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Nanoscience — Potential and Threats*

Paul Alivisatos[1]

As the world's population continues to expand, scientists are working to address the energy needs and challenges that accompany growth with environmentally responsible approaches. Nanoscience is helping to provide solutions to energy and environmental concerns in a number of ways.

Keywords: Nanoscience; Energy; Environment; Carbon Cycle 2.0 Initiative.

It's really fun to be part of a Molecular Frontiers Symposium. This is where you can think about deeper questions that maybe come up in your own discipline each day by joining with others and of course to interact with people who are early in their careers and try to get them interested. The title of my talk which was given to me, seeks an explanation of nanoscience, both its advantages and its potential problems, and to do this within the context of the energy and environment problem. So this is not an easy task and, and we will have to move kind of quickly here to go through some aspects of what is nanoscience in a short period of time.

In fact it puts me in mind of a famous TV character that used to be on the television in the United States called Father Guido Sarducci. He had a funny comedy routine once which was called "The Five-Minute University." In the Five-Minute University you learned in five minutes everything that you would still remember five years after you attended a full course at a university. This is going to be our Five-Minute University version of what is nanoscience but hopefully in the context of energy and environment.

And I think that you can appreciate that in coming decades, problems of energy and environment will really intensify as the 10 billion people we've been talking about will be an increase in the population. But, as well they will be having greater energy intensity because all of the people who are today in the low economic stratum will be pulling themselves up every way they can in order for their families to be better off. And so we will have greater and greater energy use by a larger number of people and therefore we know that there's going to be a big crunch coming. And the question is how can we also organize ourselves, as a science community, to meet some of those demands. And I wear another hat as a laboratory director with a laboratory that has a few thousand people working at it, so many of them on energy and environment problems, and there too we have to think how we can organize ourselves. We also know that any solution that we come up with in order to be important actually has to operate on a massive scale and therefore it could have unintended consequences, and we need to have a system for learning how to think about the consequences of our technologies and the unintended consequences as early as we can in order to be able to be proactive.

So to give it some context, today we operate in our energy world with an open-ended carbon cycle. That means that we burn fossil fuel and put CO_2 into the atmosphere. About half of the molecules that we put into the atmosphere, 30 gigatons of CO_2 per year, about half of that stays in the atmosphere changing the radiative balance and the heating of the planet, and about half of it enters into the biosphere into the oceans and into the land masses causing various changes there. It's important to know that, that this number of sort of eight and a half gigatons of carbon or 30 gigatons or so of CO_2 is massively larger than the net carbon fluxes that normally occur in the planet that would restore things you know in other words

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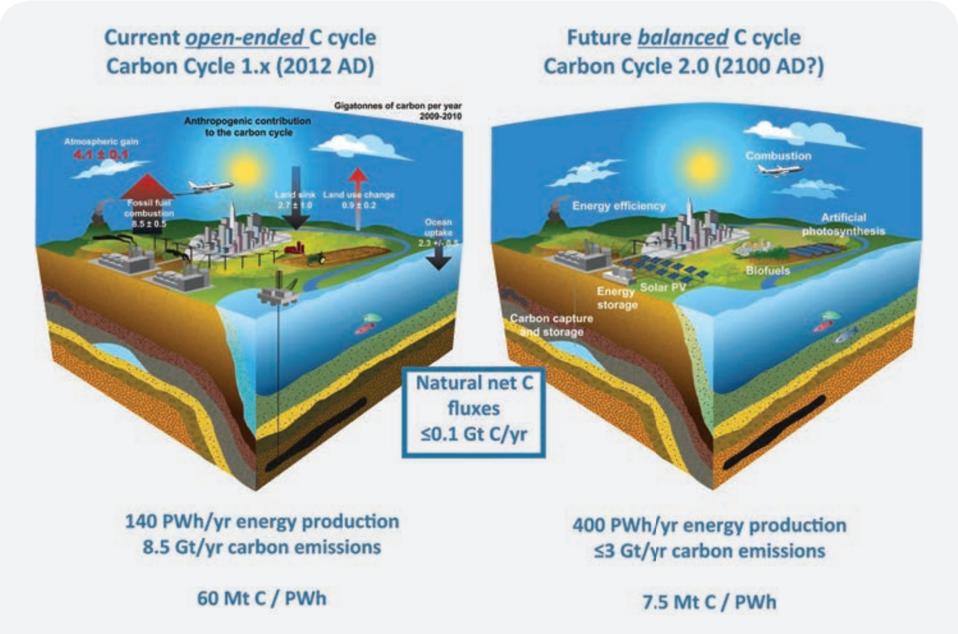
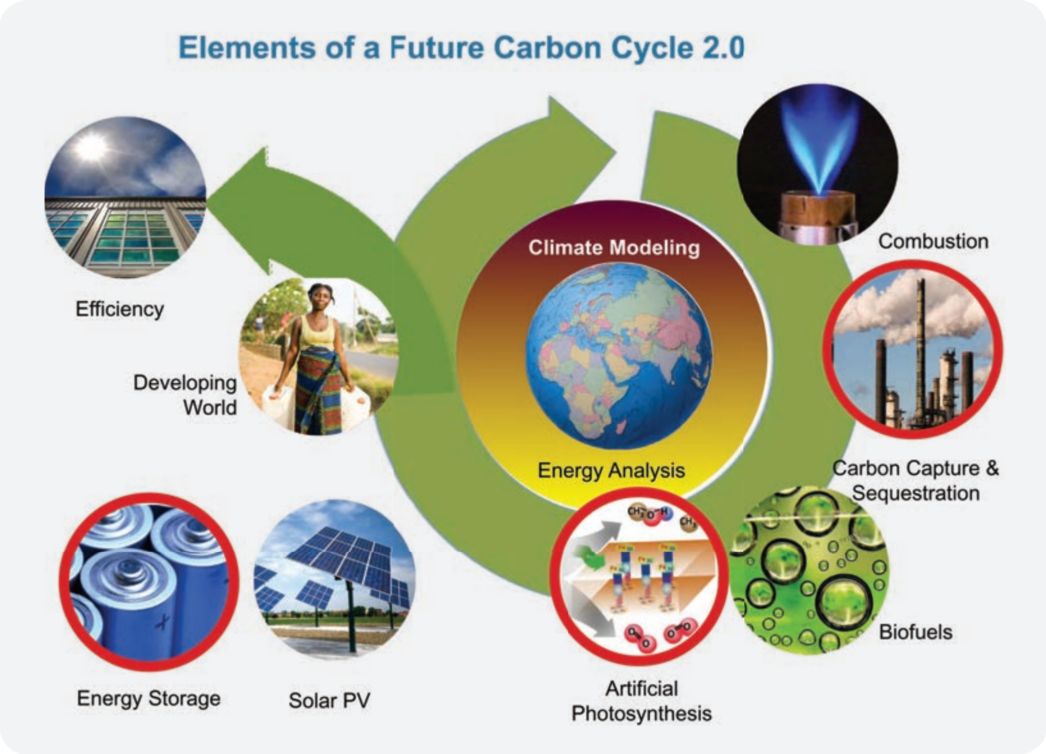
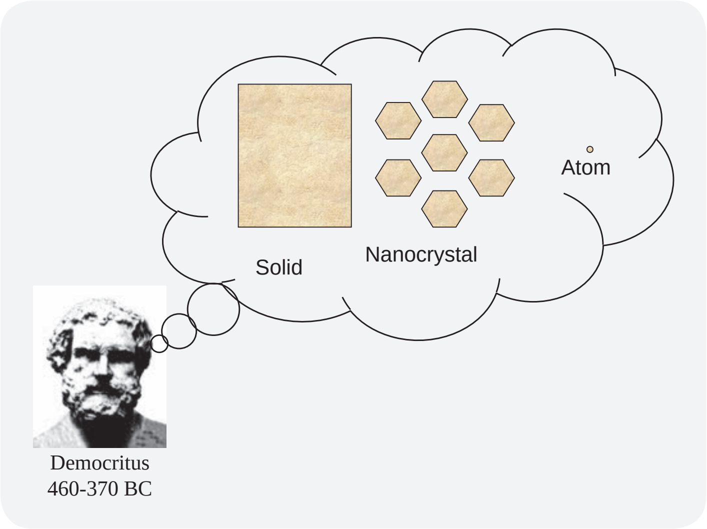


The current carbon cycle is out of balance, producing global climate change. Nanoscience will play a key role in creating new technologies for a future balanced carbon cycle. The numbers at the bottom show that in addition to decreasing C emissions over this century, we also expect to need to produce 3x the amount of energy. Also, all of the current net C fluxes between reservoirs are much much larger than natural fluxes, which in general are near zero, but even during periods of rapid natural change they are seldom much bigger than 0.1 Gt C/yr (Don DePaolo. private communication).



in periods when people are not putting so much carbon into the atmosphere, the net fluxes in any given period of time in past history were much, much smaller. And so this is a large perturbation. And as we imagine moving towards year 2100 perhaps then we will have created a balanced carbon cycle and to get towards that we will need to develop a variety of new approaches. But especially we will have to find a way to very significantly increase our energy production and at the same time very significantly decrease the carbon emissions. So the intensity of carbon use has to go up by at least one order of magnitude. So it is very challenging.

And so at the lab, at Berkeley Lab, we've organized ourselves into what we call The Carbon Cycle 2.0 Initiative. The goal being to try to provide the science that's needed in order to have a more stable carbon cycle in the future and it's organized around each one of these circles that you see here and they are laid out in this way. Along this line here you can see combustion, carbon capture and sequestration, biofuels and artificial photosynthesis. You can think of this is the arc of carbon. This is how we use carbon today. And these are some solutions that we will be using in the interim. And then this is a longer term solution that would be carbon neutral. This is carbon neutral but limited in



its scope perhaps by the land availability this might be scalable to much larger areas. And then over here we have the off-ramps especially efficiency which is of course in many ways the most accessible means we have for bringing the carbon cycle under control.

