A Conversation with Prof. Angela Belcher: Leader in Biotemplated Nanomaterials

IMAGE COURTESY OF PAUL S. WEISS

Prof. Angela Belcher in front of her laboratory at MIT.

I met with Prof. Angela Belcher at her office at MIT last month. We talked about her work using viruses to template materials, where the field is going, and the challenges ahead.

PSW: What first made you think about templating structures with viruses?

Angela Belcher: It really started with my Ph.D. work, which was on how abalones make shells [Figure 1].[1−7] I was and still am fascinated by how biology is so good at making really exquisite structures at the nanoscale. Abalones make $CaCO_3$ and they can control [its] crystal structure. Calcium carbonate is very fascinating considering that you do not have to have a change in temperature or a change in pressure, but you can grow and control two different crystal structures of materials. As a graduate student, I isolated the proteins that can grow one crystal structure *versus* another.[6]

Then, looking at the periodic table and isostructures of $CaCO_3$, you quickly realize that there are isostructures of $CaCO_3$, but none of them are very interesting technological materials. I started thinking, "How do you get proteins controlling any kind of material you want on the periodic table?" because nature's only done this with a handful of materials (silica, calcium phosphate, iron oxide, calcium carbonate).[8] I started thinking about how we could make that connection between protein structure and inorganic materials.

I first started thinking about antibodies; basically, "Can you inject rabbits with semiconductors and try to raise antibodies against them?" And that is hard for a couple of reasons: it is a pretty messy unknown, and I'm a vegetarian, so I do not like to do animal research if I do not have to.

About that time I heard about phage display, which is a pretty simple system, using bacteriophages that have DNA inserts into genes that code for proteins that make up the coat of the virus. And wow! In a 1-μL sample you can have a billion different possibilities! We tried that when I first got to the University of Texas and it worked really well.[9] We got from binding materials to growing materials. We got to where we could bind five particles on the head of a virus—very fun but not that practical!

We started thinking about how nature already gave us this wonderful template, which is

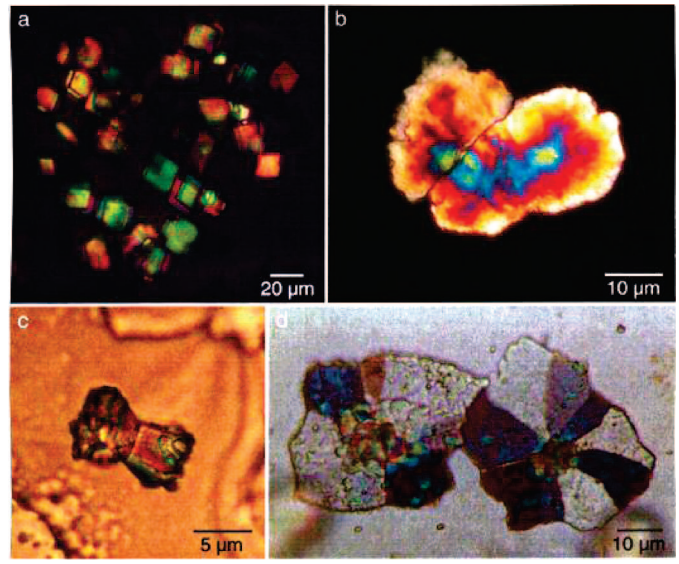

Figure 1. Abalone shell structures are composites of biomolecules and calcium carbonate. Light micrograph (under polarized light) of crystals grown *in vitro* using proteins from abalone, including nuclein (all), and (a) producing calcite; (b) calcitic proteins producing calcite; (c) aragonitic proteins producing aragonite; and (d) a mixture of calcite and aragonite proteins producing aragonite.[1] Reproduced with permission from ref 2. Copyright 1996 Macmillan Publishers Ltd (http://www.nature.com).

To hear Prof. Belcher's advice to young scientists, please visit us at the audio page of http://www.acsnano.org/.

