Big Picture Podcast – Episode 24

Solar Fuels (Chapter 11A)

Interview with Professor Rajeshwar, Electrochemist

Co-hosts John and Tracy Suchocki interview professor Raj Rajeshwar, one of the leading researchers in the exciting area of solar fuels, which are fuels generated directly from sunlight. We explore the chemistry behind the many challenges still faced in the development of solar fuels. We talk about the prospects. About the possibilities. This is perhaps one of our more technical episodes. It assumes the listener has a basic understanding of chemical reactions, particularly oxidations and reductions. But for all listeners, much value and insight is provided. Duration: 47:39.

Podcast 11A

John: Prologue. Tracy?

Tracy: Roof top solar panels produce electricity. We know that.

John: Yup

Tracy: But imagine a not too distant future where roof top solar panels produced hydrogen fuel instead.

John: Hmm

Tracy: This hydrogen fuel can be used to supply your household fuel cell powering all your electrical needs, including a recharging of your electric car.

John: You’d be self-reliant. Off-grid

Tracy: Off-grid. Stronger against the dangers of storms, fires, and international interference.

John: And you know, communities would no longer need electricity from centralized fossil fuel or nuclear driven power plants.

John: And our collective carbon dioxide output, it would fall. We’d have few nuclear wastes. And we could export this solar technoloy to developing nations leading to better economic and social stability across the world. If only

Tracy: If only we had an efficient way to transform the energy of sunlight into a storable solar fuel. Then all these things could become actual.

John: For today’s episode, we interview professor Raj Rajeshwar, one of the leading researchers in the exciting area of solar fuels.

Tracy: Together, we explore the chemistry behind the many challenges still faced in the development of solar fuels.

John: We talk about the prospects.

Tracy: About the possibilities.

Tracy: Now hang tight through the technical jargon and you’ll be rewarded with a bright new perspective granted to you by your understanding of the basic concepts of chemistry.

John: Welcome to the Big Picture podcast, we're here with Krishnan Rajeshwar, distinguished professor of chemistry and biochemistry at the University of Texas, Arlington, and founder and director of the Center for Renewable Energy and Science

Technology, as well as past president of the Electric Chemical Society. Raj, thank you so much for joining us here.

Raj: Glad to be here. Thanks for having me.

Tracy: Welcome. Nice to be here with you. And I'm excited to learn more about solar fuels.

Raj: Thank you, Tracy.

John: Raj works with a topic dear to our hearts known as solar fuels. Perhaps we could start Raj. You could just describe your main research interests.

Raj: I've been involved in energy R&D for close to four decades or so in some form or the other, and first foray was the area of oil shales. This was just after the mid 70s, after the oil embargo and there was a lot of interest in the tri state area. The resources shales trillion barrels of oil locked up in the mountains in Colorado, Wyoming and Utah. This was during my postdoc training and the idea was to be to somehow take the sea organic matter out of the shale formation. And the problem with the shales, were they submerged a few thousand feet below the ground? So you don't want to disrupt the landscape in the process of recovering the oil. So the idea was to somehow liquefy the organic convert the organic matter into a flowing fluid which could be pumped up. So we were looking at the electrical properties, microwave type heating, for example. So this is what started me, got me started in energy R&D. And soon afterwards, I would say in the late 70s, there was this notion of the perfect energy conversion system that is use a split water into hydrogen and oxygen using an external energy source, and then you could simply recombine that hydrogen fuel on demand,

John: So it's a way of storing the energy.

Raj: Storing the energy. A big problem with renewables, as you can appreciate, is the fact that the renewables are intermittent. So, for example, let's take solar or energy. It's not constant.

John: Photovoltaics?

Raj: Photovoltaics. The sun doesn't shine all the time. So we need to have a way of storing that sunlight somehow. I call it bottling sunlight, keeping storing the sunlight in a bottle. How do we do that? One of the ways would be to convert that incident optical light energy into an energy rich chemical product, which could be, for example, hydrogen. Hydrogen has many things going for it. It's not optimal in terms of being a guest. That's one of the handicaps it has, but it has many other things going for it. You can appreciate hydrogen was the fuel of choice. People point to the Hindenburg disaster as a negative aspect of hydrogen energy, but it is not the hydrogen which was the culprit. The Hindenburg was the material that was used in the dirigible, plus the lightning. It was the perfect storm. Literally

John: The static electricity.

