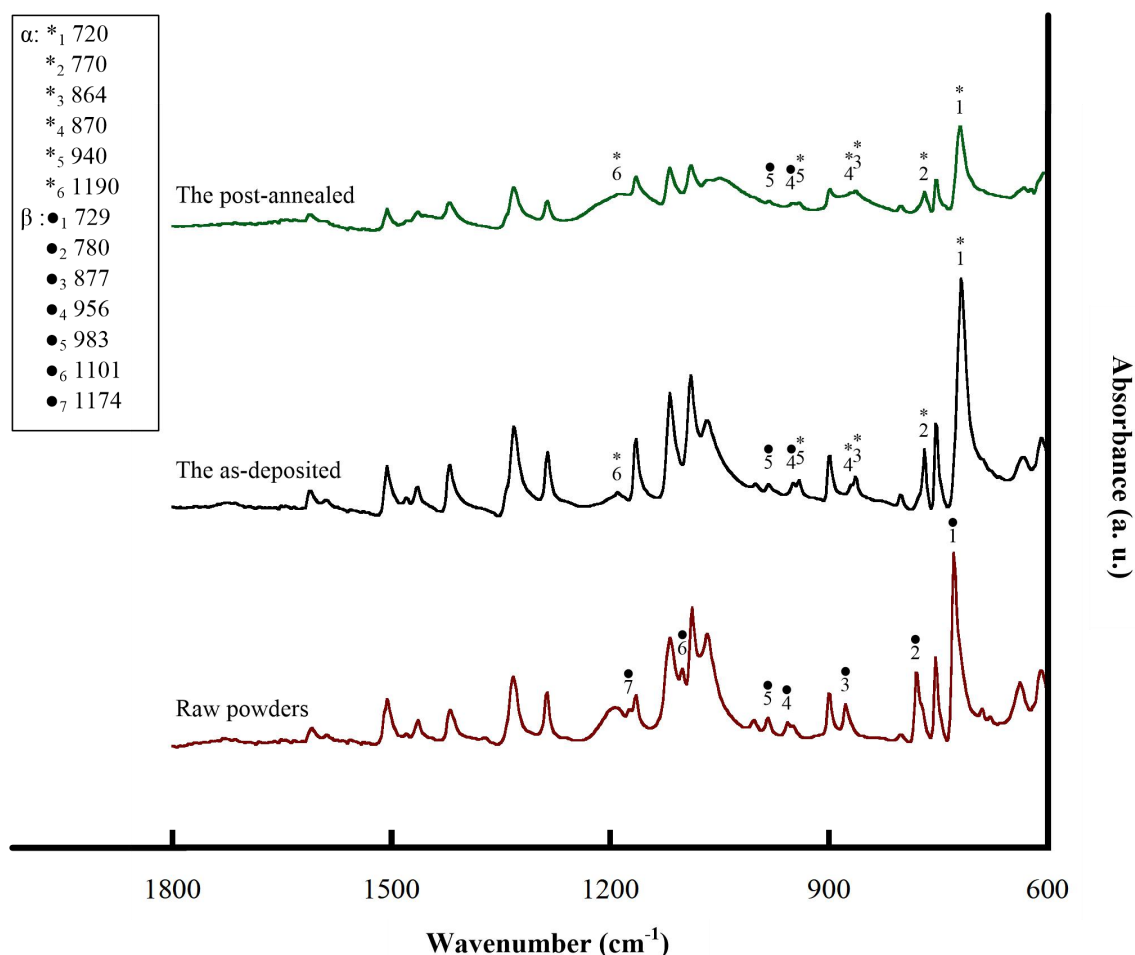


Fig 3. FTIR-responsive crystal-structural characteristics of raw powders and recrystallized frameworks of copper phthalocyanine.

