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Nanocomposites: general discussion

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Yogesh M. Joshi opened a discussion of the paper by Marc Couty: It is indeed a very novel way of manufacturing the composite: first dissolving and swelling Styrene butadiene copolymer in styrene and subsequently crosslinking the latter. Does such assembly have any special benefits in terms of mechanical or other properties over the usual Styrene butadiene copolymer?

While it has been claimed that post swelling occurs, it is possible to separate the filler into the small aggregates. The SEMs in Figure 3 in your manuscript do not show any appreciable change in aggregate size. As expected, it seems only the average inter-particle distance has increased.

Marc Couty responded: After polymerisation, the polystyrene content is so high that the sample is glassy at room temperature and of no use for tyre properties. The experiment should be repeated at a lower swelling ratio to test the mechanical properties of such a material.

Indeed, SEM does not show any reduction in size of the object. We must keep in mind that since SEM is revealing only 10 nm under the surface of the material, for such branched objects made of primary particles around 10 nm it gives only informations on cuts of the “branches”. If one assimilates the aggregate with a human hand, SEM would be equivalent to image finger cuts.

B. L. V. Prasad enquired: 1. During the preparation process some reagents are added to the filler silica particles and it is seen that these reagents then adhere to the silica particles. What happens if these silica particles are pre-grafted with these reagents?

2. Is the chemical nature of the interactions between the grafted silica particles and then polymer well understood? How important is this for the final quality and function of the material?

Marc Couty responded: Some silica are pre-grafted with silanes. The main difficulty comes from adapting the melt mixing process to incorporate these fillers. I don't know any study of silica pre-grafted with polymers. It would be difficult to make because the polymer grafting step must be done before the silica aggregates are agglomerated. The chemical nature of the interactions is still debated. However, for silica dispersion what matters is tethering the chains to the surface whether it is chemical grafting or physical strong adsorption. For the final quality in usage like wear or tear resistance, it may make a difference.

Sanat Kumar asked: 1. If you fix the amount of functionalising chains, then, is the domain size fixed as an equilibrium quantity? Or, does this depend on the processing? How do I think about such data? Overall, how do I think about this problem? 2. You have previously said "I know I'm not at an optimum" presumably in terms of the dispersion state of the nanoparticles and hence the properties you achieve. How do you know that?

Marc Couty answered: I know, today, that I am not at an optimum, because I have glasses that allow me to see that the material structure is evolving with a strong coupling between processing conditions and raw materials used. My task is to master all these coupled mechanisms to gain in terms of material performance. We do have a dependence on the processing conditions at a fixed amount of functional chains because melt mixing is not just mechanics but chemistry. Depending on the temperature during the mixing cycle (and all the processing tools on the material transformation chain), one can activate or not the grafting at given stages of the process. The complexity goes one step further when one thinks that grafting can take place before fragmentation of agglomerates and thus generates "Janus" type aggregates *in situ* with one "face" grafted while the other, previously connected with the agglomerate, stays free of the grafts. I do not know how to characterize this type of object in the material but it would be very interesting to state on the existence and their probable impact on the material properties.

Yogesh M. Joshi commented: Polystyrene dissolves in styrene, but whether butadiene dissolves in styrene or not, I do not know. In case there is a different extent of swelling of the styrene part *vis-à-vis* the butadiene part in styrene, some of the parts of the chain will be more swollen than the other. It may lead to interesting scenarios and possibly residual stresses in the resultant crosslinked material. Any comments?

Marc Couty commented in reply: Unfortunately, I am not using block co-poly (styrene-butadiene) but a statistical polymer and I cannot give any hint on that interesting comment.

Rajdip Bandyopadhyaya asked: (a) In our paper on "Dynamics of chain aggregates of carbon nanoparticles in isolation and in polymer films: Implications for nanocomposite materials",[1] we had shown the role of a linear chain of nanoparticle-aggregate on enhancing mechanical properties of a polymer composite. This mechanism has direct implication in car tyres. Have you conducted any similar elongation and reinforcement type experiment for your silica-filled nanocomposite? Can you study mechanical properties by considering only laboratory-made individual nanoparticles, which will behave differently to the actual commercial silica aggregate?

(b) How do you define and distinguish between agglomerates *vs.* aggregates? In our case, individual carbon-filler nanoparticles were formed by laser ablation; it eventually generated a chain of carbon nanoparticles bonded at the particle-interface by C–C covalent bond, which were well-dispersed in the polymer matrix. Such a chain of carbon nanoparticles is called an aggregate, as it cannot be broken into individual nanoparticles, due to the strong C–C bond. On the other hand, agglomerates are reversible structures, which can be broken down by sonication. Are your definitions similar?