Raj: The static electricity, which set the skin on fire. And then, of course, the hydrogen ignited. But it does not the hydrogen. In fact, there are videos of hydrogen burning and gasoline flame, and there are many positive aspects of hydrogen flame. It's not as hazardous as gasoline. But any way you convert the incident solar energy into high didn't somehow then we have a way of storing that and then we can recover that energy, though the fuel cell, which would be recombining the hydrogen with oxygen in an electoral chemical device, or we can simply burn the hydrogen. In fact, there are even prototype cars in the market. Now, BMW has one which is based on a hydrogen combustion engine and you have to modify the engine somewhat to accommodate the hydrogen instead of gasoline.

John: And you would store the hydrogen and nanofibers?

Raj: That's a roadblock right now so we can talk about the roadblocks in due course, but one of the problems right now is storing the hydrogen onboard. If we have plentiful space like in a bus as so, then it's easier because then you have a lot of spare room where you can pressurize the hydrogen and store it onboard. But if we're talking about cars, then we have to somehow squeeze a large amount of hydrogen in a small volume

John: And that requires energy.

Raj: It cost energy, but, for example, space application. They simply don't. The economics don't come into play. Right.

Raj: In the space industry, they use liquid fuels, so they pressurize these gases. But the price is not a factor, doesn't come into play. They are worried about the mass then less worried about dollars. Of course, for terrestrial applications. That's what you're pointing out is absolutely a critical factor. We need to have an economic way of doing everything. In fact, ultimately, it's going to come down to what is the alternative, which is the price of gasoline per litre. It has to be competitive to that which it is right now. So but the road one of the roadblocks is the way of storing the hydrogen onboard in a car, for example. And there are many options are being bandied about, converting the hydrogen, storing it in a solid form.

John: Into zeolites?

Raj: Or as a hydride

Raj: So that's an ongoing technology which is evolving.

Tracy: So you started with talking about how to capture the solar energy. And you said it could be captured in hydrogen. And then the hydrogen could be burned.

Raj: That field has now evolved into something everybody calls it a solar fuels. It need not be just hydrogen. For example, another option. We can talk about is converting a greenhouse gas like CO2 into fuels, you know. So what you're doing there is you're not only mitigating the harmful effects of CO2 accumulation in the atmosphere, but you're converting it into a value added product. If you can generate, for example, methane or methanol from CO2. Then you have a fuel you're generating from waste material or material you want to dispose of like CO2.

John: So you went initially toward hydrogen as a potential solar fuel. What are the benefits of hydrogen versus methane or methanol?

Raj: You know, you can argue that converting CO_2 ultimately into a carbon based fuel and then burning it again. It's a circular argument. You're not really minimizing the carbon footprint. Ultimately.

John: You're still in the game of playing with carbon. So if you go toward hydrogen, you're pointing out is you could just forget about carbon altogether.

Raj: And that's that's a drastic transformation. That’s a challenge.

Raj: A sea change in terms of thinking this whole energy business. Obviously, there's a lot of resistance, but every oil company says that they have a renewable portfolio. Is it for PR or is it is it a honest effort? The crossroads, the turning point will be when we are going to have a carbon tax. If we if we have a tax on carbon emissions said that's the time when people will be forced or industrial will be forced to make a change, because right now I think you can argue, well, there are a lot of electric cars coming into play, but if you look at the total fraction of the transportation sector and you ask the question, how much has electrification? What percent of the total has. It's might minuscule,

John: Miniscule.

Raj: Right? It's less than 10 percent of Sunday. In spite of all the Teslas and Chevy Volt and Bolls and all the products.

John: I would love to look at this as a story. If we could, beginning with sunlight coming down to the earth and the challenges that we would meet along the way to creating a solar fuel. So the first step we can all imagine, the sun is shining, putting out a lot of energy and some have calculated enough energy actually per square meter or that close to the sun. So the sunlight is coming down. And the first thing that's going to happen in my mind, I'm seeing it's going to hit some solid state chemical and we would call that

Raj: A solar absorber.