Merged microstructures prove our framework is not a pile of loose copper phthalocyanine micro-rods (**Fig. 4**). Self-weld features were found in the focused neighborhood when a droplet of slurry gradually vaporized on a glass slide. Micro-rods or smaller-scale particles of copper phthalocyanine bind each other at their contacts. In the technological aspect, this combination between solid particles is a self-weld process. The self-weld indicates that the construction of our copper phthalocyanine deposit is a framework. At this size-level, an observable change in microstructures should accompany the detectable phase transformation. When particles aggregate, the transformation from β to α at contacts in the acidic or mechanical process was TEM-imaged [17]. Under SEM imaging, a heap of combined wires from thermal evaporated η -crystalline nanowires during annealing was reported [9]. But, what cohesive adherence contributes to our oddball is undetermined due to a lack of more informative diffraction or structural analyses.

Interestingly, we obtained the β -subsisted α -frameworks in a merely dry process at the room temperature. At present, we only can claim the mechanism of our self-weld should be different to the reported ones [9, 17]. Also, two micro-structural states during self-weld in solvent-processed copper phthalocyanine are first-time imaged by us. Indeed, the crystal- and micro-structural changes in our self-weld during dehydration have to be addressed. To this end, correlative research is in progress.

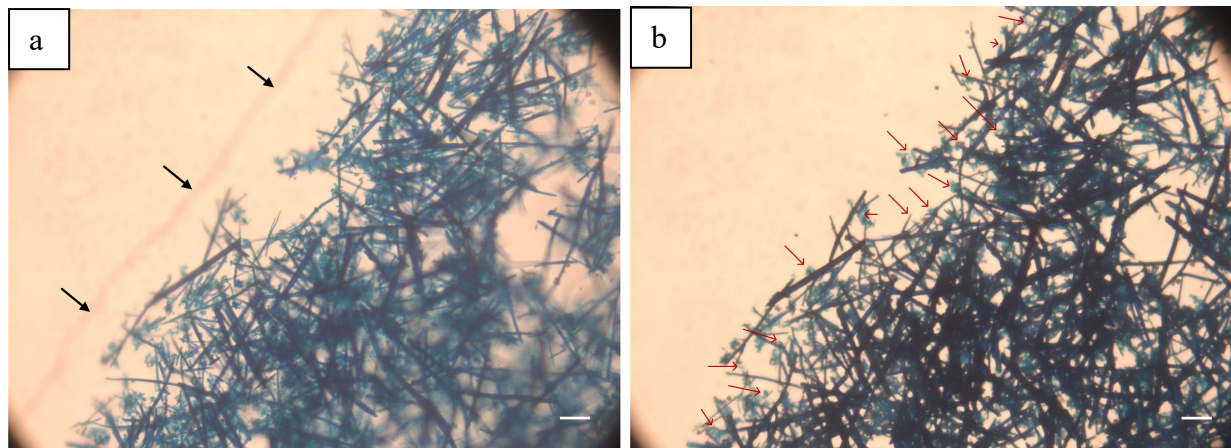


Fig 4. Merged microstructures in a framework during dehydration under optical microscope. a. A droplet of slurry of acicular copper phthalocyanine and RO-water. Black arrows indicate the droplet-substrate-air boundary. b. The droplet of slurry in 20-minute dehydration. Red arrows point out the counted difference in microstructures. The scale bar is 50 μm . A glass slide is used for the substrate of a framework.

To inspect the flexibility, framework-coated transparency film was bent and fixative to image in the middle of the arch (**Fig. 5**). Peeled framework was not observed as well as cracks in the solid rods. This only reveals the potential of our framework in flexibility. To commercialize it as a free-standing framework, flexibility-related properties have to be improved.