(c) How do you interpret the terms "dispersion" and "distribution" separately, while discussing your processing results at different steps of the nanocomposite study?

1 R. Bandyopadhyaya *et al.*, *Chem. Mater.*, 2004, **16**, 3147–3154.

Marc Couty replied: We have done many studies of mechanical reinforcement using shear or elongation since many of the material properties in tyre are linked with mechanics, and indeed the shape of the aggregates have a strong impact. In toy model systems of nanoparticles, we are mostly interested to extract parameters transferable to more complex systems and in general not looking for their direct mechanical properties that are in general very different for industrial commercial silica. In my "definition", agglomerates differ from aggregates essentially by their size. I suppose both are rigid objects and that the process of evolution from agglomerates to aggregates is irreversible. If there is a reversible process then I would associate it like you with an interaction between primary objects that I (implicitly) consider as rather weak compared to covalent bonding and not refer to these objects as agglomerates, that may not be rigid and evolve while applying stress.

As you point out, "dispersion" and "distribution" are extremely coupled since it is a matter of interaction strength between aggregates. The swelling process I have used allows to separate what is a direct (strong) interaction and a polymer mediated (weak) interaction.

Ajeet Srivastav questioned: What is the reason behind choosing nanoparticles rather than nanowires, though it has been established very well that the fibrous reinforcements are the most preferred way to enhance the mechanical properties of the composites?

Marc Couty answered: Again, melt mixing has some limitations: it is often difficult to separate wires at the nanoscale when they are assembled before mixing and it results in a poor dispersion with reinforcement properties that do not reach the ones with nanoparticles. When the wires diameter is in the order of 100 nm to 1 μm, they get fragile and one ends up in a dispersion of objects with no cylindrical character.

Sanat Kumar remarked: We, in academia, do research and work on problems we imagine that you, in industry, are interested in. For example, you say that it is not feasible to completely disperse nanoparticles into a polymer – but this is almost exactly what we (in academia) have been focusing on as our Holy Grail and end goal. What else are we missing/ignoring? What should we be thinking about in the big picture? Processing? Anything else?

Marc Couty responded: The tyre industry deals with huge quantities of materials (million tons per year) and investments have been made for robustness and efficiency. Using melt mixing techniques, it is probably difficult to achieve a dispersion of nanoparticles. Working on other processing techniques to achieve the ultimate dispersion of particles is itself very interesting for the industry to measure the distance to the asymptote or to access some parameters transferable to the industrial case of aggregated particles. Academia could address the industrial problems more and in the case of the present paper, focus on the driving mechanisms of agglomerate (or aggregate) fragmentation under shear. This requires accessing the mechanical stresses acting on "fractal" aggregates under shear and the material resistance of nanoscale silica to rupture that is today a field with limited research. I think that you, as representative of academia, are working on the right subject to generate a dispersion of particles and derive the thermodynamic mechanisms that drive the self assembly of the particles at the nanoscale.

Rajdip Bandyopadhyaya addressed Marc Couty, Jacques Jestin and Sanat Kumar: In order to study the reinforcement of polymers with filler nanoparticles, use of spherical, filler-nanoparticles is good as a toy system, as there is no isolated, spherical filler-nanoparticle in a real polymer nanocomposite sample.

The latter almost always has a short network of filler particles – like linear (or branched) chains of spherical, filler-nanoparticles. These chains are few hundred nm in length. They are also desirable, as the anisotropic, linear-chain of nanoparticles as they have more reinforcement, compared to spherical, filler-particles.[1]

It would be interesting to study dynamics of such linear chains, although polymer dynamics is well known for years. However, the dynamics of such linear chains (which constitute almost 30% of the polymer nanocomposite in the car tyre) is hardly studied or understood. Has there been any such development or observation in your work?

[1] R. Bandyopadhyaya *et al.*, *Chem. Mater.*, 2004, **16**, 3147–3154.

Marc Couty responded: We haven't looked at the dynamics of the aggregates in the materials. There are a few studies of SAXS/SANS studies under deformation or XPCS under quiescent conditions but not much in terms of interpretation of the obtained signals.

Sanat Kumar replied: We have looked at the role of particle dispersion state on mechanical reinforcement.[1,2] What we find is that the optimal reinforcement occurs when the nanoparticles form percolated, system spanning structures. While this is a necessary condition it is not sufficient. In addition to percolating we find that chains need to be adsorbed on the particles, and the particle–particle overlap (necessary for percolation) be mediated by the presence of adsorbed polymer chains. It is the resulting "entropic spring" contribution to elasticity that we find increases the modulus and also toughness.