I mention here developing world, I hope it's still okay to call it that. In this context, it's intended to mean what does happen with the at least 2 billion people living under $2.00 a day. As their energy develops we need to have thoughts on how to help them because the first thing that they may do is use the easiest energy technology that comes to hand and that often can be one which is damaging to the environment. Perhaps, we can think of ways to enable the folks in the developing world to have a different pathway to their development.

And then of course there are these two off-ramps as well which take us off of carbon energy storage and solar PV. In the center sit our scientists who do climate modeling and especially those who do energy analysis and we'll see more of these towards the end. Energy analysis is what's going to help us think about all of these as well as the life cycle assessments and some of the risk assessments that we'll be talking about.

So today I'm going to talk about these three subtopics and the question that we're going to ask is, how can we have some positive outcomes here? We don't want to just be thinking about the environment as being the sort of horrible bad nightmare about what's going to be in the future. In fact actually it's a very exciting period of time because we have the opportunity to think about new ways, new and exciting problems that will enable us to have energy in a more friendly environmental way that can really advance the state of our thinking and of our science. So we're going to ask how can nanoscience specifically contribute solutions in areas of energy and environment and I'm going to give these three examples, one each in batteries, artificial photosynthesis and carbon capture and sequestration. So first of all I'm going to back up and say what are some themes of nanoscience and here are some; scaling laws, synthesis and properties of building blocks, the power of one, a deep connection to biology and the current era of building. Hopefully, by the end of the talk you'll see what each one of those means.

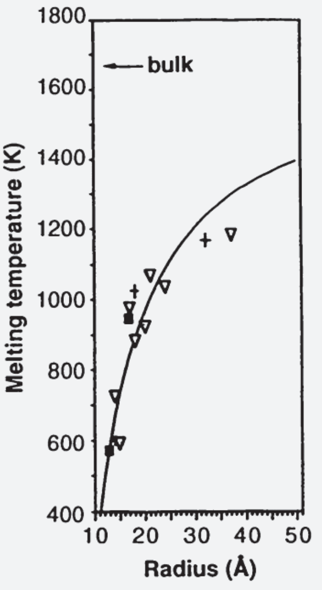
Now let's back up and think about the basis of nanoscience. We're going to take a slight break here, and just go back to the beginning of nanoscience which in this case we're going to attribute to Democritus in 400 or so B.C. He was a philosopher who was the first person to use the word atom. Atom meaning "that which cannot be divided," and so the literal meaning of the word atom. And what was Democritus thinking about? Well, he was simply trying to understand the nature of matter. He was trying to think what is stuff? And he thought okay, in order to understand it he would suggest a though experiment. If I followed the instructions of his thought experiment, I would start with an ordinary piece of gold. I would take the gold and just chop it into two pieces and ask the question if I now have two pieces of "gold." Are they the same as the one big piece that I started with or not? And the fact is that for all intended purposes if you were to measure any fundamental property like say the melting temperature, the hardness, any of those kinds of properties, and you break the gold into two, the answer would be yes, they're the same as long as they're macroscopic. But somehow Democritus was able to intuit the idea that if you keep breaking it in two, break in two again and again and again, eventually you would get to a point where when you break the gold up it would now be, matter would be grainy and you would reach a point where you could not divide it any further. And that's the indivisible, that's the atom.

And it turns out what is nanoscience? Nanoscience is the study of matter that's in between matter where it doesn't matter how big it is anymore, whether it's twice or half the size all the fundamental properties are the same, and matter where it's truly atomic and it cannot be divided anymore. In between those two, there are a lot of sizes that are very small, you can't really see them with your eye, but every time you make the material a slightly different size, all of its properties change. And that is what nanoscience is about is to try to study matter in that very tiny regime because of course it's so interesting that you can change the properties by changing the number of atoms. So Democritus really set the stage for the study of scaling laws of nanomaterials. Scaling laws will describe how you smoothly go from here to there in properties as you change the size, in the event that it is a smooth variation.

So we're going to see some scaling laws in action and then from seeing those scaling laws, we're going to be able to make conclusions about energy technologies and that's going to be the goal of this lecture. We're going to look at four scaling laws; melting temperature, structure, energy level spacing and the concept of "artificial atoms," and charging energy. And these are four very powerful scaling laws and they relate of course going from structure to function. What we're going to find is all these properties depend critically upon the size and therefore control of size, shape, topology and connectivity on the nanoscale can enable new functional materials for energy and environment because we can control the properties by changing the sizes. We can make new materials that could have many of the properties that we want them to have.

So let's go through and see one example of a scaling law and let's start with melting temperature, I mentioned that earlier. Imagine a solid and if you think about the solid, all the atoms are holding each other together. They're all bonded with each other. So if you have a big solid, it has a "cohesive energy." How much energy it takes per atom in order to start to really get it to melt is going to depend on the size when the crystal is very small because all of the atoms on the surface are not bonded to any on the other side. So the total bonding of that crystal will become weaker when the crystal becomes very, very tiny because of all the surface atoms, okay. And we'll see that here in action.

This is an example of the melting temperature of a solid. In this case it's a semiconductor as a function of its size. And what you can see is that as the crystal becomes smaller and smaller the melting temperature is dramatically reduced. In this case the nanometers scale bar represents 40 angstroms, or 4 nm. As we go to smaller and smaller sizes you can see that the melting temperature drops off. And there's a scaling law for this which goes roughly like one over the radius which is the ratio of the surface to the volume. In other words if there's more surface then the melting temperature is reduced, the crystal is held together not as tightly when it becomes very, very small. Hopefully, that's reasonably intuitive.

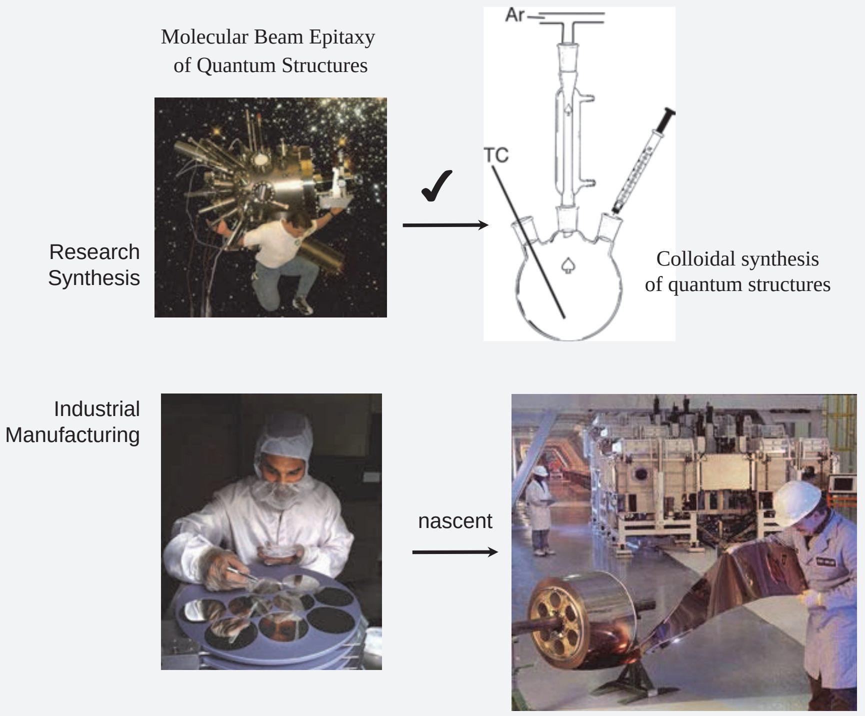


Example of a scaling law for melting in nanocrystals case of colloidal quantum dots.

Now the consequence of that for materials is that we can make high-quality crystals under very simple cheap conditions and that's going to be quite important. So one thing that we've seen in recent years is that structures which previously had been made by very, very intensive and complicated techniques when they were made in large scale, when you make them as tiny crystals are amenable to being synthesized by very low tech, very simple means, in this case just growing in a simple fluid, a material which previously had to be controlled at very high precision in ultra-high vacuum. And so in the research world, in the synthesis of nanoscale materials in the research world, there's been a tremendous transition where very advanced quantum structures are being made in simple liquid solutions. In industrial manufacturing this is a transition that's actually occurring where instead of fabricating devices one at a time in a very serial and complicated way, there is an evolution towards being able to make large areas and great big sheets of them and both of these flow from the reduction in the melting temperature.

Let's take a look one step deeper and that has to do with defects. If you can, imagine going to the jewelry store to buy a diamond for somebody that you care about very much. And there's a scaling law that you immediately encounter. You have a certain amount of money. And it turns out you cannot double or quadruple the amount of money very easily and therefore, the price of the diamond, how it depends on the size really matters to you. And if you go and look at the De Beers website where the diamonds are sold, they'll tell you right away big diamonds are much rarer. So a diamond of double the weight costs four times more. That's an economic scaling law of price with volume. But why is the bigger diamond that's perfect so much more rare? Well, it has to do with the time scale for annealing a defect out. Imagine that there's a defect inside a crystal and you ask the question how long is it going to take to move out of the crystal if I warm the crystal up? Eventually, the defect will go out, it will leave, it will be pushed out. How long will that take? It turns out it will scale exponentially with the volume. And so this is why a big diamond will be so much rarer.