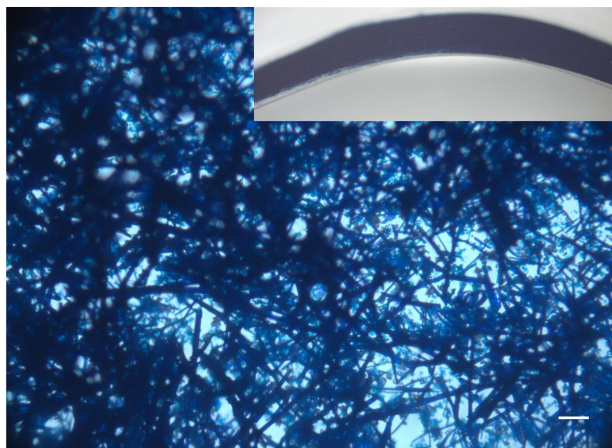


Fig 5. Optical-microscopic plain images of a framework on a bended transparency film. The scale bar is 50 μm . The microscopically zoomed image of the bended multilayers (a framework on a transparency film) is corned.

Our recrystallization of copper phthalocyanine differs to well-established patents [36-39] fundamentally. After 7 days, precipitated sulfates were not detected in a randomly sampled droplet of bottled blend (**Fig. 6**). In optical-microscopy, the bulk solution of the droplet is still clear, transparent and green-yellowish. The droplet IR-spectrally resembles to the one of aqueous sulfuric precursor [40-42]. Additionally, instead of concentrated sulfuric acid, an approximately-51 % aqueous one was used by us. To synthesize copper phthalocyanine sulfates, a blend was poured on a petri-dish. The poured solution was spontaneously separated into a colorless region and a green one in an hour. All of them disobey the claims: copper phthalocyanine sulfates form instantly during mixing or diluting. Our acicular copper phthalocyanine sulfates certainly precipitates in a different mechanism. Also, the sulfuric copper phthalocyanine blends hydrate somehow unlike the related publications. Moreover, the observed transparency of the as-poured droplet can inform us qualitatively. In α -sulfuric modification [20], this entirely soluble state of copper phthalocyanine in the hired solvent provides clarification. The phase of powdery precursor unlikely remains to be detected in one α -modified precipitate when the limit of solubility is satisfied. In consequence, our β -crystallites are recrystallized in an unknown path of α -modification. Consequently, the possible origin of the oddball is narrowed down since raw β -powders are irrelevant to our frameworks. Of course, delivering the mentioned mechanism or path is ongoing.

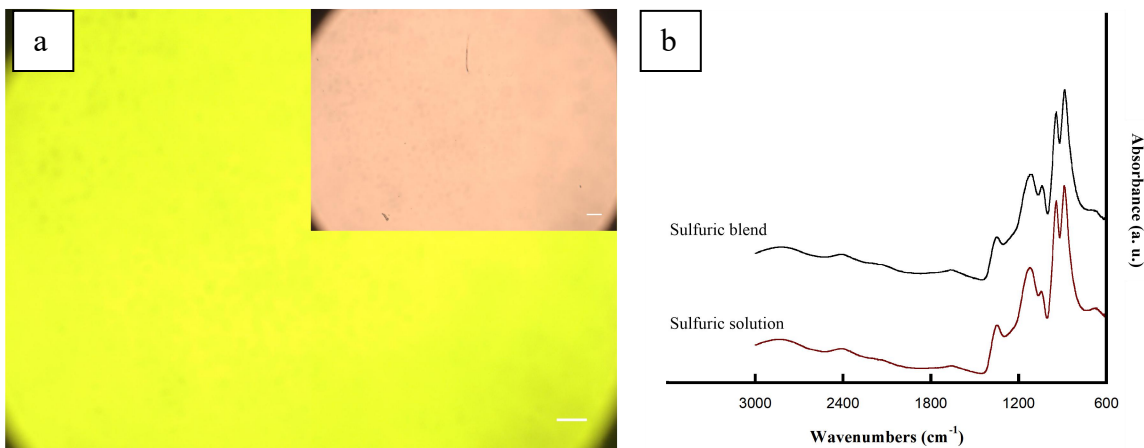


Fig 6. a. Optical-microscopic plain images of a droplet from the bottled 7-day-old sulfuric blend. The scale bar is 50 μm . The same-condition-imaged glass substrate is corned as reference. A glass slide is used for the substrate of a droplet. b. The FTIR-responsive characteristics of a droplet by the bottled 7-day-old sulfuric blend. A droplet of the applied sulfuric solution is shown as a reference.