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the crystalline structure of M13 bacteriophage.[10] If you could capture that crystallinity of an organic molecule and *translate* it into an inorganic material, then you would have something. It was luck. I would love to say it was completely planned, but it was luck that we picked such a beautiful virus to work with; it is great at templating wires [Figure 2].[11−15]

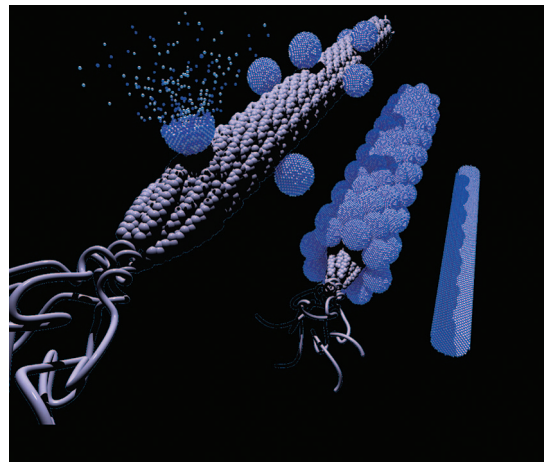

Figure 2. Schematic of nucleating, growing, and annealing a templated nanowire on the M13 bacteriophage.[12] Reprinted with permission from from ref 12. Copyright 2004 AAAS.

PSW: What are the biggest challenges when you choose a new material or a new structure as a target?

Angela Belcher: *Binding* a material is easy; we can bind a material to almost anything. One of the biggest issues always, even with binding a material, is what that surface looks like under the conditions of your selection, because it is always about surfaces. The first material we ever started with is probably the hardest, which is GaAs. Gallium arsenide is great at forming oxides, and at least from what I can tell, the oxides are not that uniform. Trying to find a material that forms a predictable surface is important.

We've spent some time and effort over the last couple of years working in nonaqueous conditions and we've done two things: (1) evolve our organisms to be in nonaqueous conditions and (2) modify them so that they can be in other solutions as well and at the same time still maintain their selectability (we have not published this yet). That is going to go a long way toward pushing us in directions that we could not go before based on no longer being as limited to a [particular] solvent system. That is always one of the main things that we look at.

We used to ask the question, "Wouldn't it be *interesting* if...?" We spend a lot less time asking that question now because we have to make *useful* things. We have to make useful things that are at least competitive with how things are made now. Making a really beautiful material biologically that functions at least as well as it is made now is not useful. A couple of years ago, it was useful. A couple of years ago, it was something you could get funded to do. Now it is not; at least I cannot get funded to do it.

We look at problems. That is the way we approach the universe now. What are the big problems in the world? Are there any materials problems? Most problems that I can come up with are materials problems; if not chemistry, they are materials problems. We're pretty lucky in that way. Then, we say, "Is there something about our process that we think can improve the performance of a material, device performance?" Also, "can we do it in a way that is environmentally friendly? At room temperature?" Things like that. Unfortunately, those issues, room-temperature synthesis, maybe even less expensive [methods], have to take a second seat to device performance. We're asking, "*Can* we make a device or material that has better device performance than can be made any other way, and do it under these other conditions?"

PSW: What do you see as the biggest materials problems, and most significant areas where you can contribute, or where nanoscience more generally can?

Angela Belcher: I'm not looking at materials problems as much as looking at world problems. One of the main areas we are focused on is energy. It is definitely a problem, but it is definitely an *opportunity*. As far as I can tell, it is a chemistry problem (although I'm trained as a chemist, so everything is a chemistry problem!). There are a lot of materials and chemistry problems or opportunities.

Most of these are about device performance, whether it is device performance of something like solar [energy], which is a device performance problem, and an efficiency problem, but it is *also* a cost. It is environmental issues as well.

Batteries are a very active area of research for us right now, so, energy storage [is a significant area].[14] We're also in catalysis, and water-splitting, for example. All of those are about catalysts, the active materials are from chemistry and materials science.

Where we see we have an advantage in a lot of these systems is in if you want to put two kinds of materials together in close proximity, in particular locations, so that they're either electronically or optically coupled. That is something we think biology can add, because we think biology or the virus or proteins has a soft template. If you can grow, nucleate, or place something together with a soft template, a lot of times that is going to get around some of the strain or compatibility problems that you might encounter. We call it "nanoalloying" or "biological nanoalloying" materials for improved device performance.

We see [the need for proximal design] all the time. One reason I'm so excited about this particular work on Ag nanowires is that it is the first time that we've been able to grow single crystalline materials by *matching* the biological template. That is the way biology does it; biology grows single-crystal $CaCO_3$ materials over a pretty large scale and that is hard to do. We're excited about being able to grow those materials just over the fact that they are beautiful materials, but at the same time they are re-

ally key in some of the battery work that we are doing right now. An issue in battery work is how to get good electrical conductors and ionic conductors right next to each other, to get the best device performance. I think we show 40% improvement in device performance over some of our other work adding 4−5% Ag wires into these kinds of structures. So, it is all about alloying.