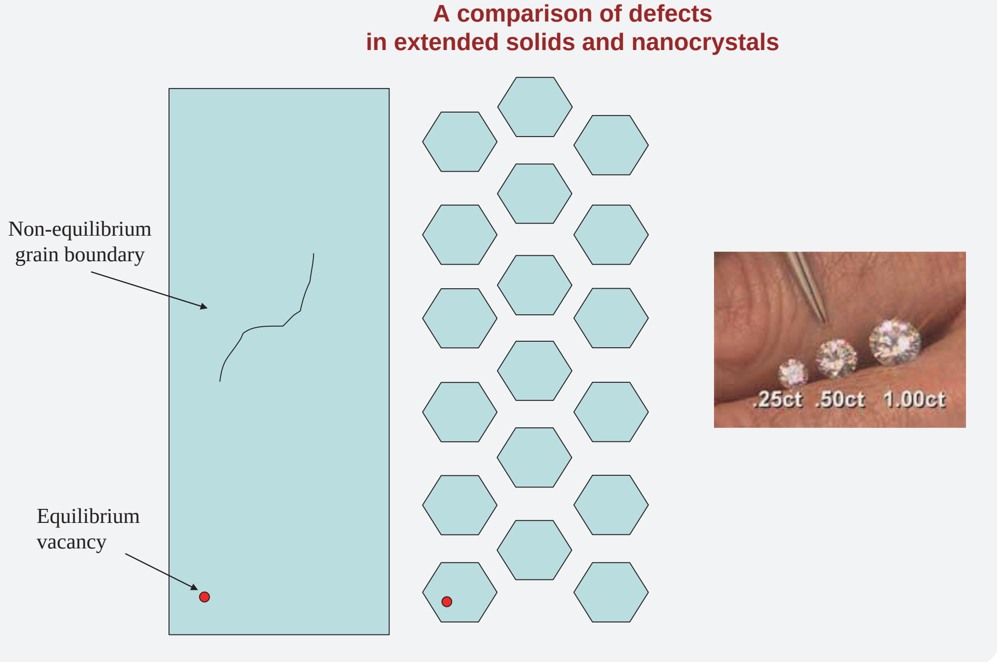
Now let's turn that around. If I want to make a perfect material, should I really make a giant crystal? What if instead I said, okay, I'm just going to make a very tiny one, it's only going to be 5 nm in size. Well then it turns out I can grow a very perfect crystal very, very easily, very, very quickly and it won't be rare at all. I can make lots of them. And that turns out to be a fact that you can make extremely perfect tiny crystals very easily. Now I mentioned here on average, nanocrystals can be made to contain no equilibrium defects. That's not to say that nanocrystals never have defects in them but if you take reasonable care and you just warm a tiny crystal up a



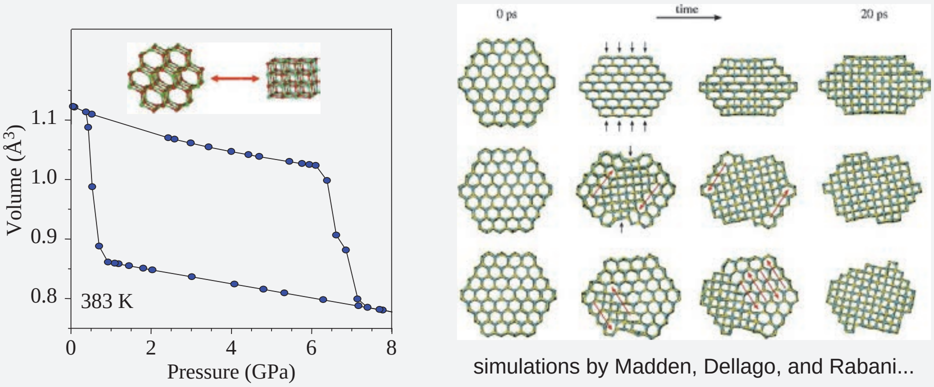
Nanoscience may enable fast and inexpensive synthesis and manufacturing on enormous scales of high quality materials...

little bit, all the defects will be pushed out to the edge. That means that a very simple cheap process can make a material of extremely high quality. And that for energy turns out to be incredibly important because energy is all about huge volumes. And therefore, the costs and the rates really matter a great deal. So that's a scaling law that really matters to us that we can make crystals that are highly perfect.

How do we know if these crystals are so perfect or not? Well, here's another scaling law which is going to take us to batteries in a moment. Imagine taking a crystal, this is one shown here, where each atom is bonded to four others. And we'll simply press the heck out of it. You just push it on all sides. And the crystal now would like to become smaller because it's being pushed from every direction and so it's trying to compact itself. And what will happen is the volume will decrease as you increase the pressure. The volume will decrease and then all of a sudden at a certain pressure "boom" there'll be a big volume change and it will go from one atom bonded to four others to one atom bonded to six others. Now that can be studied in all kinds of materials but in a nanocrystal something very special happens which is that this change, which corresponds to an 18% change in the volume, it's an enormous change in the volume. This change is completely reversible in a tiny crystal. If you now release the pressure, it will pop back. You can pop between one structure and the other, despite the 18% volume change without the crystal ever having a new dislocation or a new defect generated. If you take a big crystal



A comparison of defects in extended solids and nanocrystals



simulations by Madden, Dellago, and Rabani...

Annu Rev Phys Chem **46**, 595–625 (1995).

Science **276**, 398–401 (1997).

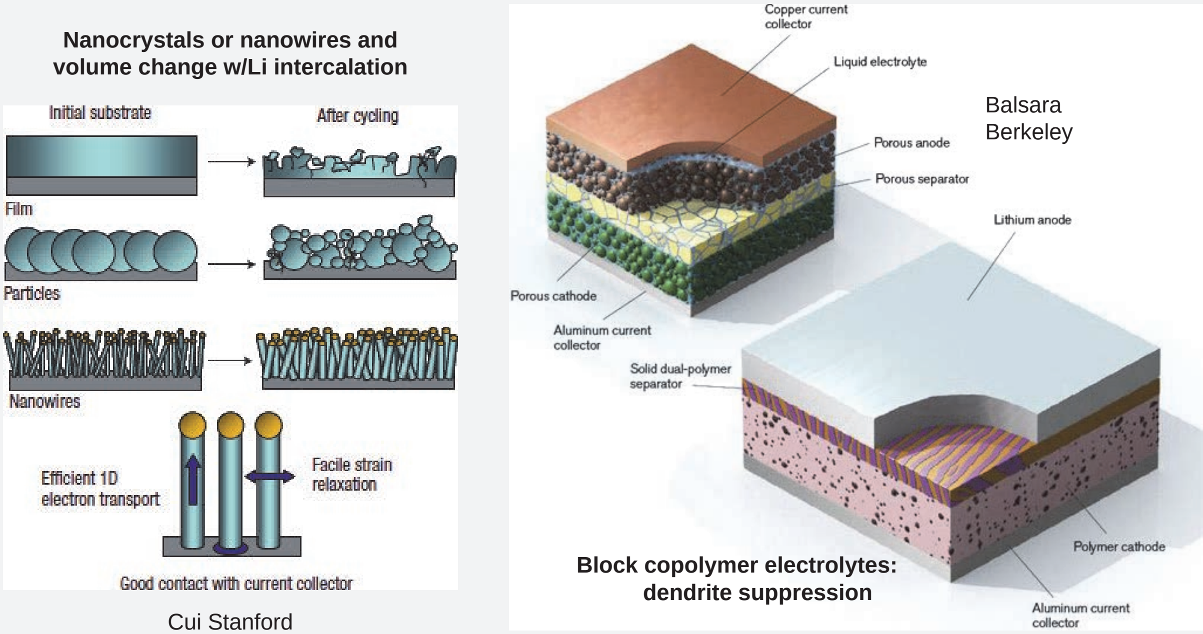
Nanocrystals as "Single Structural Domains." A nanocrystal can reversibly change volume without creating defects. This scaling law can be used to design new reversible batteries.

and you press it like this to the point where it undergoes a phase transition of that volume change, the crystal will break up into lots of little domains, but a tiny crystal can just pop between one structure and another. If you like you can think of that as a molecule "isomerizing" between two different stable structures. What this means is that the nanocrystal acts as a "single structural domain." This is incredibly important for nanocrystals and it has lots of implications for how we think about them.

Now let's think about that in the context of energy storage. Here's a battery and a former coworker of mine, Yi Cui, who's now at Stanford, one of **Dick Zare's colleagues**, was thinking about this idea of the nanocrystal as a structural domain and he realized, oh my gosh, when I take a battery, what do you do inside a battery? You flow lithium ions from one side to the other, you need to store them some place on the other side of the battery, what you do is you "intercalate" the lithium in an electrode. The lithium will enter into another phase so it will enter into a carbon phase or into a phase of silicon as was described in this particular case by **Yi**. When that happens, the volume of the crystal changes and it might change 20%, it might change even more in some cases, in any case a big volume change.

Well, we know now from our studies of nanocrystals that if we take a very tiny crystal, it will be able to change its

Nanocrystals or nanowires and volume change w/Li intercalation

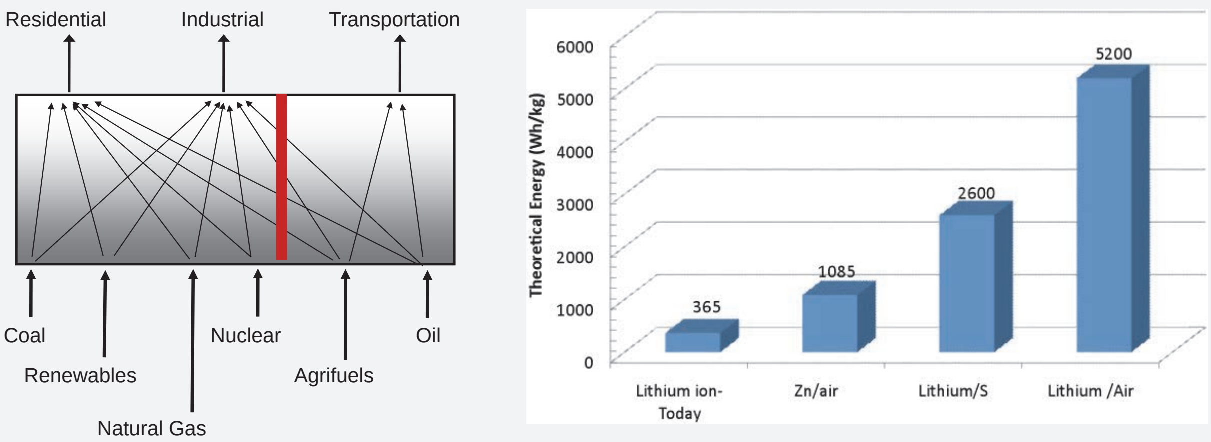


Cui Stanford

Balsara Berkeley

Block copolymer electrolytes: dendrite suppression

Batteries and control of nanoscale structural domains. Nanotechnology enabled anodes, cathodes, and transport media have the potential to revolutionize battery technologies.