John: A solar absorber. OK. The solar absorber. What are the challenges right there? First step of the way, the photons hit that solar absorber.

Raj: Mm hmm.

John: Why is that so difficult?

Raj: Here is a direct demonstration of quantum chemistry, if you will. Right. So we all when we were students, we we were very confused, too, at the idea of quantization. But here is a practical demonstration of that.

John: Ok.

Raj: So you have light coming in. The simple fact is that the light absorption process is quantized in the sense that only certain photons are absorbed. Some are just transmitted. So based on that, a single junction, people have done the calculation that the maximum efficiency you can get for a single junction photovoltaic cell is only is only 30 percent. It's only that's the maximum theoretical efficiency.

John: That's your maximum.

Raj: If you are doing close to 30 percent, you are doing extremely well. The average photovoltaic switch is on your rooftop. It's operating at about 12 percent.

John: Taking into account the peak spectrum of the Sun.

Raj: This is based on the integrated output of the sun at a certain time of day, at a certain elevation.

John: All that U.V. light coming in.

Raj: Yeah. Taking into account all the filtering effects of the atmosphere.

Raj: And the only assumption is how much of the light is absorbed versus how much is reflected. So we talk in terms of the practical efficiency versus the actual of quantum efficiency, because you really don't know how much of the light, how much. What are the reflection losses. But even barring that, your max is 30 percent

Raj: Though, you can have what we call a rainbow's cell, where we can stack up an infinite number of semiconductors with varying

John: On top of each other.

Raj: With varying band gaps. Even then it's not a linear relationship between the number of band gaps and the efficiencies.

Raj: Up, but it still doesn't creep up. You're talking about 50 percent max versus 30 percent for a single. When I mentioned Single Junction, I meant one band Gap. So if you have a silicon as the semiconductor, which is the standard prototype for photovoltaics.

John: Yeah.

Raj:, you're talking about one band Gap, which is about one point one electron volt. It's in the I.R. infrared range and you're talking about a single junction. And the physics tells us that the maximum efficiency efficiency of light to electricity, that is optical photons to electric power is 30 percent.

Interlude

John: So to clarify if I can for our listeners, we're starting to get into some fancy terminology. We're hearing terms like quantum chemistry, band gap, single junction, multiple junctions. Let's start with the quantum. As you'll recall from earlier lessons, energy itself is quantized. Like rungs on a ladder. There are only these distinct levels of energy that are possible. Just as there's literally nothing to stand on between those two rungs on a ladder, there's literally no energy happening between to distinct energy levels.

We've talked about this with the energy levels of electrons within atoms. But when you're dealing with any solid, you've got way more than one atom. So what happens when you've got the energy levels of neighboring atoms all adjacent to each other? Well, first of all, it gets kind of messy. But here's the broad overview. You'll have electrons that remain close to their atoms. And all those electrons form what we call a “valence band”. Then there are electrons that have jumped to a higher energy level called a conducting band. So, got that?

In the valence band you’ve got electrons stuck to their atoms. In the conduction band, you’ve got electrons that are loose. Think of a metal. For a typical metal, the valence and conduction bands overlap, which means its easy for electrons to move upward from the valence to conduction band, which is why metals conduct electriity so well.
Now, think of a non-metal. For a typical non-metal, there is an appreciable gap between the valence and conduction band. Because of that energy gap, it becomes rather difficult for the electrons to jump into the conduction band. It’s like a rung of the ladder simply too high and out of reach. This is why non-metals tend to be great insulators. All their electrons remain stuck in the valence band.

Now what do you have between metals and nonmetals? That’s right, the metalloids, such as silicon. For these elements the gap between the valence and conduction bands is real but quite small, which is why these elements work well as, wait for it, “semiconductors”.

Okay. Almost there. So what do we mean by a junction? For this, I’ll refer you to the textbook where you’ll read about n-type and p-type semiconductors and how when you stack them on top of each other, the interface between the two serves as a one-way valve, which means electrons dislogded by light are forced to flow in one direction through a circuit. Et Voila, the eenrgy of light is converted to energized electrons now flowing through an electric circuit. So, what’s a junction? It’s simply the interface between n-type and p-type semiconductors.

