Ultrafast Processes in Chemistry
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Module No # 12
Lecture No # 63
Multiexcitons in Semiconductor Nanocrystals – Part 2

Right this is where we stopped 7 excitons at the cost of 1 and now we want to know how did they even know that they have done it? Well they knew it from transient absorption data.

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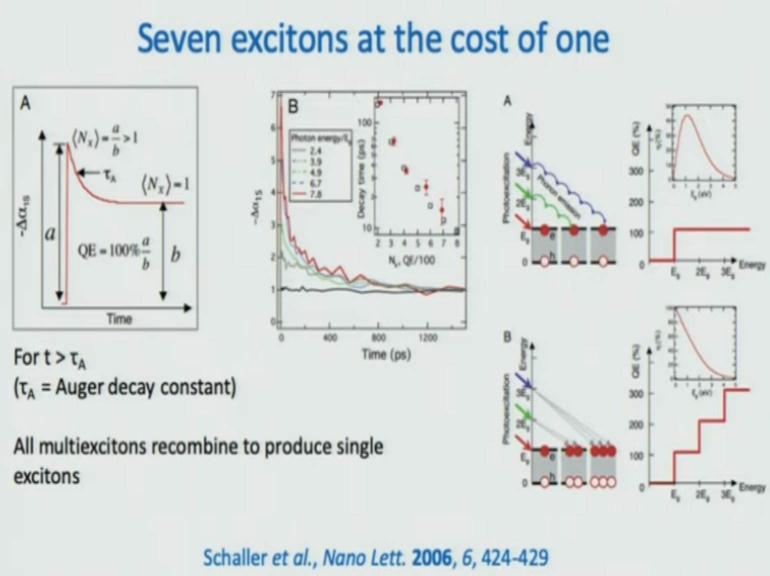

Seven excitons at the cost of one

For t > τ_A
(τ_A = Auger decay constant)

All multiexcitons recombine to produce single excitons

Schaller *et al.*, *Nano Lett.* **2006**, *6*, 424-429

And to understand what they did it is instructive to follow this schematic that they had been presented in that paper what they say is this? As we saw earlier in 200 picosecond or so the hot excitons have cooled down. So whatever we have beyond 200 picosecond is has got to do with exciton and here we are talking about transient absorption right. So transient absorption beyond that initial decay is quite long lived and that is entirely due to well if I may call it mono excitons not bi-exciton not anything else.

So what they said did is this delta a or what they have written delta alpha the designated this as b and here this Nx = 1 basically it is a regular excitons not bi-excitons or anything. And then what do you get after this instantaneous excitation you get this hot electron well hot electron then bi-exciton so on and so forth. So what they said is that this instantaneous excitation is designated as a and this Nx = a / b this is what they call well that multiplied by 100 that is percent quantum efficiency for formation of exciton which is what happens when everything is a regular exciton this is in the initial stage you have hot excitons and then you have your so on and so forth.

So what they say is that this is a measure of quantum efficiency and then once again what they did is they tail matched and the tail matched at 1 why? Because Nx = 1 at long times and then when after tail matching in fact you see the tail matching has done at longer times here it is not even 200 picosecond it is 1200 or more. As we have discussed earlier excitons can actually have a long component of life time.

So here if you go from bottom to up you actually go from 2.4 times eg to 3.9 times eg, 4.9 times eg, 6.7 times eg, 7.8 times eg are super imposed. And at 0 time they are super imposed at a value of 7 remember normalization has been done to 1 at long time so basically this 1 is b so whatever we get from the well Y intercept if I may call it well it is Y intercept is that the Y is delta alpha that is your efficiency that multiplied by 100. So this is how they arrive at 700% efficiency might sound strange to people working in fluorescence spectroscopy let us not forget more than 100% efficiency is quite common in photo chemistry right.

Number of molecules produced per photon absorb that can be more than 100% the only reason why we cannot have a quantum yield more than fluorescence quantum yield more than 100% is that you use 1 photon you cannot get more than 1 will always get less actually. So this is different here whatever extra energy has been so you are using a photon of higher energy and the excess energy is being used to generate a more excitons that is why we get this 200, 300, 500, 700% quantum efficiency.

This quantum efficiency is for formation of excitons not fluorescence is this is the efficiency of formation of charge carriers actually no that will come later. And what have in the insert is that they have super imposed for every case the short time constant obtained by regular fitting and by this Nx normalization and they have shown that it is consistent. So what we have arrived at is that there is a difference between bulk materials and nano materials I mean there are many difference between bulk material and nanomaterial’s.