PSW: How about growing heterostructures and hybrid structures? Is that something that works?

Angela Belcher: It is pretty neat that in the example that I just gave, you can think about growing two different kinds of materials or different kinds of wires and mixing them together to get improved device performance. Or, you can think about growing two materials interdispersed on a single wire. Our greatest improvement in device performance comes in the latter, where we're *stochastically* growing them side-by-side. Mixtures of the two [different materials] together makes them good ionic conductors and electrical conductors at the same time. That is the case for all our work right now. It is the case for our solar work; it is the case in our catalysis work. It is coupling these two different materials with two different properties together.

PSW: Can it be done in a more organized way? Can you make larger heterostructures?

Angela Belcher: We can definitely make larger heterostructures. Something that is hard for us and is an area that we have been looking at is more like "digital structures" and making "digital alloy" structures on a small scale. That is actually more difficult. We're working on that and we have some promise in that area, but again it is a change of thinking. We say, "We're really good at *this*; where are the applications where things don't have to be perfectly ordered?" One of the things we started to look at around 2005 were at materials that have to be really good but not perfect. That is what we've been focusing on. If you think about batteries and things like solar energy, those materials have to be really good but not perfect. The same is true for catalysts. This is different than if you are trying to build a transistor or something where everything has to be working in order for the whole thing to work.

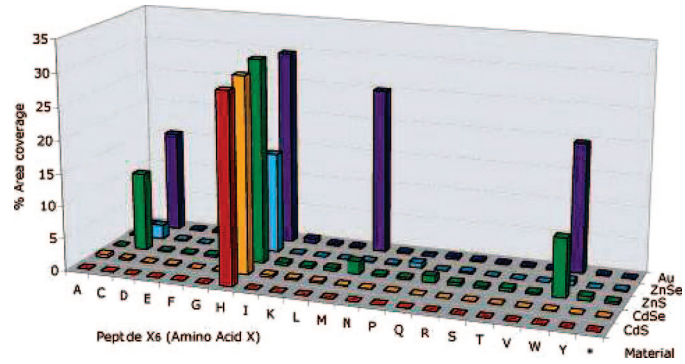

Figure 3. Homohexamers of each of the 20 natural amino acids were tested for binding to 5 inorganic materials: single-crystalline CdS, CdSe, ZnS, and ZnSe, and polycrystalline Au. The peptides were displayed on the surface of yeast.[16] Reproduced with permission from ref 16. Copyright 2005 American Chemical Society.

PSW: To what extent is there a predictive understanding of what will produce a particular material?

Angela Belcher: That is a really good question. We've looked at that on a couple different levels. I have a paper sitting on my desk that we have not sent out yet, which is our first modeling paper on amino acid sequence and structure and is targeted toward metal oxides.

We did some experiments a couple of years ago where we asked, "What's the right length of amino acids to use?" because it is something that we really did not know. We know from natural biological systems the lengths of those protein structures that actually maintain the structures of the proteins. We did some experiments with random length libraries (we did this in yeast instead of using bacteria). We let the proteins tell us what was the ideal length. We did from about 25 or 30 amino acids to 6 amino acids. What fell out of all that (fortunately for us) was that about 10−12 amino acids was the right size, which was the size that we had been using.

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Then, we did some experiments again where we said, "How important is the particular functional group?" When you think of amino acids, you think of positive and negative charges; you think of hydrogen bonding. What are the kinds of things that are important? We made all the one-amino-acid peptides and tested just those against a bunch of II−VI materials and Au.[16] What we found from that was (not surprisingly) cysteine is a good binder, histidine is a good binder, but those poly-amino-acids are not good *discriminators* [Figure 3], and that was pretty interesting. Then, we started looking at not only what is a good binder but what is next to it. We found that was equally important—maybe not so surprising. While there are things that are good binders, what's *next* to that binder has a big influence to how well it binds to that particular type of material.

What we found is that every material has its own "fingerprint". You can look at CdSe *versus* CdS; they have the same kinds of binders, but the modulators between them (up-regulators and down-regulators) would be different. We've been modeling that for the last year or so. We've made some peptides completely from scratch based on lessons learned. We can make some completely from scratch and tell if it would be a good binder.

Now, backing up a little bit more is what makes a good nucleator. That is a much harder question. Modeling a good nucleator is not something we've even attempted yet. We're pretty excited about modeling good binders now. But, one of the things that we have learned by working on metals and metal oxides is that something that nucleates one metal oxide has a good chance of nucleating another. So again, that is a part of our lessons learned.