Batteries — gateway to transportation in Carbon Cycle 2.0. today's technology 100–200 W·h/Kg 400 W·h/Kg would give a better driving range.

volume by that amount without generating any new defects and therefore, I can make a much more reversible structure for storing energy than I could ever have made if I took a big bulk material and tried to do it. So you can see the scaling law is really in action now, it's teaching you how to go and make something that could be more reversible. That's important for cycling a battery many times.

Here's another idea from a colleague of mine at Berkeley, Nitash Balsara. Instead of using inorganic things he's using organic media, but what he has shown is the following problem. You'll be familiar perhaps or I hope some of you will remember. A few years ago, Sony was making the batteries better and better and what they were doing was you take a film and you wrap it into a cylinder. And so you have the source of the lithium and where the lithium goes to, and in between you have some region that the lithium flows through and you figure, well I'll just make that thinner and thinner and thinner then the energy density will go up and up and up because when I wrap it all into a cylinder, the same amount of lithium will be transferred but in a smaller volume. So I'll make the separation zone smaller and smaller and smaller. At some point what happened was the battery started to catch on fire. You may remember that. Why was that happening? Why was the battery catching on fire? Well, what would happen is the lithium ions would start to condense into lithium metal on one of the electrodes, a little dendrite. And then the dendrite would sneak through and connect to the other side and short out the battery. And the moment it shorts out, it's all over, current flows through there, a lot of current through a small area, and it gets hot and then it's a combustible material and you get a fire.

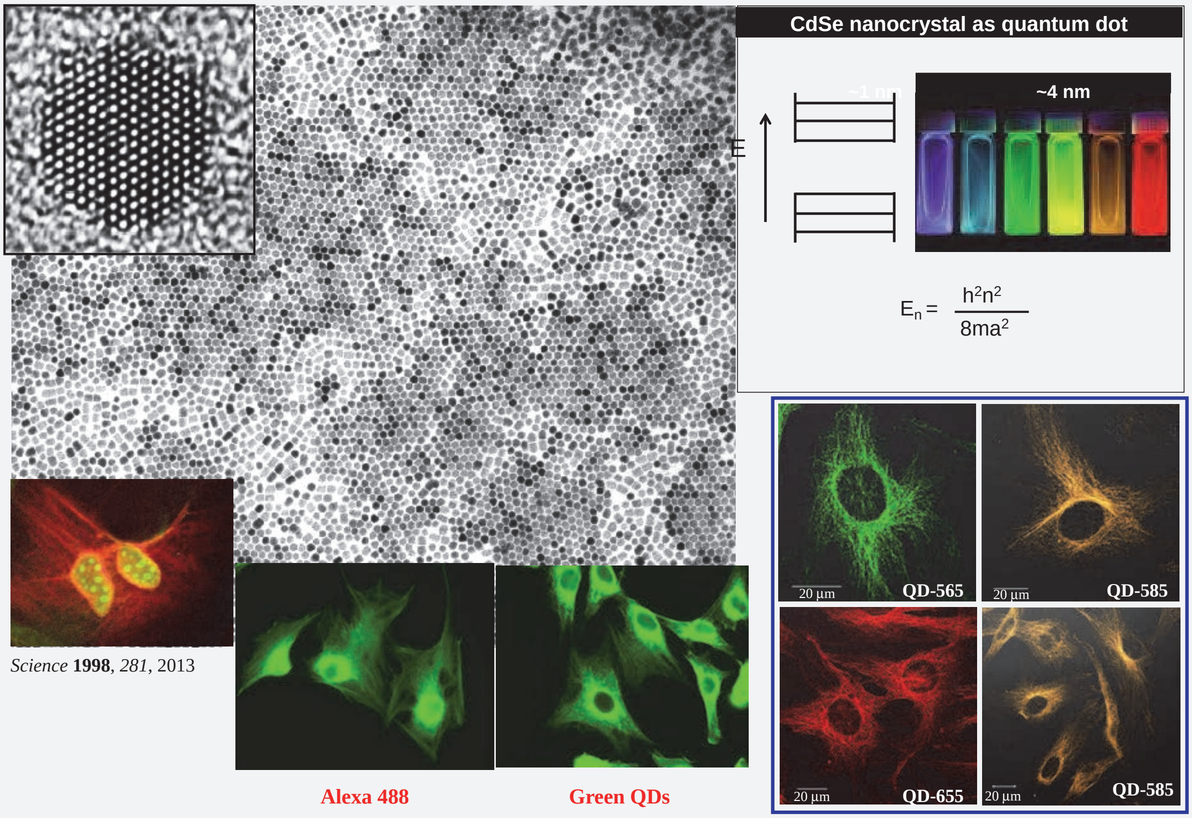
Now, Nitash was able to think about this problem, using his knowledge of nanoscience and mechanical properties, in this case of polymer material. And he showed that what he could do is make a mixed material out of two polymers. One would transport ions but it would be mixed together as a block copolymer polymer with another component that is very, very stiff, mechanically quite stiff. So now the ions can move through but the lithium cannot make a dendrite because it can't push its way into the polymer. So what you can see here are some simple ideas which tell you that nanotechnology enabled anodes, cathodes and transport materials can change entirely the way we make batteries. And that's happening today in many areas.

A little bit more about batteries before we go on. Why are batteries so important? And this is now starting to think about how do we decide what problem to work on. Batteries are incredibly important and the reason is the following. If we look at the energy sector, it has inputs like coal, renewables, natural gas, nuclear, biofuels, oil. These are all in energy inputs and then there are energy outputs. What are the energy outputs? Well, a third of energy goes to homes, a third goes to big industry and a third goes to transportation. And it turns out that if you look at this, I can take any of the inputs and feed residential or industrial. I can feed a home with electricity from any one of these sources. But it turns out for transportation, only biofuels and oil can feed transportation. I can't feed it from these other sources presently. And that means it's a huge economic opportunity if you can figure out how to take electricity which would then allow you to have any source feed one-third of the economy of energy. It's a big deal.

Lithium ion it turns out may not be the answer and it may be new chemistries. Today's technology is about 100 to 200 W·h/kg. That may not mean much to you, but it would give you about a third of the driving range of a typical gasoline car. So if we want to have a car that has a decent driving range, we have to get up to hundreds of watt hours per kilogram, which means we probably have to change the chemistry that we use from lithium to something else. So this means the battery area is just full of excitement right now and people are trying to do all kinds of neat things there. Okay, so we've seen now the exercise. We can take a scaling law like melting temperature or what happens when a crystal is very tiny with respect to its volume change and then we can use those to design energy materials. Let's do it with the last two scaling laws, two more scaling laws here. One is going to concern the artificial atom concept, band gap and the charging energy. There are two more concepts there, we're going to see them in action in true energy technologies, okay.

So first the artificial atom concept. This is a crystal of a small semiconductor. And if you look at it you can count the number of atoms across one, two, three, four, a certain countable number across. Now it turns out in quantum mechanics, we know something very important, which is electrons are not just particles, they are waves. So the electron is a wave. And it's an undulating wave inside a big crystal. What happens when the size of crystal becomes comparable to the wavelength of the electron is now the electron will be "confined" inside it and the smaller the box that confines it, the faster the electron will move inside. Just like if you've ever been to one of the science museums where they have those parabolic containers and you can put a ball in it and it will start to roll around and then as it gets in towards the center, it will go faster and faster. That's what happens to an electron when you confine it in a very small box. And its energy levels in a small box become discrete. They separate out and they become "quantum confined" and the energy level spacing scales like one over the box size squared. And that's called the quantum size effect and leads to the "artificial atom" concept. This is a very powerful concept and these materials now are widely used for biological imaging. These small crystals are used because they make colors that don't bleach. Here's an organic dye and it bleaches very quickly. These inorganic nanoparticles which can be introduced inside a cell do not bleach and therefore they're very, very stable.