End Interlude

Raj: That's when we have a solid state photovoltaic device. We are not talking about converting the light energy to a chemical energy yet. OK, so now now we need to convert that electrical energy into some useful chemistry.

Raj: What could that be? That could be a reduction of protons by the electrons to hydrogen. And that's the electoral chemistry part

John: So

Raj: Of it.

John: Reduction meaning. “Leo the lion goes Ger”. **L**oss **o**f **e**lectrons is oxidation, reduction is a **g**ain of **e**lectrons is **r**eduction. And so reducing the proton means you have a lone proton and you are giving it an electron, creating a hydrogen atom.

Raj: And two hydrogen atoms then have to combine. This is where you asked about this. What is a catalyst's do? That's where the catalytic function comes in. So now you can see we are muddying the water a little more and more and more

John: Getting more difficult.

Raj: Getting more difficult.

Raj: Let’s start out with having a semiconductor which could harness the sunlight. We generated electrons and we converted electrons to two hydrogen atoms. Let's say now, unless the hydrogen atoms are in close proximity on a surface, they're not going to recombine to hydrogen. We want hydrogen molecule, which is H2. And that's what we want to store because hydrogen atoms are not stable. They are high energy intermediates, if you will. So we need to convert the hydrogen atoms which are formed by the initial reduction into hydrogen molecule. There you need a catalyst. So the semiconductor surface also has to have a catalytic property that it's able to store multiple electrons because each of the electrons say reduce the hydrogen proton to two hydrogen atoms. You're really storing multiple electrons in the surface in a way that's another way of looking at it. So then you form the hydrogen and that process has to be kinetically fast because otherwise we're going to have losses in the in the overall cycle. But most importantly, we overlook the fact that the semiconductors contacting a liquid that means it has to be chemically and photochemical is stable.

John: So this is happening in water because that’s where the hydrogen is coming from.

Raj: Exactly,

Raj: The protons are supplied by water. So you do this experiment with silicon surface. The cell will probably last a few seconds because what happens is you immediately form a silicon dioxide layer on top of the silicon and the cell dies. So you've got to have a stable or a stabilized semiconductor surface in contact with the water. And this is where the surge has been. And I mentioned this in the talk. We the community, we, meaning the the community worldwide have been looking for possible materials, semiconductor materials, which are stable in contact with light and in contact with water, unlike silicon. So silicon works very well in a solid state photovoltaic device,

John: With no water around.

Raj: But no water.

John: Yeah.

Raj: But it does not work. It's not very happy in contact with water. So so people have tried. What they've done is they've also explored this notion of Burri junctions. So you remove the photovoltaic junction from contacting the water. So it's burried underneath. So the top surface is designed for catalytic function. It's a metallic surface, let's say, which can do the electrochemistry part. In other words, it can transport the electrons from the underlying junction into to the water surface where the electrochemistry happens. So that is much like

John: Mm hmm.

Raj: An electrolysis

John: Yeah.

Raj: Device.

John: Nice.

Raj: Electrolyte, for example, electrolytes does exactly that. An electrolyte that has two metal electrodes, metallic electrodes and one junction the protons reduced to hide it in the other junction. Water is oxidized to oxygen. So you splitting water into hydrogen and oxygen. This is exactly the idea. So you use spatially removing the photovoltaic junction from immediate contact with the water. We we are exploring multiple options in our laboratory,

John: That's

Raj: Like

John: Almost like pushing it towards just plain old electrolysis. Take the

Raj: Electricity.

John: Electricity from this photovoltaic and electrolyte some water. And

Raj: So,

John: There's your hydrogen.

Raj: Yeah, you so you make the argument this is nothing, but you're hooking up a photovoltaic cell to a electric Litsa. But those are two disparate devices here. You're trying to integrate the whole thing

John: Into

Raj: Into one

John: One's.

Raj: Single device. There are multiple advantages to that in terms of wiring and losses and optimizing two separate devices as opposed to optimizing

John: What

Raj: One.