In this context the difference is that for a bulk material what happens is when you excite at eg you have 1 photon absorption and generation of 1 exciton so efficiency is 100% if you excite and 2 eg or 3 eg or wherever this efficiency does not change 1 photon is absorbed and an exciton is regenerator that is what happens most of the time in bulk. And the inset here is the actual efficiency of charge carrier generation and that efficiency has been worked out already in turns out that it can be maximum of 0.044 sorry 0.44.

As you see excited very high eg value you get nothing you excite at 0 which means you do not excite then of course you get nothing when you excite at eg that is when you get the maximum efficiency because if you excite at more than eg then non-radiative process is take over. See in all the discussion so far in the previous module and this one we are not for once talked about other kinds of dissipation.

Well we have in a way because they talked about cooling but we really did not think about it so much we kept thinking that we generate 1 excitons somehow that exciton will give one charge carrier it is not necessary they can re-combine they will re-combine right. So the competition always between recombination of electron and hole by themselves and the separation by applying an potential difference.

So 0.44 the best one can do I am talking about efficiency of charge carrier generation can at best 0.44 in bulk. In nanoparticles however what one can think is that if you use smaller eg nanoparticles so this plot is I understand it in the in a different way if you use photons of higher and higher energy so compared to that this eg is smaller and smaller what we were saying is that as you use material with band gap as much smaller than the energy of the photons that you use efficiency can in principle can go up.

What which efficiency? Efficiency of charge carrier generation an in principle go up to 100% okay that is the ideal scenario this is the reality.

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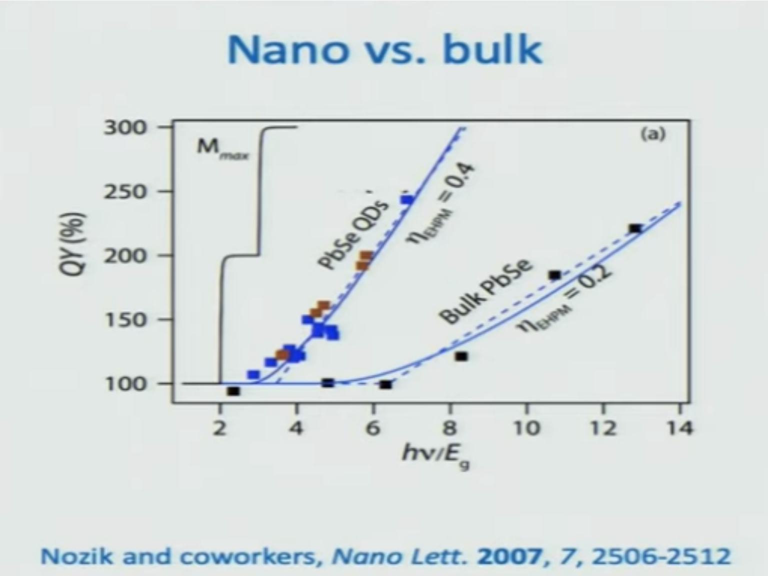

Nano vs. bulk

Nozik and coworkers, *Nano Lett.* **2007**, *7*, 2506-2512

In this 2 modules we are going to take the names of certain people who have really made advances in this field over last 2 years you must have heard of Nozik because he one of his works actually made it to the newspaper I think last year or a year before. So what Nozik's group showed was that this is what you expect a step wise increase in efficiency of charge carrier generation and well efficiency quantum em and then efficacy of charge carrier generation is determined this is what they get for PbSe quantum dots this is what they get for bulk PbSe.

So see bulk PbSe also it is not flat right what is the expectation quantum yield should just the same that is not correct and if you look at the efficiency of charge carrier generation. In bulk it is 0.2 in nanoparticles it is 0.4 it is definitely more but the picture is not really as row Z as we might have thought it is. It gets double does not get 100 times but never the less the efficiency of charge carrier generation does go up if one goes up from bulk material to its nanoparticles.

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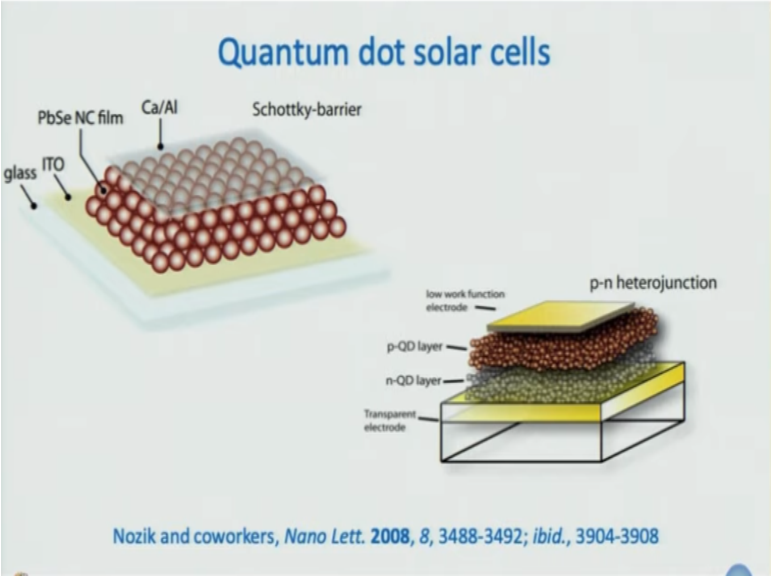