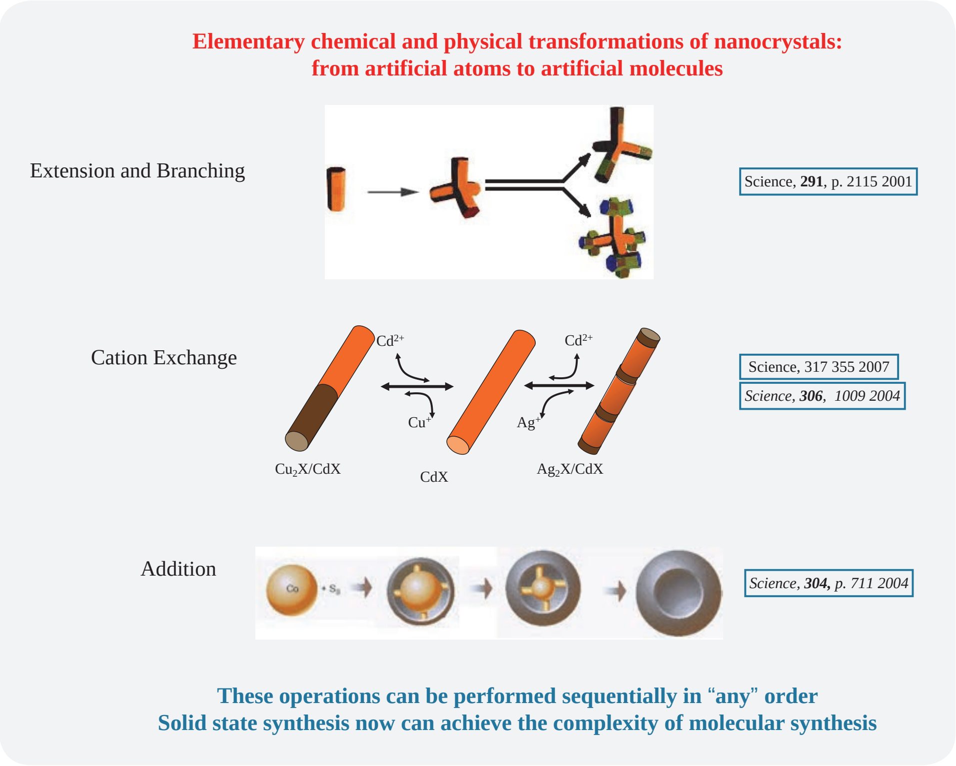
Now from atoms, I hope you know if we have atoms what's the next thing that you want is molecules, right? So if we have artificial atoms I want to take two atoms and put them together and make a molecule. Then I can build things. And that's what nanoscience wants to do for energy. We want to build things. But at first when you start you have to have a mechanism for building. So for us, in my group, we have spent many years learning how to go from artificial atoms



Science **1998**, *281*, 2013

Quantum confinement, Artificial atom concept — impact in the chemistry of nanomaterials.

Elementary chemical and physical transformations of nanocrystals: from artificial atoms to artificial molecules



These operations can be performed sequentially in "any" order
Solid state synthesis now can achieve the complexity of molecular synthesis

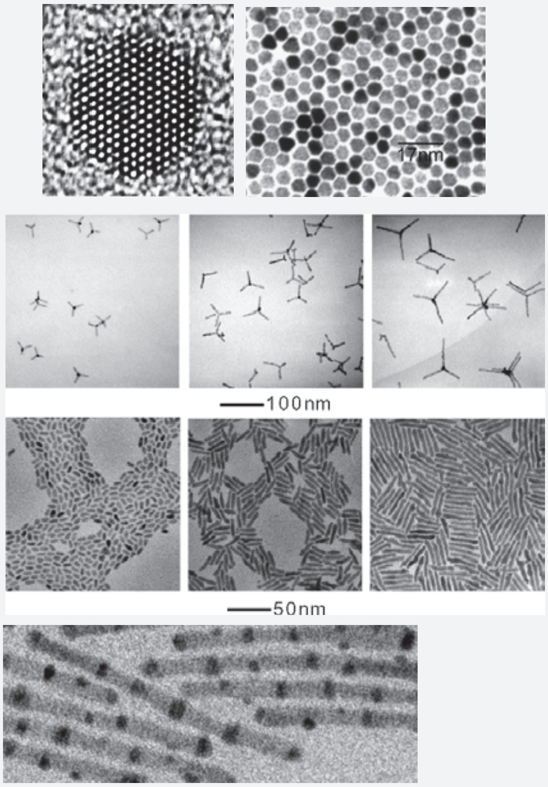
to artificial molecules by developing chemical systems, reactions, which produce reliably certain types of shapes like hollow particles or striped particles or branched ones, or all kinds of little funny shapes like that. And as we learn to form these into a system then it turns out that becomes like molecular chemistry. In molecular chemistry, we can start with a set of molecules and with well-defined rules, hopefully, we can add one to another and build up, for example, a drug molecule. In that same way what nanoscience would like to do is to take artificial atoms and learn how to put them together into intricate arrangements which allow the energy flow to be controlled in a very specific way on a very small length scale. And that's by making an artificial molecule. So that's one of the big goals of nanoscience.

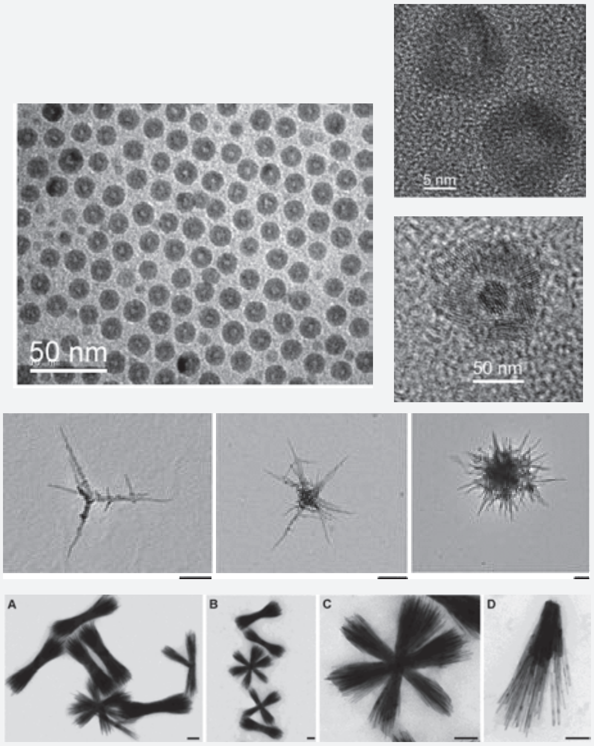
Now Rutherford, the very famous physicist who discovered nuclei, okay, Rutherford once made a very famous quip about science, when he said there are only two branches of science: physics and stamp collecting. And I don't know whether he felt good about the stamp collecting or not, but it turns out I'm a stamp collector and so are all of my friends. And this is our stamp collection and these are the nanoparticles that we learned how to make. We made branched ones, hollow ones, one completely inside another like Russian dolls, ones that look like P orbitals and F orbitals and stripes and so on, okay. And what I wanted to say to you about this is that I think Rutherford was exactly right in the following sense that when a field of science starts, the first thing that it has to do before you can systematize it is, you have to scan and just see what is possible, what happens, and that's called stamp collecting. So this was a fit. Then the second phase is now you know approximately what the land looks like. Now you can start to perform a deep analysis and understand the principles that underlie it. So that's why his saying makes a lot of sense. And we've gone through the stamp collecting phase, so now we can be in the science phase of building things on purpose because we know how to make all of these structures.

So what would be one we might want to make? Well, here would be a challenge and I said there's a deep connection to biology. I mentioned before that nanoparticles can be used to image biological systems. For example, in the imaging of biological systems today if somebody that you know has a biopsy for a tumor, they take a piece of tissue out to see is the tumor benign or malignant. A pathologist will stain it, in order to image and see what it is, and it is very likely that they will use a nanoparticle to do that imaging in order to see what that is. So that is something valuable, imaging, that nanoscience offers to biology. It goes the other way, too. Here's a very famous biological system, the photosynthetic membrane. And it is an incredibly intricate device which takes photons and creates new molecules. And people cannot do something that rivals that. It's very, very difficult for us. So it's interesting to try to dissect it and see if we could imitate nature, and make an artificial material for photosynthesis. One reason is because then we could make a complete carbon cycle for energy, but also because it's a deep intellectual challenge, can we do something as complex as that. And just look at all these arrows, I don't even know what many of them are either. It's such a beautiful complex system. It's got many, many characteristics to it. Could we make an artificial system that has some of those characteristics completely from scratch? Okay, we have to find out.

So let me say some characteristics about what you would like to have happened in an artificial photosynthesis system. You want to absorb light, separate a charge, you will make an electron and a "hole" (the absence of an electron) and then you want to use these to drive a reduction and

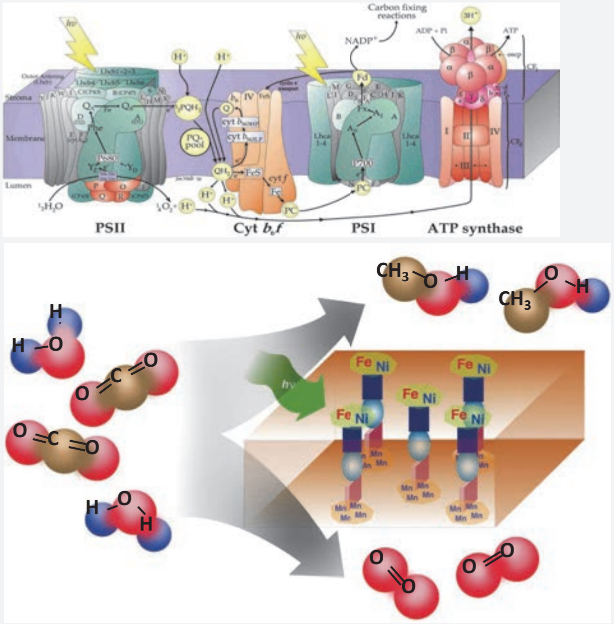
A nanocrystal “stamp collection”...





Symmetry, topology, connectivity, directionality...

Artificial Photosynthesis and Nanoscience



- •High density of reactants (photo-generated charges) leads to more products
- •10 k_BT dissipation required to ensure directionality of energy flow
- •Catalysis and flow of reactants and products must match solar flux

an oxidation reaction. And in the natural system that's that's driven across a membrane.