John: Kind of hope do you have for that? I mean, the default, it would seem to me, would be just get your optimize your photo cells and have generate the electricity to electrifies water all you want.

Raj: Which is where the industry's leaning toward. At this point,

John: Because it's a sure fire

Raj: It's

John: Done technology.

Raj: An easier problem to solve right now. The alternative in terms of integrating a monolithic

John: An

Raj: Single device

John: Island, one

Raj: Which

John: Integrated

Raj: Can all

John: Device.

Raj: In one, the challenges seem very steep. I'm not honestly I'm not hopeful in my lifetime that we're going to crack this problem because, of course, the payoff is huge.

John: So

Raj: So

John: Here.

Raj: I'll be foolish to stop working on it. We are all optimists at some level or the other. But if someone wants to make a real money out of this, the prudent option would be have that parallel thing of combine what we call a hybrid device, a hybrid foldable takes cell hooked up to a water, electrolytes to drive the solar fuels. Of course you can extend this argument and you can say we can not only do the water splitting, but we can also do CO2 reduction. This way

John: Yeah,

Raj: We can we

John: Yeah,

Raj: Can

John: Couldn't do that with the photovoltaic cells.

Raj: Sell there again for the same similar problems because they you're reducing CO2. The electrochemistry challenges tend to be a little more complex than water

John: The

Raj: Splitting.

John: Water.

Raj: Simply speaking, for example, CO2 reduction can occur in many steps. So two electrons step would generate carbon monoxide from CO2.

John: Yeah.

Raj: So the option there would be convert CO2 to carbon monoxide, which can be used to create a synthesis gas along with a variety of carbon-based fuels using Fischer-Trope technology.

Raj: Well-established technology. That would be the other option would be to do Aseel plus H to generate that in our photo electrochemical cell and then do the conversion of further conversion to gasoline separately.

John: But for for the photo catalysts that you're talking about, you have some leads in terms of what it might look like and you look to the periodic table and you see what elements you have to work with. Because what we're needing to build here is an electrode that has all these marvelous properties together, all in one. And you looked at parent table and you see what you got. It's not going to be any one element, likely some sort of ceramic or alloy of various elements. Could you talk a little bit about combining

Raj: So,

John: That?

Raj: Yeah, that's a very good point you raise, John, because there's also this other notion we don't want to have elements like platinum. The single most factor keeping back fuel cells from cars on the road right now is platinum. All of the platinum is controlled by one or two geographical locations around the world. There's not a whole lot of platinum around. South Africa controls most of the platinum deposits. So and that's a huge effort going on now to reduce the amount of platinum needed for fuel cells.

John: So even though platinums

Raj: That is

John: Really

Raj: Really awesome.

John: Awesome, it's

Raj: It's

John: Just

Raj: Just.

John: Not available

Raj: Yeah. This is

John: As.

Raj: A God's way of doing a trick on it.

John: It's.

Raj: It's it's it's called a volcano plot, which has the catalytic activity versus the elements,

John: And listeners to see that plot and check our show notes.

Raj: The tip of the volcano. Plot is all elements like platinum, rhodium, osmium,

John: You heard it

Raj: Iridium.

John: Here

Raj: And

John: And

Raj: Nicole

John: Nicole is.

Raj: Is so on the on the

John: A

Raj: T

John: Periphery

Raj: Lids, much

John: Must.

Raj: Less. So that's a challenge. That's the other challenge is the catalyst for hydrogen production. They all happen to be noble metals

John: Expensive,

Raj: And expensive,

John: Rare noble

Raj: Rare,

John: Metals.

Raj: No novel metals. Things like nickel worked reasonably well. In fact, iron works to an extent. So that's what the industry or the research community and fuel cells is a huge effort going on to find non platinum group metals as catalysts in the fuel cell, of course, is the reverse. What we are talking about is the oxygen reduction and hydrogen oxidation. The hydrogen oxidation is an easy process, relatively

John: It's downhill.

Raj: Speaking. Yeah,

John: Yeah,

Raj: But

John: Yeah.

Raj: Both

John: Water

Raj: Are downhill.