Quantum dot solar cells

Nozik and coworkers, *Nano Lett.* **2008**, *8*, 3488-3492; *ibid.*, 3904-3908

And that is what as they made the quantum dot solar cells very attractive these are 2 kinds of quantum dots solar cells are commonly studied commonly made Schottky-barrier and pn heterojunction. In Schottky-barrier what you have is you have glass ITO is transparent electrode so light has to get in right and what at the same time there has to be an electrode inside that you have this semi-conductor nanoparticle film. And then you have the other electrode calcium aluminum that is what it is that is what it gives you a Schottky-barrier.

And in the other one you have a pn junction so you have a p quantum dot layer you have an n quantum dot layer and rest of it is pretty much the same. There has been a lot of study of not only efficiency but also a ultrafast dynamics of charge carrier formation in quantum dot solar cells this is in itself is has become of hot field of research over the last 10 years or so. Before quantum dot solar cells people used to talk more about dye sensitized solar cells.

Well again let me digress a little bit why is it that we need all this I mean solar cells are there all around we can see solar cells and from here if we go to well look at the roof of almost any building you see solar cells. What is the need of further research in solar cells? The problem is the solar cells are actually very expensive solar energy works because of huge amount of government subsidy. It is really not a commercially viable proposition even more and then it is very easy to break those cells also.

Somebody gets unhappy of solar energy and can go with the stick energy and mash up this cells and it is very expensive. So one approach that had been taken was will use a dye excite the dye and that dye is going to transfer its energy into things like titanium dioxide nanoparticles and then charge carrier generation would take place and there has been lot of work in from late 90's well of course people started working with things like porphyrin's other dye molecules it was found out that your dye molecule has to have a COS functionality otherwise it can anchor itself titanium dioxide nanoparticles.

So people tried other things like vegetable dyes somebody proposed goat blood that contains a lot of dyes so on and so forth. But there is a problem dye with sensitize solar cells. Dye sensitize solar cells can actually be bought for I think few 100 Rupees may be few couple of thousand Rupees. You can buy it everything will come assemble and you are done it is very nice thing to demonstrate the problem is this.

The whole idea of this your dye sensitize solar cell comes from photo synthesis. In photo synthesis you have light harvesting you have reaction center where charge separation takes place and that is how it works. So if one can mimic photosynthesis before the step of production of glucose then one can harvest in sun light and all this processes are ultrafast right absorption light of course and then there is always this fret that takes place and electron transfer everything is ultrafast that is why the ultrafast community got into this field.

Now the problem is this that even chlorophyll by the way is something that degrades in sun. But the advantage of plant is that it is a living thing so it can grow morely so it can produce more chlorophyll. Dye sensitize solar cell cannot grow cannot produce more dye and really miss if you have to change the dye all the time that is why whatever dye is used in dye sensitize solar cells so far is found to be not stable to the point of satisfaction in sunlight.

So the cell would work for 1 hour or 2 hours or 2 days 5 days and not any more. So it is once again not a very practical thing that is why focus move to solid state solar cells. And quantum dot solar cells have been explored for a long time because quantum dots are more stable than dye's. And secondly what we saw is being nanoparticles there is his advantage of formation of multi exciton's okay.

So ideally this module should have ended here but let me just for the sake of completion also go ahead and say that quantum dot solar cells as many of us would know already are slowly making way may be not even slowly for another kind of material solar cell with another kind of material and that is Perovskites.