And here are some things that we could think about. Now I want to try to make an argument that says, if it's optimized, it probably will be made out of nanoscale components. Here's my argument. Imagine that I start with a really big semiconductor that absorbs the light. And now I want to do chemistry with it. The chemistry has to take place in one molecule, and that energy of the photon has to suddenly find itself localized into a chemical transformation in just one bond. Okay, so that means that if the excited electron in the solid is a wave and the electron is very large compared to one bond, I have to localize it now again into that one bond and I already showed you it takes energy to localize an electron. So I'm going to lose energy if I do that. Okay, so that means I'd like to use the smallest object possible to make my artificial photosynthetic system. I'd like it to be one bond, say. Well, what would happen if I did that? Well it would be more likely to fall apart (remember how the nanocrystal quantum dots are more stable than molecular dyes?) So there is an optimum nanoscale size for the light absorber.

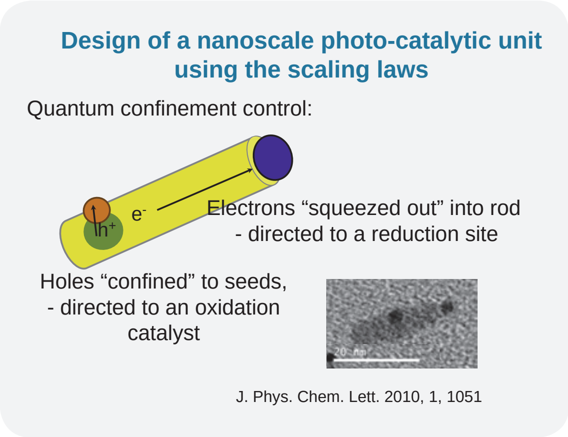
It turns out it's very important that the energy flow directionally. If I'm going to do photosynthesis I need to have a direction because I can't have the two sides of the electrodes shorting each other out. The reduction has to be on one side, the oxidation on the other. It turns out I can do an entropy calculation and say it costs me a certain amount of entropy to have the energy go in a specific direction. And that turns out to be around 10 KT. That means, I'm going to lose a certain amount of energy every time a photon gets absorbed no matter what. From thermodynamics I know every time the photon gets absorbed I'm going to lose a certain amount of energy. That says if I have a molecule that's got say 20 atoms in it, I'm going to lose that 10 KT and I have to do that billions and billions of times. The odds are that molecule will fall apart are quite significant. So if I take an infinite solid, it will be very, very stable but I have to pay the energy to localize the electron. If I take a really tiny one, I can absorb the photon just fine, it but I'll probably have an event where I'll break the molecule after a little while. So this is an argument why in the end if you look at the natural photosynthetic system, it's operating with 4 or 5 nm size components. Probably that's what we want to do too.

There's one other thing that we have to be able to do, which is photons just keep on coming from the sun and you have to keep up with them. And by this I mean you may not know it but if you look at the plants outside, when the sun comes up, the photosynthesis starts and it tracks the sun, more sunlight, more photosynthesis, and they track each other up to about 15% of the total noon time solar flux. Beyond that, actually the natural photosynthetic system cannot have the catalysis and the flow of reactants and products keep up. It's too slow. So nature throws out 85% of the sunlight! Maybe we can avoid that problem in our design.

So here's an example of trying, in an early stage, to design a photo-catalytic system. We will use quantum confinement, quantum phenomena of confining electrons, and we will see yet another scaling law pop up, which now has to do with "charging energy." So let's make a system which has a direction to it. We will make a nanoparticle which has in it two catalyst particles, one on the side here and one on the other end. And so here's the one side and there's the end. And we'll build the crystals so that there's a little semiconductor here attached to another one. Remember I told you we can build all kinds of stuff. So there'll be one semiconductor embedded in another and these are organized, these semiconductors such that when a photon is absorbed, holes will stay here in this green zone but electrons will like to be in the yellow zone. And electrons will then want to flow here to this blue area which is where the reduction events could take place. And holes will go to this orange attached catalyst, which will then do the oxidation. So then I will have ensured the directionality of energy flow. And one way that I'll do this is I'll make sure that by quantum confinement that this little zone is so small that the electron doesn't want to be inside it anymore. It really prefers to go outside. Remember if I squeeze on that electron, its kinetic energy is going to go up. If there's another place for it to go, it will jump out and go there. So I built my structure in such a way for this to happen. And here you can see that something like this kind of works if I make this distance larger and larger between the seed and the reduction catalyst. The quantum efficiency for hydrogen production in this case goes up and up and that means that it's working better.

Now I told you I have to keep up with the photon flux and there's some technical things here that I don't want to go into it necessarily in detail, but what we can do in this particular case is measure the light emission from one of these structures. And whenever it emits light that means that the electron and the hole — okay whenever it emits light, it means that the electron in the hole recombined. When it doesn't emit light, it means that the electron and the hole are doing chemistry because the electron went to do a reduction and the hole went to do an oxidation and that's a good thing. Now it turns out if there's no catalyst attached, this semiconductor, if I put in more light, it will just emit more light. But when the catalyst particles are attached, remember there's an oxidation one here, and a reduction one here, I see this very funny non-linear dependence to the light flux. And it turns out if I look at it in some detail what I find out is that at this photon flux, when the photons are coming often enough, I reach the point where on this side the oxidation can no longer keep up. I can't take the holes out of the system as quickly as the photons are generating them. And this zone here is actually a zone where the electron chemistry cannot keep up. I start to build up electrons on here.

And I just want to tell you about this one because it's another one of the scaling laws. I promised you a fourth scaling law and that's the charging energy, so here it goes a real quick qualitative explanation, but very important if you want to think about nanoscience, it shows up all the time. Imagine I have a piece of metal and I stick an extra electron on it. What's happened is, now there's one extra charge and I can



Design of a nanoscale photo-catalytic unit using the scaling laws

Quantum confinement control:

Electrons "squeezed out" into rod
- directed to a reduction site

Holes "confined" to seeds,
- directed to an oxidation catalyst

J. Phys. Chem. Lett. 2010, 1, 1051

ask what is the new charge density? It's increased by one charge divided by the volume of that crystal. If I go to add a second charge, it's repelled by the first one, but if the crystal is quite large they'll hardly feel each other because it's a big volume and they won't feel it, but as the crystal gets smaller and smaller once I've added one charge, if I go to add a second one, the Coulomb repulsion will be great, because they're both confined to the same tiny volume. This is why the charging energy scales like one over the radius, the smaller the radius, the larger the charging energy. These little particles that are doing the catalysis are quite tiny, so small that they can never have more than or two extra electrons on them. In fact they can really only have one. So I can very easily see a saturation event in the photochemistry. If I turn the photon flux up at some point, the catalysis won't keep up anymore, either for the holes or for the electrons. And I can see at exactly what laser power that happens and then I can compare that to the solar flux and try to see, is this going to work or is this not going to work in full sunlight? So that's the exercise that we do to try to make an artificial photo-catalyst work in progress.

So here's the algorithm to build on the nanoscale: design using scaling laws and then measure at the single molecule level. Now why do I say measure at the single molecule level? This is the next very important thing that I want to tell you. This can be a virtuous loop. The reason is because, when we make artificial materials, it's very hard to make two of them exactly the same. Now in nature, the DNA will make a protein and almost every single time they'll be exactly the same, if they're not the natural system has figured out how to repair them or else how to get rid of the bad copies. Although occasionally, you know we have problems from that, we have illnesses from that, but when they work right, most of the time, they're atomically exact. In nanoscience, there are just a few very specialized cases where we can make something atomically exact. They would involve things like picking an atom up and putting it down. That can be atomically exact, or they can involve synthesis of very small molecules which have 10, 20, maybe 30 atoms in them. But as number of atoms becomes large, tens and thousands, which is what we need for these kinds of structures, we cannot achieve true atomic precision yet, but we will. It's possible to. We know nature does it and we will too one day. But how can we get there? How could we get to the point where we could actually make atomically precise things? Well, we'll follow this algorithm and we'll look at each one and see how it's different from the next. But another thing that we need is observation methods which operate at the single molecule level so that we can see what's different from one to the next. So that's a big part of nanoscience is developing new tools.

I'm going to share with you today the tool that we made most recently. This is called a graphene liquid cell and what it is, is just a very simple thing. This is a movie of the growth of nanoparticles and I'll show it to you. Again there's never been a movie like this before. And this is what it's like. We take a piece of graphene, it's a single atomic layer of carbon, and we trap liquid between two of those graphene layers. It turns out graphene in one layer really sticks to the next. So if I have a graphene layer, and I put a drop of liquid on it and I take another graphene and put it on top, what will happen is that the liquid will break up into little pieces, and the graphene will seal around each drop. And now I have a little pocket of liquid that's trapped between the graphene layers and I can do electron microscopy in there and I can go in and look at every nanoparticle as it's forming in the liquid. So here you can see all of its crystal structure and you can observe directly the growth of these particles in solution as it takes place in real time. This is the graphene liquid cell, and it's going to enable us to do all kinds of things in the electron microscope that previously had not really been possible. So it's a way to see.