[1] P. Akcora *et al.*, *Macromolecules*, 2010, **43**, 1003–1010.
[2] J. Moll and S. K. Kumar, *Macromolecules*, 2012, **45**, 1131–1135.

Jacques Jestin answered: The dynamic of the chains in the presence of the particles in nanocomposites is indeed a critical point. Neutron scattering experiments offer the possibility to label the chains and to separate the contribution of the chains close to the particles from the ones in bulk. It allows also to probe a broad range of typical times by combining backscattering and spin echo experiments. However, such experiments are difficult to design properly because it can be difficult to find the right polymer with the convenient time scale while knowing and controlling the structural organization of the NPs inside the polymer. We can find some nice experiments of spin echo for high particle loading by Richter and of backscattering on silica/PMMA systems by Robertson and Ackora. Alternative approaches use dielectric spectroscopy (Sokolov) or NMR (Long/Lequeux). As far as I know, there are different scenarios which are discussed to explain the reinforcement: gradient of chain mobility, glassy layer or glassy bridges, increase of the entanglement density, entanglement between the grafted and the free chain.

Nicholas Kotov addressed Marc Couty and Jacques Jestin: I wonder if you tried the classical Halpin-Tsai model for description of these composites?

Marc Couty answered: There is no general model that can accommodate all the physics of these materials. The ideas behind composite models work well in general for macroscopic composites. When it comes to nanocomposites where dimensions of particles, interparticle distances and polymer chain characteristics are comparable, they tend to be crude. Several ideas are currently debated like the existence of a glassy polymer shell around particles and slowed down dynamics of polymers due to entanglements in a crowded environment, which are much more promising.

Jacques Jestin replied: We used the model of Takayanagi[1] which is a series parallel model combining the modulus of a reinforced phase (the filler) with the one of a soft phase (the matrix). The general idea of this model is very close to the Halpin-Tsai model but for isotropic fillers. The fillers are here spherical nanoparticles that are forming clusters (also more or less spherical). There is indeed no orientation parameter like in the Halpin-Tsai model more dedicated to anisotropic fillers than fibers.

1 M. Takayanagi *et al.*, *J. Polym. Sci., Part C: Polym. Symp.*, 1964, **5**, 113.

Guruswamy Kumaraswamy asked: I am curious about the effect of the molecular weight of the grafted polymer chain on the dispersion that is achieved. As the polymer molecular weight increases, there is a decrease in the concentration of the terminal groups that graft onto the nanoparticle surface. However, it is likely the stretching of high molecular weight chains (tethered to the nanoparticle surface) in the flow field that results in effective nanoparticle dispersion. Is there, therefore, an optimum molecular weight of the telechelic polymer chains to achieve dispersion?

Marc Couty responded: We have shown in previous work[1,2] that the grafting density is a key parameter impacting the dispersion. Indeed, when one decreases the polymer molecular weight, the grafting density is increasing which results in a reduction of material dissipation through a better dispersion. In the meantime, the number of free chain end increases and the dissipation due to the viscoelasticity of the matrix is higher and has to be balanced. As you mention, decreasing the polymer molecular weight decreases the viscosity and probably, the ability to rupture the agglomerate should decrease. Such an optimization has not yet been performed.

1 G. P. Baeza, A.-C. Genix, C. Degrandcourt, L. Petitjean, J. Gummel, R. Schweins, M. Couty and J. Oberdisse, *Macromolecules*, 2013, **46**, 6621–6633.
2 G. P. Baeza, A.-C. Genix, C. Degrandcourt, J. Gummel, A. Mujtaba, K. Saalwächter, T. Thurn-Albrecht, M. Couty and J. Oberdisse, *ACS Macro Lett.*, 2014, **3**, 448–452.

Priyadarshi Roy Chowdhury communicated: Is the dispersive process limited to SAXS?

Marc Couty communicated in reply: Swelling the material and separating the aggregates can also be used in TEM and SEM studies since one can image individual objects.

Priyadarshi Roy Chowdhury communicated: Which analytical technique do you think gives confirmation about particle-growth?

Marc Couty communicated in reply: Particle growth is one stage of the filler synthesis process and I don’t have any access to this information.

Priyadarshi Roy Chowdhury communicated: Please discuss the low “Q” concentration associated with SAXS.