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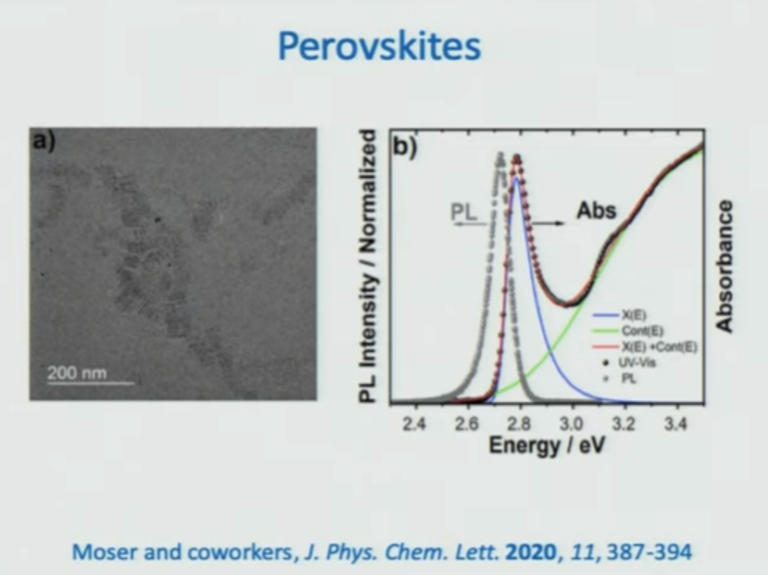

Perovskites

Moser and coworkers, *J. Phys. Chem. Lett.* **2020**, *11*, 387-394

Again the problem of Perovskites is stability so far 2 problems one is that perovskites contain lead. So one major focus has been to make perovskite without lead the other issue is stability to water moisture stability to light and so on and so forth. But quantum dots perovskites turned out to be very promising so once again let me just show you a piece of data not really going into the detail of perovskite but there is another reason why I want to show it.

Moser and coworkers this is the paper that has been published this month 2020 so again perovskite quantum dots have been made you can see images here and generally when you have perovskites quantum dots you see squares nice squares they are very good looking. Only last week there has been a paper from the group of Narayana Pradhan where they have made perovskites quantum dots of shapes other than square that itself as an interesting advance.

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But here since it is a nanocrystal anyway you have similar absorption and PL spectra that you expect for nanocrystals. So what Moser and coworkers have done is that they have studied ultrafast dynamics in this perovskite nanocrystals.

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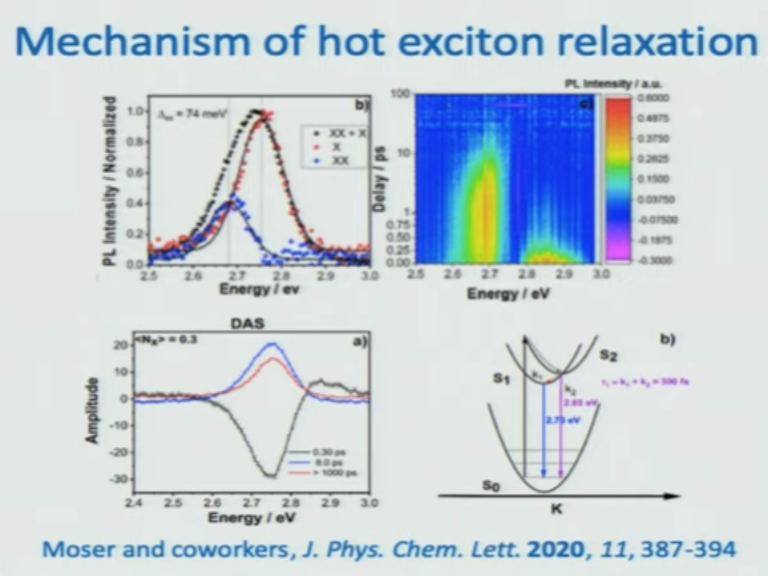

Mechanism of hot exciton relaxation

Moser and coworkers, *J. Phys. Chem. Lett.* **2020**, *11*, 387-394

Using transient absorption as well as fluorescence up conversion but the fluorescence of conversion data here actually looks like transient absorption does not it? I am talking about top panel there are 2 axes actually 3 axes third access is pointing towards you intensity and then 2 axes are time and wavelength okay. So the way it has been done I think I mentioned it in the passing when we talked about fluorescence up conversion is that they have used a different kind of crystal.

In the sum frequency generation crystal that they have the optic axis is horizontal and that makes it possible for some frequency generation over a broadband. So what you can get is that you can get the florescence spectrum entire fluorescence spectrum at whatever delay you want rest of the instrument is same there is a delay which delays the gate pulse there is an excitation pulse the only different is the fluorescence is focused on to a sum frequency crystals along with the gate pulse where the some frequency crystals allows phase matching independent of frequency.

So for a given delay you can get the entire florescence spectrum that as we have understand makes life much simpler makes data acquisition maybe 100 times or 1000 time fast that is what they have done and what is of interest here is that if you look at the transient absorption time evolution and fluorescence up conversion time evolution there are more or less the same. Once again as you go higher in energy pump or excitations wavelength you get this ultrafast component.