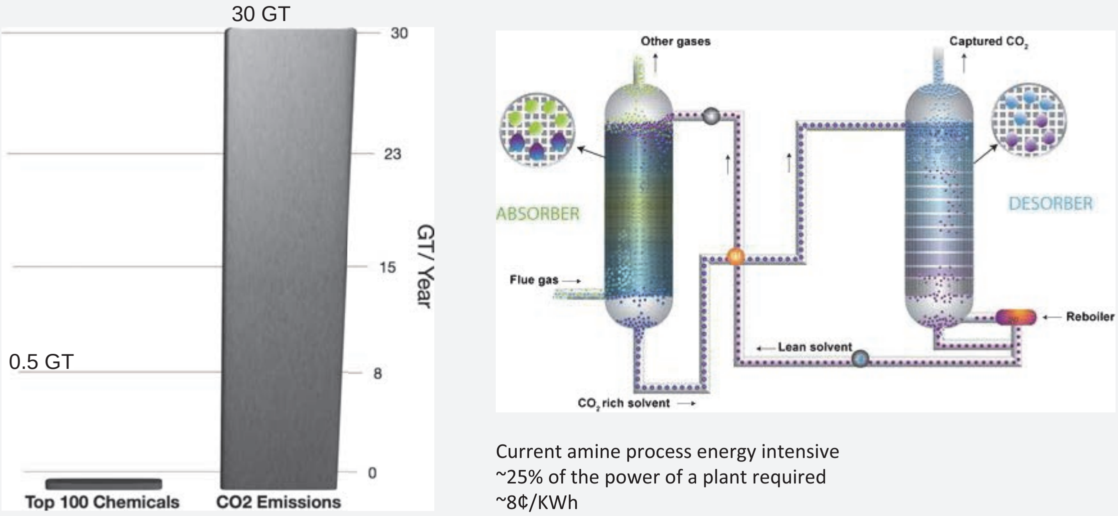
I'll give you an example of one thing that's seen here. This is a case of two nanoparticles coming together and fusing. And Sir John, I know this is of interest to you. Here is a case where there were certain kinds of defects in the nanoparticles. Here is something that happens very commonly when metal nanoparticles are formed. They come together and they fuse, you might have seen some of those events in the movie of the growth of the nanoparticles. Here we can see two particles that come together, and they fuse. And what we can see is that we can image the actual fusion event and what you can see is I can measure the end to end distance of the combining particles, and the thickness of the neck between them here. And what you can see is as the neck thickens, the end to end distance become smaller, okay. So as the neck thickens the end distance becomes smaller. So I can see that what is happening is atoms are moving around the edges of this particle and coming together and making this crystal. So now I'm actually observing the growth in real time. That's going to enable us to go back later and create much more precise structures than we have previously. So we've seen two, I have a third one if my time is okay. Is my time okay? Five minutes? It's okay.

Okay so let's do capture and sequestration. And this is something I have to tell you about energy that is very, very important. I mentioned to you earlier 30 gigatons of CO_2 is emitted every year. Now what do you do with a thing like that? 30 gigatons, I mean it's an impossibly large number. You can't really imagine what it means, okay. It turns out you can take the top 100 chemicals produced in the world, the top 100 chemicals, add them all up and they're half a gigaton. So now you know there's a factor of 60 difference between how much energy we use and anything that we make to use, pretty much, okay. This is why the energy problem is so complex. You can't just take the CO_2 that's emitted and say I'm going to make something with it because there's nothing we want on that scale except energy. So if you can make a complete cycle with the CO_2, with a photon and make a fuel again, then that matches, it's fine, okay, but absent to that, there's a lot of CO_2 leftover, and we have to put it somewhere. So people are thinking about how to capture the CO_2 and put it somewhere. So let's talk about that.

The current process for capturing CO_2 involves taking the CO_2 and putting it into a liquid water that contains an amine. The amine binds the CO_2. And now you want to release the CO_2. Well, you say why don't you just leave it bound, what you already know why we can't, because there's nothing I could bind it to that we have enough of. So you have to release the CO_2 somewhere away from the atmosphere after you capture it. How do you release the CO_2? Today, you boil the water and that's what we heard about earlier today that, it consumes an enormous amount of energy, therefore it costs too much, about one-third of the energy of the power plant would have to go into releasing the CO_2. It's too much.

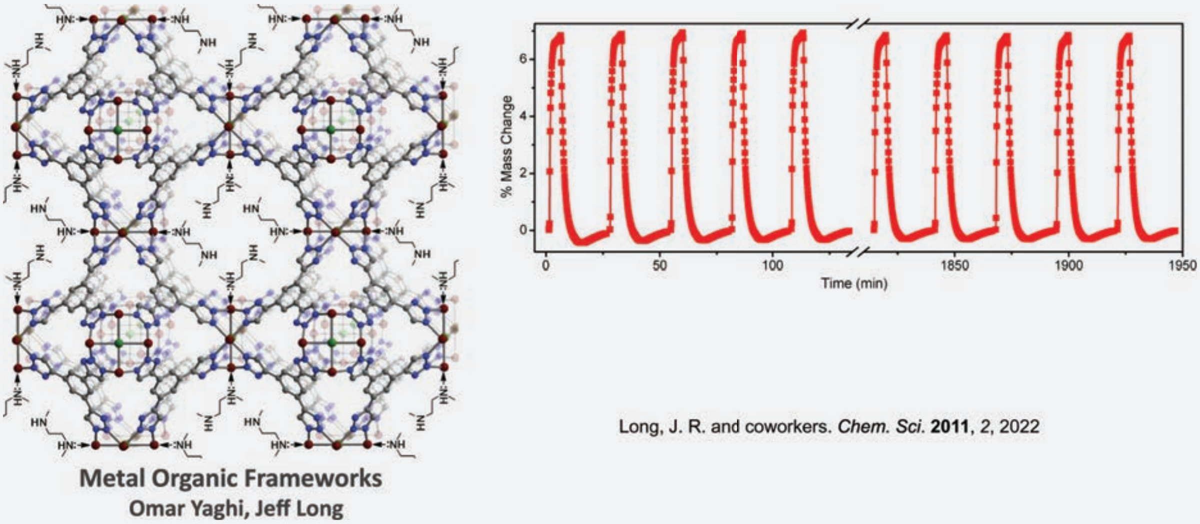
So you try to make new materials. So here are another class of nanoporous materials, metal organic frameworks, they're very similar to the ones that was shown by Sir John earlier, but these are materials that combine organic molecules and inorganic atoms in very intricate ways. And in this case my Berkeley colleagues, Omar Yaghi and Jeff Long, have made MOFs which contain carbon dioxide binding amines, but which are solid state compounds, so you never have to boil a liquid. And with these they've achieved now some very promising properties. They can release the CO_2 with one third of the energy that's typically used. So that is a design of a new nanoscale material for energy applications. And in fact you can make many others, but time is not going to allow me to describe them.

So now let's go to the section on energy analysis and risks. So what would you do with all that CO_2 after you capture it, to prevent it from going into the atmosphere and warming the planet. One of the proposals is that you stick it underground. So you take CO_2, you stick it underground and then it stays there. Now why would a geologist think that's a good idea? Well, it turns out our current energy technology is based on taking gases and liquids that have been sitting underground for millennia and they're not going anywhere. So if we pull gases and liquids out, we should be able to put others back in and if it's a formation that normally holds gases or liquids, a geologist will tell you it's got an excellent possibility of holding it for a very, very long time. Is that correct? Is that not correct? Well, so at the Berkeley Lab what we do is we now get a whole group of people to think about this from many, many different disciplines. And so for example, they'll



Current amine process energy intensive
~25% of the power of a plant required
~8¢/KWh

Carbon Capture and Sequestration — scale and scope of the problem.

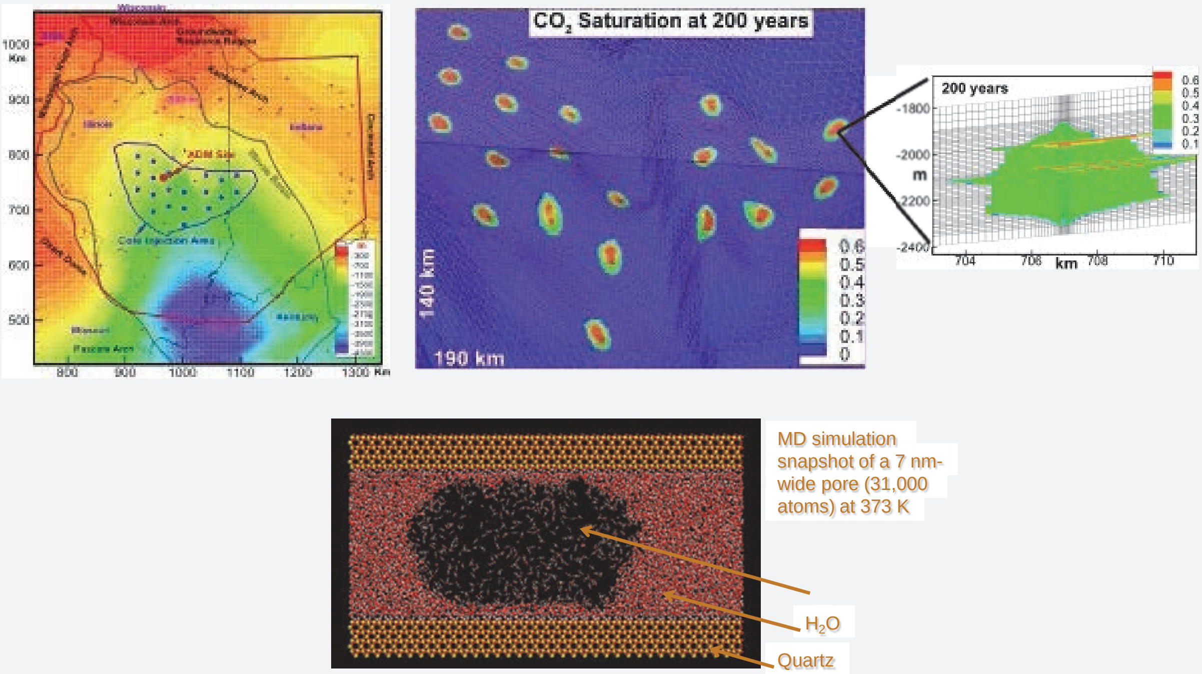


Long, J. R. and coworkers. *Chem. Sci.* **2011**, 2, 2022

Metal Organic Frameworks
Omar Yaghi, Jeff Long

Carbon Capture — New materials. The challenge: develop a material that can capture and release vast quantities of CO_2 at 1/3rd today's cost of ~8¢/KWh — Current technology involves capture using 30% solution of monoethanolamine (MEA) in water with regeneration carried out at 120°C. The working capacity for these solution is also much lower: only ca. 2 wt% CO_2. — We now have a related material that shows cycling at 11 wt% capacity with a similar low regeneration penalty.