4. Conclusions

In summary, we have developed a method to construct alternative frameworks for high-porosity electrodes and substrates. Our novel method and framework can be a paradigm for the series of phthalocyanines. In our approach, copper phthalocyanine frameworks were drop-stacked on substrates from slurry of rinsed precipitates. A morphological difference in the post-annealed framework is not observable. On the glass slide, β -characteristics were spectrally detected in the α -predominant frameworks under dehydration or annealing. One high-possibility transitional behavior between α and β polymorphs was exposed in X-ray-diffractive record. Hypothetically, our process is responsible for this unidentified peak. Fused features were found at the contacts in rod-constructed frameworks. Bending the framework coated transparency film shows the potential flexibility of frameworks. We are attempting to characterize the copper phthalocyanine framework's responses under applied stimulation. Optimizing our proposed process for large-scale free standing frameworks is ongoing. To recrystallize phthalocyanines, our procedure suggests that the sulfuric precipitation should be better understood.

References

- [1] Shobana, M.K. and Y. Kim, Improved electrode materials for Li-ion batteries using microscale and sub-micrometer scale porous materials - a review. *Journal of Alloys and Compounds*, 2017. 729: p. 463-474.
- [2] Biesheuvel, P.M., Y. Fu, and M.Z. Bazant, Diffuse charge and faradaic reactions in porous electrodes. *Physical Review E*, 2011. 83(6): p. 061507.
- [3] Liu, P.S., X.B. Xu, W. Cheng, and J.H. Chen, Sound absorption of several various nickel foam multilayer structures at aural frequencies sensitive for human ears. *Transactions of Nonferrous Metals Society of China*, 2018. 28(7): p. 1334-1341.
- [4] Rao, Z., Y. Wen, and C. Liu, Enhancement of heat transfer of microcapsulated particles using copper particles and copper foam. *Particuology*, 2018.
- [5] Zhang, Y., F. Chen, X. Tang, H. Huang, M. Ni, and T. Chen, Preparation and characterization of paraffin/nickel foam composites as neutron-shielding materials. *Journal of Composite Materials*, 2018. 52(7): p. 953-962.
- [6] Latorre, N., F. Cazaña, V. Sebastian, C. Royo, E. Romeo, M.A. Centeno, and A. Monzón, Growth of carbonaceous nanomaterials over stainless steel foams. Effect of activation temperature. *Catalysis Today*, 2016. 273: p. 41-49.
- [7] Yang, F., K. Cheng, K. Ye, X. Xiao, F. Guo, G. Wang, and D. Cao, Au- and Pd-modified porous Co film supported on Ni foam substrate as the high performance catalysts for H₂O₂ electroreduction. *Journal of Power Sources*, 2014. 257: p. 156-162.
- [8] Choi, W.S., H.R. Jung, S.H. Kwon, J.W. Lee, M. Liu, and H.C. Shin, Nanostructured metallic foam electrodeposits on a nonconductive substrate. *Journal of Materials Chemistry*, 2012. 22(3): p. 1028-1032.
- [9] Zou, T., X. Wang, H. Ju, L. Zhao, T. Guo, W. Wu, and H. Wang, Controllable molecular packing motif and overlap type in organic nanomaterials for advanced optical properties. *Crystals*, 2018. 8(1): p. 22.
- [10] Katsumi, N., Y. Shin, and N. Tomonobu, Controlling molecular condensation/diffusion of copper phthalocyanine by local electric field induced with scanning tunneling microscope tip. *Japanese Journal of Applied Physics*, 2018. 57(2): p. 020301.
- [11] Kumar Ghorai, U., S. Saha, N. Mazumder, N.S. Das, D. Banerjee, D. Sen, and K.K. Chattopadhyay, Experimental and theoretical investigation of enhanced cold cathode