John: Down

Raj: The

John: The

Raj: Oxygen

John: Oxy.

Raj: Reduction is a difficult process because it involves four electrons. That's where the best catalyst right now is platinum. So to go back to the water splitting is the same thing. Water splitting is doing it in reverse. It's the same idea. So you want to have what we call earth, abundant elements, non-toxic elements. So that's the other side of the coin.

John: It's got to be abundant. It's got to

Raj: It's

John: Be

Raj: Got

John: Non-toxic,

Raj: To be about non-toxic.

John: Safe. It's then it's got to work

Raj: Yeah.

John: As

Raj: For example,

John: Well.

Raj: Prof's guide, solar cells. There's a lot of concerns would led. And you can argue, well, lead is used in the lead acid batteries in the cars, but that's not soluble. Led in the Petrowski solar cell case. The lead is soluble and so the toxicity concerns are much worse. Much like chromium 6 was a huge

John: Fxe

Raj: In

John: Kurumi.

Raj: Hexavalent

John: Yeah.

Raj: Chromium in California because once it until it's soluble enters into the water stream. So the toxicity is a huge problem. Things like cadmium cannot be used mercury. So it rules out many, many elements

John: Would they explore those elements anyways, just to learn the chemistry?

Raj: We have done people. We meaning the community, has worked with things like selenium, copper, indium dicipline inside. Selenium is toxic in high amounts hiam concentrations of selenium

John: Not good

Raj: Or hazardous.

John: As a.

Raj: But still people are working on those materials on the notion that we can do efficient recycling, that we don't let the. But that's in the solid-state case solid-state photovoltaics. There's not much concern that they're going to be soluble. But in a in a photo,

John: You have it

Raj: Electrochemical

John: In water, it's going to dissolve in

Raj: Itsaid

John: That water,

Raj: Says.

John: What are you going to do with that water?

Raj: Exactly. So it's a whole game. It's the game changes there. So that that's that adds to the challenges. So not only do we need a champion photovoltaic material, we need a champion electrode material with these elements which make up these materials have to be earth abundant and they have to be non-toxic. And so the DOE, those are some of the challenges. That's what makes me a little worried that they're going to crack this problem in the foreseeable future. But the payoff is huge. You're

John: You remain optimistic

Raj: Optimistic.

John: Based upon.

Raj: I remain optimistic on the basis of history that when our species have sought out to solve something, we have done it right. At what cost? That's a whole different matter. But if we wanted to land on the moon, we did land on Mars. Maybe all we going to do that. Maybe we will. But we have set out these challenges over the. And we have solved them in these solar fuels. KS It has to be borne in mind that we haven't had a sustained history of funding over the years. So we have it's been in fits and starts. Unfortunately, the whole renewable business. Renewables business is tied to politics. So it's every four years. You know, the solar or renewables. When the liberals are in control, there's much more funding. But when it tends to be conservatives, it tends to be more fossil based. There's a strong fossil lobby. In fact, you can see that in the in the legislations which have been passed in the on the EPA front

John: So from that comes a lack of predictability?

Raj: Which makes it all the more difficult.

Raj: The saving grace now is the environmental fact, the fact that the younger generations are worried about what we are doing to the planet.

John: Yeah.

Raj: And

John: Needs to be sustainable.

Raj: That is what's probably going to save this research effort and it's gonna sustain it. I've gone through these boom bust cycles over the last few decades before we were not concerned about the environmental aspects. All we were concerned about was the price of oil. So it was just tied to economics and nothing else. So right now, it's not just that the price of oil is important, but more than that, it's also what harmful effects are the wreaking on the environment by burning fossil based fuels? That's definitely going to be a factor. The other the point of this equation we did not talk about is worth exploring is this plan so doing it. We call this artificial photosynthesis and the argument can be made. Well, plants are doing it, but the plants don't care about the economics. They don't care about the efficiency plant. Photosynthesis happens to be a very inefficient process

John: 3 percent.