Marc Couty communicated in reply: We have not been able to understand clearly the origins of the strong intensity at low q. We suspect that we still have few large compact agglomerates that generate a strong diffusion.

Priyadarshi Roy Chowdhury further communicated: Do you think cross-linking or twisting is possible in the synthesis of the polymer nanocomposites, which you have mentioned in your paper?

Marc Couty communicated in reply: I don't think that cross-linking occurs during the synthesis of the nanocomposites since we don't have any chemicals that have an action apart from reacting on silica, and chains carry at most one functional group.

B. L. V. Prasad opened a discussion of the paper by Jacques Jestin: Studies similar to those carried out by Dr Marc Couty and Dr Jacques Jestin may have been reported in the literature. How useful are these for industrial applications? If they are not very useful what are the reasons? Are they too “ideal”? Are the academicians missing to include important stuff, that is relevant for industry, in their studies?

Marc Couty answered: I don't have much to add to the answer I made to Prof. Sanat Kumar's previous question. The fundamental knowledge gained on an "ideal" system is very important for industrial application. The industry is focused on technical processes to make materials at large scale based on that knowledge.

Jacques Jestin replied: The collaboration between academicians and industrials are supposed to permit avoiding to miss important stuff relevant for industry. Those studies are useful for industrial applications by providing quantitative directions to optimize the processes and to delineate boundaries of the relevant parameters.

Alison Edwards asked: Would you wish to comment on the need to actually undertake some experiments on systems of interest in order to verify that the expectation and the experiment actually match? In particular, I would value your views regarding how much extrapolation from one system to another can be relied upon when working with nanoscale materials where new and novel properties are sought.

Jacques Jestin replied: We can benefit from methodologies and tools (synthesis, sample processing and analytical or numerical analysis) given by such studies for extrapolation to other systems, either fundamental nanoscale or applied materials.

Alison Edwards questioned: It is not clear to me why you would do some of your SANS work at Saclay and some at ILL. Could you clarify for us whether the instruments were chosen to optimize particular aspects of your experiments, or whether there was insufficient beam-time available to complete the work at one or other location (if indeed this would have been preferred)?

Jacques Jestin answered: We have tried to optimize the beam time as function of the samples and the performances of the spectrometers between Saclay and ILL. The isotropic samples were measured at Saclay and the anisotropic stretched samples that required more flux were measured at ILL. We did not suffer from insufficient beam time at one or the other location.

Erika Eiser remarked: Did you also look at the mechanical properties of you polymer–nanoparticle composites in the presence of hydrogenated chains? Deuteration in polymer chains with high molecular weights can lead to phase separation even in apparently identical polymers, as shown by the group of Jacob Klein and others. Moreover, the replacement of H-atoms by deuterium along the polymer chain can alter the van der Waals attraction between the chains and the nano particles and therefore affect the nano-particle aggregation.

Jacques Jestin replied: The H/D mixtures are fully miscible due to low molecular masses (40k). We do not see any significant differences between the pure H matrix and the H/D mixtures for mechanical properties and nanoparticle dispersion.

Priyadarshi Roy Chowdhury addressed Jacques Jestin and Marc Couty by communicating: What are the effects that play a significant role in conformational changes associated with the polymeric chain?

Marc Couty communicated in reply: The grafting density has probably the major impact. The chain length of free and grafted polymer has also a great impact.

Jacques Jestin communicated in reply: The main conclusion of the study is that the mean chain conformation is not affected at rest by the presence of the particles whatever the nanoparticle loading and the polymer/filler interactions. Under deformation, for the crosslinked elastomers, the chain relaxation is reduced by the NPs that act as additional cross-linking junctions.

Priyadarshi Roy Chowdhury opened a discussion of the paper by Ramanan Krishnamoorti† by communicating: What will be the effect of small-angle neutron scattering on moderate dispersions of POEOMA-SiO_2?

Ramanan Krishnamoorti communicated in reply: The structural correlations between the hybrid nanoparticles will become increasingly important as the concentration of the particles is increased. For dilute solutions, as much of this study demonstrates, the scattering methods allow us to probe the single particle regime. However, as shown in the last figure of the manuscript at modest concentrations, a correlation hole scattering peak is observed and is quite well modeled using a Percus-Yevick type model.

Vandana Shinde communicated: Which type of information is received from SAXS and SANS, which are necessary for these nanocomposite poly(oligo(ethylene oxide)monomethyl methacrylate)-grafted silica nanoparticles?