- emission by plasma-etched 3d array of nanotips derived from CuPc nanotube. RSC Advances, 2015. 5(30): p. 23847-23854.
- [12] Ghorai, U.K., S. Das, S. Saha, N. Mazumder, D. Sen, and K.K. Chattopadhyay, Efficient and persistent cold cathode emission from CuPc nanotubes: a joint experimental and simulation investigation. Dalton Transactions, 2014. 43(24): p. 9260-9266.
- [13] Ghorai, U.K., S. Saha, S. Shee, and K.K. Chattopadhyay, Facile synthesis, self-assembly mechanism and field emission property of copper phthalocyanine nanowires. AIP Conference Proceedings, 2013. 1536(1): p. 223-224.
- [14] Prabakaran, R., E. Fortunato, R. Martins, and I. Ferreira , Fabrication and characterization of hybrid solar cells based on copper phthalocyanine/porous silicon. Journal of Non-Crystalline Solids, 2008. 354(19): p. 2892-2896.
- [15] Kato, H., S. Takemura, K. Iwasaki, Y. Watanabe, N. Nanba, T. Hiramatsu, O. Nishikawa, and M. Taniguchi, X-ray photoemission spectroscopy and Fourier transform infrared studies of electrochemical doping of copper phthalocyanine molecule in conducting polymer. Journal of Vacuum Science & Technology A, 2007. 25(4): p. 1147-1151.
- [16] Hassan A.K. and R.D. Gould, Structural studies of thermally evaporated thin films of copper phthalocyanine. Physica Status Solidi (a), 1992. 132(1): p. 91-101.
- [17] Fryer, J.R., R.B. McKay, R.R. Mather, and K.S. Sing, The technological importance of the crystallographic and surface properties of copper phthalocyanine pigments. Journal of Chemical Technology and Biotechnology, 1981. 31(1): p. 371-387.
- [18] Assour, J.M., On the polymorphic modifications of phthalocyanines. The Journal of Physical Chemistry, 1965. 69(7): p. 2295-2299.
- [19] Bock G. and W. Fabian, Novel pigmentary form of β -copper phthalocyanine. U. S. Patent 4370270, 1983.
- [20] Smith, F.M. and J.D. Easton, Phthalocyanine pigments-their form and performance. Journal of the Oil & Colour Chemists Association, 1966. 49(8): p. 614-630.
- [21] Hoshino, A., Y. Takenaka, and H. Miyaji, Redetermination of the crystal structure of α -copper phthalocyanine grown on KCl. Acta Crystallographica Section B, 2003. 59(3): p. 393-403.