Raj: At Max. Yeah, it's but there's enough redundancy in nature that it doesn't. But any manmade energy conversion system has to ultimately ask to come down to dollars and cents. We have an interest of the chemical engineering community yet because we haven't come up with consistent 10 percent stable device which then can be engineered. The engineers will only scale technologies which are viable if we are looking at three four-plus and it's simply not worth their time. And that hasn't happened in the solar fields. It will not happen till we deal at the laboratory level. We can demonstrate a 10 percent minimum stable. Stable meaning what, 10 years? Let's say

John: That's

Raj: So long

John: How long the electro

Raj: For

John: Last.

Raj: Industry would consider 10 years as a livable. You know, you can take it out, replace it

John: Ok. Here.

Raj: 10 years.

John: Yes.

Raj: So if it'll last 10 years, I think it should be at least viable.

John: Somehow I'm reminded of a good year back in the mid eighteen hundreds. He was searching for how to make vulcanized rubber and he was just up in the night trying to combine this and that and that and this. Then finally, bam, he got vulcanized rubber. I'm reminded of that in the search for photo catalyst for solar fuels.

Raj: We are focused on materials which can fulfill those varying requirements of stability, the appropriate electro optical properties of the carrier transport, the kinetics. So we do this. Materials design, if you will, using we I worked with a theory group. So we set out a set of properties. And this is really cutting edge. I would call materials by design. It's like you set out the properties you want and then you synthesize tailored to have that properties. If we can do that, this would be things of the order of like machine learning and things like that, artificial intelligence where, you know, it's right now we do it by trial and error. It's much like the drug industry. OK. We know what properties you want for the drugs, but a priority when you synthesize in the lab, they're not necessarily gonna have those target properties. That's what leads to things like combinatorial because then you synthesize variation variants of that in wells combinatorial well, you synthesize combinations. Hence hopefully you hit upon one sweet spot that one composition has that desired combination of properties.

John: Strong arming. Going through all the different variations you could possibly imagine. And just just testing them all to see

John: What sticks.

Raj: It's a huge try. That's where the cost comes in and that's what do you want to minimize? Ultimately, we want to reach the goal where we don't want to spend all the time in the space, which is not an optimal. You want to be able to hone in on that sweet spot.

Raj: You don’t want to waste too much time on non optimal materials. You want to hone in on that optimal combination. And we are working with, for example, turnarounds in quaternary is or even higher number of elements,

John: You fought

Raj: Four

John: Your four or

Raj: Or five

John: Five elements

Raj: Elements

John: Together

Raj: Together together

John: In a compound.

Raj: Making a compound

John: Oh,

Raj: Semiconductor.

John: Wow.

Raj: That's what we are doing in our lab. It's done pretty much by trial and error.

Raj: Because there is no crystal structure. Person or material scientist cannot tell us that if you have this combination of this chemical combination, it's gonna have that property. You can ask the question of when a mixed two elements with oxygen. Why does it have that structure? Ternary compound can be viewed as a combination of two binary oxides. Right. But the two binary oxides have certain structure. The ternary oxide turns out to have another structure. Why does it have that structure?

Raj: We don't know why. Then they combine they they form that structure. It does some with the properties that, for example, band gaps, the two binary oxides may have different band gaps.

John: But

Raj: Yet

John: They're combined.

Raj: The ternary there and they combine.

John: Oh, yeah.

Raj: There are some rules, some some cases you can predict what the ultimate band gap is gonna be. But it doesn't it's not obeyed in all the case.

John: We've talked about this earlier in terms of chemical changes, when you have one element which is yellow, say sulfur and you have another element which is colorless, which is oxygen, you think you might put them together, you have something that's a blend of the two. But during a chemical change, that's the magic chemistry as you come up with something completely different. Water, for example, is not hydrogen. It is not oxygen. It's a liquid. Its water is uniquely different from the elements from which it is made. And what Raj is pointing out here is that you can't protect all the time. What you're gonna get when you take four different elements and you put them together. It's an exploration, educated guesswork.

Raj: That's where we're trying to do this in a smart way and do the modeling and calculations and say, OK, if you mix these two. This is what you're going to get. And this other property you're going to have. Right now we are not there. We are not there yet.

John: But do you start with cause you said platinum is the ideal metal or. And so do you start trying to imitate that? And just try to.