Which is missing when a lower energy pump or excitation is used so once again very similar hot exciton dynamics is observed here and what they have been able to do here is that they have been able to show what is this spectrum of the bi-excite? And this also tell us that whatever we have discussed earlier that is not complete does here bi-excitons emit it does not have to wait to get two excitons level.

If bi-exictons emit that means what they have recombined they are not there anymore. So not all bi excitons are going to produce exciton that we had expected right the light will be emitted. So there have been able to separate this 2 and they have been able to propose a interestingly the model they have been proposed is very much like a model that we would encounter for molecules but that is because we are using a particle in a box model here anyway.

To close this discussion what I wanted to say is this there is more to life even bi-excitons we have talked about excitons we have talked about bi-excitons you can have things where that balance is not there in excitons as well as in bi-excitons what do we have number of holes is equal to number of electrons but there are other particles at this these are actually known it is not as if it not new discovery bi-excitons have been known for many decades.

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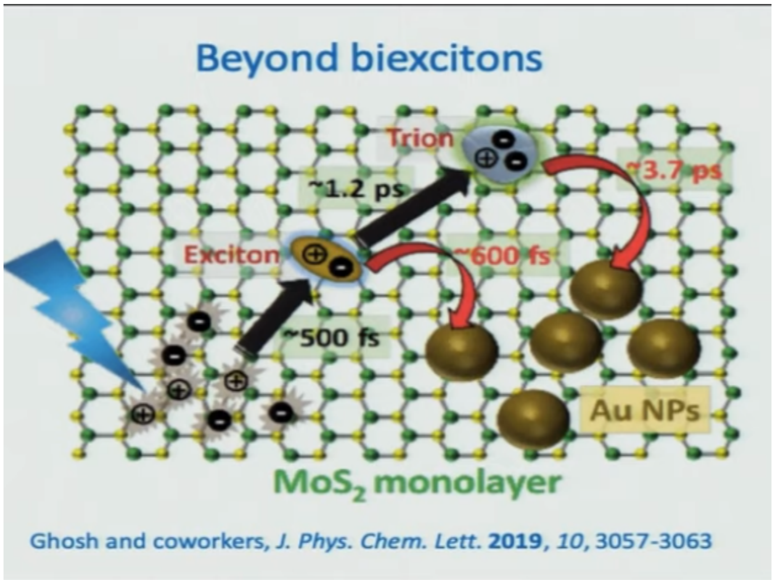

Beyond biexcitons

Ghosh and coworkers, *J. Phys. Chem. Lett.* **2019**, *10*, 3057-3063

Similarly what is also known for many decades is Trion means 1 hole 2 electron or 1 electron 2 hole we have a bi-exciton somehow an electron has been lost to a defect or something like that. And in this paper published last year by professor Hiren Ghosh and group what they have done is that now they have worked with 2D material MoS2 monolayer and it is not even homogeneous this is Mos 2 monolayer with gold nanoparticles.

And what they have been able to show using transient absorption very elegantly is what is it that happens that shown that in 500 femtosecond you get the exciton then 600 femtosecond the exciton can actually transfer the energy to gold nanoparticle or you can get Trion in 1.2 picosecond how they got Trion for that we have to read the paper we are not going to discuss this quite a loaded paper this is this cartoon is only summary of what is there and then from Trion it takes 3.7 Picosecond to transfer the energy to gold nanoparticles.

Well when I say takes 3.7 picosecond perhaps I am not really being exact time constant is 3.7 Picosecond. So let me just say that this scope of study of ultrafast dynamics in nanomaterial we have talked about plasmonic nanomaterial we have talked about semiconductor nanomaterial we have talked about perovskites well we have shown you the data on perovskites data nano crystals and here we see 2D material.

This scope is infinite at the moment a lot of new things are there that not have been explored earlier and using ultrafast techniques one can explore them and learn things that are interesting definitely from the fundamental research point of view and possibly also to device more applications like what we saw application in quantum dot solar cells. So that is where we close the discussion of system as such will have maybe 3 more modules in which we are going to talk about other kinds of ultrafast spectroscopy.

In so many lectures we might have given the impression that ultrafast spectroscopy means transient absorption and femtosecond up conversion which definitely not there are many other techniques we will not be able to go into all of them fortunately if you understand how transient absorption works then you can understand most of the other things so we will talk about only 2 kinds of experiments one is 2 dimensional spectroscopy and the other is surface sum frequency generation that is what we will do over the next may 2 or 3 modules for now this is it.