- [22] Jung, J.S., J.W. Lee, K. Kim, M.Y. Cho, S.G. Jo, and J. Joo, Rectangular nanotubes of copper phthalocyanine: application to a single nanotube transistor. *Chemistry of Materials*, 2010. 22(7): p. 2219-2225.
- [23] Norimichi, K., S. Takao, and M. Kenjiro, The effect of metal oxides on the transformation of copper phthalocyanine crystals in organic solvents. *Bulletin of the Chemical Society of Japan*, 1976. 49(8): p. 2029-2032.
- [24] Maggioni, G., A. Quaranta, S. Carturan, A. Patelli, M. Tonezzer, R. Ceccato, and G. Della Mea, Deposition of copper phthalocyanine films by glow-discharge-induced sublimation. *Chemistry of Materials*, 2005. 17(7): p. 1895-1904.
- [25] Resel, R., M. Roland, M. Ottmar, M. Hanack, J. Keckes, and G. Leising, Preferred orientation of copper phthalocyanine thin films evaporated on amorphous substrates. *Journal of Materials Research*, 2000. 15(4): p. 934-939.
- [26] Zongo, S., M. S. Dhlamini, P. H. Neethling, A. Yao, M. Maaza, and B. Sahraoui, Synthesis, characterization and femtosecond nonlinear saturable absorption behavior of copper phthalocyanine nanocrystals doped-PMMA polymer thin films. *Optical Materials*, 2015. 50: p. 138-143.
- [27] Suito, E. and N. Uyeda, Transformation and growth of copper-phthalocyanine crystal in organic suspension. *Kolloid-Zeitschrift und Zeitschrift für Polymere*, 1963. 193(2): p. 97-111.
- [28] Xu, Z., K. Li, H. Hu, Q. Zhang, L. Cao, J. Li, and J. Huang, From bulk to nano metal phthalocyanine by recrystallization with enhanced nucleation. *Dyes and Pigments*, 2017. 139: p. 97-101.
- [29] Achar, B.N. and K.S. Lokesh, Studies on polymorphic modifications of copper phthalocyanine. *Journal of Solid State Chemistry*, 2004. 177(6): p. 1987-1993.
- [30] Erk, P. and H. Hengelsberg, Phthalocyanine dyes and pigments. *The Porphyrin Handbook: Applications of Phthalocyanines*, 2003. 19: p. 106-146.
- [31] Verma, D., R. Dash, K.S. Katti, D.L. Schulz, and A.N. Caruso, Role of coordinated metal ions on the orientation of phthalocyanine based coatings. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2008. 70(5): p. 1180-1186.
- [32] Zhu, C., Z. Qi, V.A. Beck, M. Luneau, J. Lattimer, W. Chen, M.A. Worsley, J. Ye, and E.B. Duoss, Toward digitally controlled catalyst architectures: hierarchical nanoporous gold via 3D printing. *Science Advances*, 2018. 4(8): p. eaas9459.

- [33] Atwater, M.A., L.N. Guevara, K.A. Darling, and M.A. Tschopp, Solid state porous metal production: a review of the capabilities, characteristics, and challenges. *Advanced Engineering Materials*, 2018. 20(7): p. 1700766.
- [34] Singh, S. and N. Bhatnagar, A survey of fabrication and application of metallic foams (1925–2017). *Journal of Porous Materials*, 2018. 25(2): p. 537-554.
- [35] Chakravarty, U.K., An investigation on the dynamic response of polymeric, metallic, and biomaterial foams. *Composite Structures*, 2010. 92(10): p. 2339-2344.
- [36] Fredrick, G.P., Preparation of phthalocyanine pigments. U.S. Patent 2365464, 1944.
- [37] Schiessler, S., E. Spietschka, W. Tronich, and A.G. Hoechs, Process for the purification of copper phthalocyanine. U.S. Patent 4010180, 1977.
- [38] Schiessler, S., E. Spietschka, H.G. Elinkmann, and A.G. Hoechst, Process for preparing copper phthalocyanine pigments of α -modification. U.S. Patent 4056534, 1977.
- [39] Phthalocyanine copper dispersion system and preparation method thereof. China patent CN103992328A, 2014 (in Chinese).
- [40] Huntley, C.J., K.D. Crews, and M.L. Curry, Chemical functionalization and characterization of cellulose extracted from wheat straw using acid hydrolysis methodologies. *International Journal of Polymer Science*, 2015: p. 9.
- [41] Biermann, U.M., B.P. Luo, and T. Peter, Absorption spectra and optical constants of binary and ternary solutions of H_2SO_4 , HNO_3 , and H_2O in the mid infrared at atmospheric temperatures. *The Journal of Physical Chemistry A*, 2000. 104(4): p. 783-793.
- [42] Giguère, P.A. and R. Savoie, Les spectres infrarouges de l'acide sulfurique et des oléums. *Canadian Journal of Chemistry*, 1960. 38(12): p. 2467-2476.