Raj: That's a very interestrates. That's an excellent I have to think about that. Whether we are actually rashly going on, we're trying to mimic what makes platinum an excellent can we know why they function as good catalysts? In the case of there, it's the adds option strength, but the strength of the ETS option should not be too strong. So that's where the volcano comes in. So it has to have the right amount of affinity to bind the hydrogen atoms, yet had not have too much affinity

John: Let him go.

Raj: That that bond has to break and a newborn has to form between the two. IDGNS. It's a very tenuous balance between two opposing forces.

John: That you get with platinum.

Raj: Does it get platinum?

John: Yeah.

Raj: So

John: So.

Raj: That's what the terrorists are trying to do is to see whether we can make come up with an alternative for platinum which will have that same. We are talking about surface properties. These are happening on the surface because catalysis

John: Atlas's within

Raj: With us

John: Water.

Raj: Within water catalysis is a surface phenomenon. So when we talk about catalysis, it has to do with binding. And it has to do with the release and it has to do with new product formation and the kinetics of that, because ultimately a catalyst speeds up the reaction. Right, without itself undergoing any change. There's something magical about the Noble Metals surfers, which nobody has been able to quite come up. I mean, we have Kath's materials for oxygen reduction, which come within a few million gold of platinum, but still doesn't beat platinum yet. It's only the last couple of decades where we have been able to understand the atomic god, the nanoscale happenings, the processes at the surface. We didn't have the tools before. Now we have spectroscopic and microscopic tools which we can apply to understand what's happening. Why is platinum so magical? Unfortunately,

John: It's

Raj: It's also the

John: A cruel,

Raj: Most expensive.

John: Cruel joke on us. The synthesized photosynthetic processes is how is that connected with the photovoltaics?

Raj: So the plant photosynthesis process. What happens there? It's very similar to what we are talking about in water splitting. It's the photo assisted oxidation of water to oxygen in the plans. Plants don't have platinum in there, but they have these intricately designed, naturally occurring manganese catalysts, which people are only now the last two decades as we've been able to isolate and understand the structures and the functions of these manganese catalysts in the plants. So on the reductive side, it's a little different that plants don't reduce the protons to hydrogen. Instead, it takes a reductive power and reduces the CO_2, so it assimilates the CO_2 and stores it in the organism. So.

John: Sugar.

Raj: So it fixed.

John: Yeah.

Raj: Yeah. Exactly.

John: Ok.

Raj: CO_2 is fixed on the reductive side. But what's happening on the oxidative side is exactly similar to what we are talking about. Now you can argue immediately, can we take the same natural organisms and transpose it and construct? People are trying to do that, but it has not been too successful. I can recall genetically engineered or artificially engineered natural plant type catalyst being applied to a water of food oxidation. I think the maximum efficiency has been a couple of percent 3 4 percent.

John: I'd like to be clearer on the term artificial photosynthesis. How would you define that?

Raj: Artificial photosynthesis is doing the same chemistry that plants do, but doing it with the different materials. Let's say in the plant, photosynthesis, it fixes the carbon instead. We could be generating hydrogen from protons. So what the solar fuels community does can be termed artificial photosynthesis.

John: Ok, artificial photosynthesis directly generating fuels from sunlight and immensely challenging endeavor that could revolutionize our movement toward sustainable energy. Professor Rosa Shaw, thank you so much for joining us here. The big picture podcast. It’s been quite the honor.

Raj: Thanks for having me, John. Tracy.

[Theme music]

Raj: It's been a pleasure.

John: Our theme music by Zach Jeffery. Musical flourished by Patrick Wright on jazz guitar, Scott Pazira on bass, and Carrinton Clinton on drums. Productions assistnce from Greg Simmons and CPro Music. To learn more about professor Rajeshwar’s work on solar fuels, be sure to visit our show notes at ConceptualScience.com where you’ll find that ever so revealing volcano plot. A note of appreciation to all instructors using conceptual academy. Thank you for your support. To the hardworking student, our thanks to you as well for your learning efforts, which we see as the path to making this world a better place. There's a bigger picture. That's good chemistry. Good chemistry to you.