PSW: Are unnatural amino acids[17] useful or is that too broad a phase space for now?

Angela Belcher: You know, I *really* want to work in artificial amino acids, but we have a rule that we've started working on in the last three years—let us try to make things as easy as possible, not necessarily as hard as possible, which is a new approach for me.[18] So far, we have not found a material that we cannot work with, with the 20 amino acids that we have, in terms of binding. Growing is something different.

I really want to be in the III–V semiconductor growth space, and I think that unnatural amino acids may help get us there. It is a little bit complicated in terms of expressing the unnatural amino acids in the phage. I've talked to great people in that area. When I get really stuck, it might be a place that we can go, but right now it is just not my area of expertise, and it is going to take a large jump to get there. I think it is going to be *great* if we ever have the space to get there.

PSW: What do you see as the biggest challenges coming up? Do you feel like, "We have to solve 1, 2, and 3 and that will open up new capabilities"?

Angela Belcher: We're working on about 10 different things right now. [Production] scale is always an issue for us. That is always a later point, because if you cannot make the material better, and you cannot make the performance better, who cares about scale? But, it is almost always an important part of what we think about.

We're working on materials for plug-in hybrids, for batteries; we have lots of different solar projects we're working on. And eventually, "How do you scale it to a rooftop?" or, "How do you scale it to a [Toyota] Prius or something like that?" Thinking about how to take biology to scale is something that is always in our minds. We're working on capturing CO_2 from coal plants. That is a scale problem.

I do not think about that in terms of "1, 2, 3." We started working on batteries; we published our first paper on that in 2006.[14] We started working on the anode materials and did not realize the cathode materials were harder. Right now we have about five different cathode problems that we're working on. Again, we are working on device performance. One of the biggest problems there is: how do I get my specific capacity up? We got the specific capacity up. It looks *great*. How do you get your power density up? That is a harder problem. Maybe we've got our power density up, but how do we get cyclability and performance up? That is the case that we get and then go, "Let's get specific capacity." Check, got that. Now, "Let's get cyclability; let's get energy density." Once we get all of those, *then* you say, "How do you get scale?"

PSW: One of the things that you alluded to is that some materials have quite varied surfaces in terms of stoichiometry, structure, and so forth. Is that an advantage? Gallium arsenide is the one I know: it has many different stoichiometries, many different structures,[19] and according to what you put on it those would vary. Does that flexibility end up being an advantage, a disadvantage, a control element, or does it factor in at all?

Angela Belcher: I think stoichiometric control is absolutely *key* and a main part of what we try to do is control that. It is not even just stoichiometry but it is things like Fe_2O_3 *versus* Fe_3O_4, or if you look at materials for catalysis, a lot of times their oxidation states are equally as important or more important—they are active or not, depending on the oxidation state. In catalysis, it is not only the stoichiometry, but it is the number of defects on the surface, controlling the oxygen defects and things like that. That is one of the things that we're really good at; that is one of the things biology is really good at and has been a major focus for us because the difference between an active material and nonactive material is based on all of those factors. We look at our system as an advantage in that case, because we're good at when protein structure can control a particular oxidation state and that, for us, is critical.

> We're only interested in doing useful science and useful technology that can have a big impact in the world.

PSW: Are you able to use to advantage of those taking the opposite approach, nanoparticle growth with surfactants and the resulting materials? Do you learn something there, or do you have to be self-reliant in that regard?

Angela Belcher: All we're trying to do is to make things better and we use anything we can to get it to be better. We use materials and processes all the time that are made with surfactants. If their material is better than ours, then we will use that material, exchange out our protein for whatever stabilizes the surfaces and use those premade materials. We do that for some of our III–V materials for solar [applications]. We look at the world as not *only* a phage will solve it, but can we help solve a problem with proteins? We will use any means that are available to us to get the desired outcome.

PSW: What are your ultimate goals? What do you want to accomplish with this methodology?

Angela Belcher: My goals have started to change over the years because at one point my goal was to make materials and devices at least as well as you can make by other mechanisms

(high temperature, pressure, cleanrooms). I feel like that is pretty accomplishable; I feel like, in the work that has come out and is coming out, we've shown that the materials and the devices that we make (at least prototypes of them) are comparable to those made in other processes. I feel like I've checked that off the list, and so [we] have to move the bar.