try to do simulations. Here's a simulation of CO_2 on a strictly molecular scale. And so you've got some silicate material and it's got water and CO_2 and salt all mixed together and you try to simulate what is the nature of the interface and how is it is the CO_2 going to deposit, is it going to dissolve, what's going to happen. Once you understand the sort of molecular level then you can try to do a simulation at a very large length scale. Here they've taken CO_2 and they stuck it underground



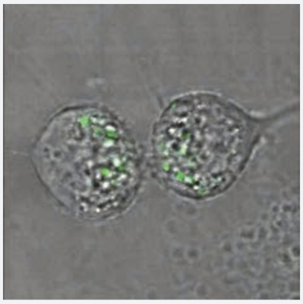
Carbon Sequestration — simulations. Simulated injection 5 Gt CO_2, Over 50 years at 20 sites. No transport between sites, gases move down. Peak pressure rise 30 bar dissipates over time — brine Zhou and Birkholzer GHGST, 2011.

in a series of wells in a particular geological formation in Illinois, all in the computer. And they inject a certain amount of CO_2 and they put it in over a period of time at these different sites. And what they find is that the CO_2 injected here, given everything they know about the rocks, what it does is it goes down vertically but it doesn't spread horizontally very much. But what does happen is the pressure goes up a lot.

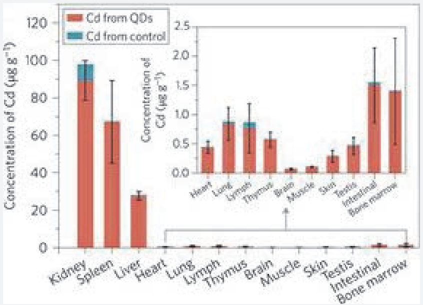
So then some economists come to help. Now we need economists. We have to have a diverse group, a community to think about it. The economists come and they say okay let's think about all this. We'll do a calculation of the cost of all of this. And they say, oh gosh you know what, you've pushed the CO_2 under there, you've made the pressure high, it's briny water, the water has a lot of salt in it. Actually, why don't you just push the water out, evaporate the water and collect the salt and then take the salt and sell it because it turns out the salt has an economic value. You can use it in the Midwest to salt the streets to melt the snow. And they can calculate the value of that, and it's actually significant. So now you start to see how you could build a system where the different parts talk to each other and one thing you do on one side starts to help with something you're trying to do on the other, but only if you thought about it, because otherwise one thing you do on one side can cause trouble on the other side. And this is why we have to change our thinking to be able to think as a system of energy, and not to think of just one part of the problem. It's very tricky, not at all easy to do.

So in fact now they start to think of all these other ideas, the geologists, and they say well gosh you know, there's another thing that I could do. It turns out I can take air and compress it into a big reservoir and I can store energy that way on a massive scale. And then they say, okay well what's the pressure-volume curve for that? And they say, if I put CO_2 in at pressure, the CO_2 can go supercritical. And when that happens that changes the pressure volume relationship and turns out you can store more energy if you have 20% CO_2 and 80% air then you can't if you had only air. That's very interesting, because now it means that I could take those air energy storage reservoirs and start using them 20% for CO_2 and I could actually have a positive solution again. So you start to see how the community really thinks about interactions in complex ways that are really very, very interesting.

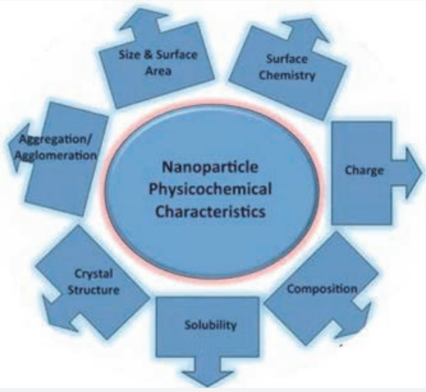
The very last topic here. I was asked to talk about health effects of nanomaterials and I do want to. They're very interesting and they're important, but it turns out we don't know near enough about it. So what can I say about this. Here's an image from my lab from about 10 years ago. This shows, a cell dividing, and it had quantum dots in the "mother" cell. And so the two daughters cells have separated we see that the quantum dots are going into the daughter cells. At the time we were very excited about this because what it meant was that we could take a certain cell type and load it with quantum dots, for example, it could be healthy cells and they could divide and we could have a separate set of cancer cells in the laboratory and they could divide and there wouldn't mix their quantum dots from one to the next and therefore we could track, for example, the cancer cells as they move through a tissue because they'd be the red ones inside a green or something like that. But when you look at a diagram like this, you start to think, hmm, I wonder if this is all okay or not because there was this inorganic thing sitting around inside these pockets and the nanoparticles just go right in their too very easily and you start to think, well what are the facts of that. And it turns out that people don't completely know. It's a very nascent early topic. Here's a book just came out. This is the first book I know of, that's a real book on this topic, Adverse Effects of Engineered Nanomaterials. And one of the things that it points out which I think everybody in our business knows which is if you have a nanoparticle, it's one thing to say, oh I have a quantum dot, but I can make a quantum dot that has completely different surface chemistry such that it will like to go inside a cell or it will run away. And



Quantum dots in cell division



"A pilot study in non-human primates shows no adverse response to intravenous injection of quantum dots"
Nature Nano May 2012



From "Adverse Effects of Engineered Nanomaterials,"
by Fadeel, Pietroiusti, and Shvedova, Academic Press 2012

therefore I have to take into account all of these properties of agglomeration, surface chemistry charge and so on before I could even begin to know where a nanoparticle goes. There are studies which show things like this shows nanoparticles which were injected into some monkeys in this case, and some of the studies have gotten to that point and they follow where the nanoparticles remain as a function of the time. In this particular case a paper that just came out couple of days ago. Pilot study in non-human primates shows no adverse response to intravenous injection of quantum dots. Well, for every paper like this you'll find another one that says something rather different. It's a very chaotic moment. It's a very chaotic moment. The science isn't settled yet.

So that the UK Royal Academy in 2004 issued what I think is the best statement about this to date that hasn't really changed. Treat nanomaterials as if they are hazardous. Seek to remove them from the waste stream. Don't apply free nanomaterials to the environment unless the benefits clearly outweigh the risk. Now what do we mean by free nanomaterials? That would be like particles that are just free to move about, but for example, in a battery they're not going to be free to move about, they're going to be embedded and you can recapture that material and use it later on. So for the vast majority of uses, in fact we can use these materials in a way that I think will be quite reasonable but in the meantime this science has to advance or else we're eventually we're going to get something very, very serious. And they say something very serious here as well, assess potential impact throughout the lifecycle of the nanomaterial. And now I think is a key thing and we certainly need to do that.

Okay, so I'm going to wrap up here. I hope that you have seen the scaling laws, the synthesis and properties of the building blocks, the power of one that means we have to have tools for looking at single particles and their trajectories and what they do, the very deep connection between artificial nanomaterials and biology both benefiting both biology and nanoscience. And right now we're in this era of we just learned how to make stuff, so now we're practicing making it and we'll just have to see what comes out of that, but here's a very, very famous phrase from another person, I said Democritus was the father of nanoscience okay, a more recent candidate would be Richard Feynman, a famous physicist, whose lecture on nanoscience really assured in the field in some sense and a very famous phrase of his, "what I cannot create I do not understand". That's a kind of model for nanoscience and it sort of stands as like what we try to do in this field and how it works. Thank you.

Audience: One small question, you mentioned the metal organic frameworks and the way that you can sequest a CO_2 into them. I've read somewhere recently and I can't remember where that this, although attractive from the purely scientific standpoint, is economically not good in the sense that the MOFs, the metal organic frameworks, are pretty expensive in relative to generate, is that true?

Paul Alivisatos: I'm not totally certain but I don't think so. I will say that the MOFs themselves at this point are finding some very interesting potential uses, for example, they can be used to put in a gas tank to make natural gas, you know, you can store it. And in those cases, the MOFs, the specific MOFs that are being used are quite low cost. BASF is now making some of these in tonnes scale. And I believe that the materials that are being used here are not especially ones that ought to be anything more unusual. So I don't know the answer completely but I don't think that's, you know there's nothing about the composition there that suggests, I mean it's got some means, the metals, I think zinc is being used you know it's not something that ought to be so pricey.

Audience: There are some interesting questions from the internet and here is one; What do you think is one, V1 application of nanoscience most likely to lead to a truly revolutionary technology? Is that the space elevator?

Paul Alivisatos: So let me say this. First of all that if you look at the world around us, today there are many nanoscience activities already in evidence. I mentioned a specific case which I personally have been involved in, biolabeling. Every pathologist pretty much uses quantum dots for looking and that you know many people personally will benefit from being able to see what type of tumor is there. But if you look inside a computer or inside a whole variety of technologies that we have today, the concepts of nanoscience run all the way through them and if we look, you know, much of catalases also as I think you know very heavy components of nanoscience built into it. So it's all over the place. With respect to space elevator, that's a fun concept. You know one of the great thinkers of the field, Rick Smalley, Nobel laureate who's passed away now, was a huge fan of the space elevator and nanotubes and was trying to push that idea. So it's an interesting idea. I personally haven't spent a lot of time thinking about a space elevator. I don't know where it's going to go but it's an idea that's out there. What I do want to say is that nanoscience is a very broad field and already it's finding lots and lots of applications. So I think it will be in a sense I think somebody earlier was talking about the pervasive impact that polymers have had in the world of materials. In the sense I think nanoparticles in particular are going to have a comparable impact over time because the range of applications that they can have is so huge.