We're only interested in doing useful science and useful technology that can have a big impact in the world. Right now, that is why we are focusing primarily on energy, but we're also focusing on medicine. We've accomplished some of what we initially set out to accomplish in that it is no longer a wacky or crazy idea that this is achievable. It is being done in more mainstream places than just academia now, which is pleasing to me.

On the next horizon for us is making materials that can repair themselves, making them "smarter", [*i.e.,*] not only making good quality materials, but materials that can correct themselves and heal themselves. Now all of a sudden, that is reaching too far, people say. I cannot always see the direct pathway there, but biology does it. We have to be able to figure out a way to do that.

Again, scale is an issue. Getting things into the marketplace eventually. Clean chemistry, clean processing. How do you not add waste back into the environment? Some of the battery materials [problems] we're working on with Paula Hammond here at MIT are "can you make them as biodegradable as possible?"

PSW: In the self-repairing materials you mentioned, are you keeping the biological components in, and then keep operating?

Angela Belcher: We're working on this a couple different ways. One of the things that we're looking at is how to repair cracks in large equipment. In that case, I'm not thinking about it as repairing by a cellular mechanism, because that is a bit harder, but how do you make materials or coat them with paints and things like that so as a crack starts to develop it heals itself. That is the place we're starting. We have a program on finding "mistakes" in materials and then trying to heal those mistakes.[20]

I go through BlackBerrys a lot, because I break them all the time, and it is *such* a pain. Healing things like that would be a big advantage.

> How do we harness the potential of this country's youth to get them fired up about science and engineering?

PSW: When you realized your goals were attainable in the near term did you find that disturbing?

Angela Belcher: I have three main life goals. One of them, on the scientific side, is to use biology to make useful materials with clean processing to change the way things are manufactured. That is attainable to me or I can see that as being attainable.

The second goal has to do with my companies, which is commercialization and having successful companies.

The third is having a very large impact on education, mostly in grades K-12. I think that is the hardest of all. That is the one that is going to require the most time. How do we harness the potential of this country's youth to get them fired up about science and engineering? We have a couple of hundred students come through this laboratory and involved in projects, but how do you scale that? How do you have an impact on *millions* of kids? To me, the other two are much easier than the last.

PSW: Do you differentiate between chemistry, self-assembly, nanoscience, and any of the other fields in which you have a part?

Angela Belcher: I do not differentiate at all. I think we're living in a time that is great for young people coming up now, because you do not have to differentiate yourself. When I got my first degree in biology, I had someone say, "What makes you think you can be an inorganic chemist?" It did not seem like a very large jump to me. I consider myself a chemist because I think in terms of unit cells and I think about bonds, but then again I feel so lucky to be trained as a chemist because what in the world is not chemistry? Not everything, but most everything is chemistry. I do not think those differentiations matter at all. I think the key is to find out what you are really excited about and apply yourself in that area.

If people ask me to define myself, I say that I'm a materials chemist, which I am not sure that the head of my Department of Biological Engineering loves. I do not think I've ever called myself a nanoscientist, because to me it is all about atoms, it is all about bonds.

PSW: I'm sure your department head is not too unhappy with you! (This was a question suggested by your colleague, our Associate Editor Prof. Paula Hammond.) What do you see for self-assembly in the future?

Angela Belcher: Paula Hammond is one of my favorite scientists; she and I work a lot together on self-assembly and devices.[14,21]

I think self-assembly is going to become much more of a norm in terms of manufacturing. "Self-assembly" is such a bizarre word anyway. What do you consider "self-assembly"?

I keep coming back to scale, but doing it all in scale is going to be really important. I would really like to say "no assembly required" for the battery work. What if you just put all the ingredients together and it just formed? You can always think about doing that on a really small scale, but then to have it happen with your iPod battery and to have that completely self-assembled. How do you take that to a larger scale? How do you have your computer self-assemble? I think eventually that is not going to be so crazy. I think most of us believe that. I think that the future *is* in self-assembling systems.

PSW: Do you have advice for young scientists and would-be scientists?

Angela Belcher: My advice has always been: "Find out what you're really passionate about; follow what you're passionate about." I always say that I have the best job in the world and that I would do it for free, but instead someone pays me a lot of money to do it, which is not bad! I think it is being open to creativity. I think it is finding what it is that you really love to do, and that has always been my advice.

[Literature citations and figures were added after our conversation to assist and to direct the reader to relevant publications.]

— Paul S. Weiss, Editor-in-Chief

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