Ramanan Krishnamoorti communicated in reply: Typically SAXS is sensitive to the electron density contrast and therefore is most sensitive to the presence of higher atomic number atoms. Therefore in polymer–silica hybrids (or in polymer–particle hybrids), SAXS is sensitive to the particle–particle correlations and the internal structure of the particles. On the other hand, SANS is sensitive to the neutron scattering length density differences. It turns out that one of the largest neutron SLD differences lies between that of a Hydrogen atom and a Deuterium atom. Therefore for polymer–silica hybrid particles, by varying the amount of H_2O to D_2O, the scattering length density of the solvent can be systematically varied, so that it can be made equivalent to that of the polymer or that of the silica particle. Therefore the overall structure of the polymer, the structure of the particle and the correlations between these hybrid particles can be systematically examined.

Priyadarshi Roy Chowdhury opened a discussion of the paper by Nicholas A. Kotov: How can one bridge the experimental and simulation results in a more comprehensive manner for chiral nanoparticles in atomic scale as well as in assemblies?

Nicholas Kotov replied: This is one of the biggest questions of the field. We made an attempt addressing it in a consistent manner in our recent paper about interparticle forces at nanoscale whose complexity seems to be under

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† The paper by Ramanan Krishnamoorti was not presented at the meeting, but questions and responses have been provided afterwards.

appreciated.[1] One of the central problems, in my perception, is the development of a set of adequate force-fields for nanoparticles. They need to incorporate interaction characteristics of the inorganic and organic surface ligands. It is possible for the models combining DFT and molecular dynamics modules. These models are computationally heavy and the timescales needed for realistic description of nanoparticle assemblies are not available for them. Coarse grained models can account for characteristic times of nanoparticle self-organization (seconds to hours). The adequate transition from atomistic to coarse grained models is known to be very difficult for proteins despite decades of work put into it. It is still an art form for nanoparticles. Some approaches being used for protein interactions can be transitioned to nanoparticle self-assembly.

[1] C. A. Batista, R. G. Larson and N. A. Kotov, *Science*, 2015, **350**, DOI: 10.1126/science.1242477.

Michael Bockstaller enquired: Thank you for the very interesting contribution. Could the author please elaborate further on the origin and implications of the partial oxidation. In particular, why does the formation of a silver oxide layer enhance the plasmic response? Is it related to the dielectric properties of the silver oxide shell or would other coatings result in a similar effect? Also, could you comment on the thickness of the oxide layer and what the threshold thickness would be to retain the reported effect.

Nicholas Kotov replied: The enhancement of polarization rotation upon oxidation of silver caps on ZnO nanorods is something counter-intuitive and unexpected. We attribute it, at least in part, to the increase in the volume of the plasmonic caps that improves electromagnetic coupling with incident photons. I need to mention also that not all of the silver is transformed into silver oxide in these caps. The core remains metallic.

Charusita Chakravarty said: How complex can self-assembled structures be? At some level of complexity in nanoparticle/colloidal aggregates, would you expect emergent properties that cannot be obtained by bottom–up integration?

Nicholas Kotov responded: In my estimates, the self-assembled structures from nanoparticles can approach in structural and functional complexity self-assembled structures from nanoscale biological components, for instance proteins.[1] A recent observation of an enantioselective assembly of left or right helices from simple water-soluble CdTe nanoparticles confirms this hypothesis.[2]

[1] N. Kotov,*Science*, 2010, **330**, 188.

[2] J. Yeom, B. Yeom, H. Chan, K. W. Smith, S. Dominguez-Medina, J. Hwan Bahng, G. Zhao, W.-S. Chang, S.-J. Chang, A. Chuvilin, D. Melnikau, A. L. Rogach, P. Zhang, S. Link, P. Král and N. A. Kotov, *Nature Mater.*, 2015, **14**, 66.

G. V. Pavan Kumar asked: Your work has literally added a twist to plasmons. I have two questions. Firstly, what is the nature of plasmons in your system? Are they localized or propagating plasmons or a combination of both? Secondly, chirality can be further utilized in generating light beams with orbital angular momentum. Can your structures be harnessed for the same?

Nicholas Kotov replied: When I think about the plasmons in, for instance, two gold rods in a "scissor" configuration (*e.g.* Ref. 1), I visualize them as localized plasmons. I might draw analogy here between the surface plasmons in such twisted assemblies and aromatic electrons in biphenyl compounds. Both of them are chiral and both of are delocalized within a particular space. Chiral inorganic nanostructures can be used to generate photons with circular polarization. This is one of the most exciting areas of research now. So far it was difficult to observe circularly polarized luminescence in chiral semiconductor nanostructures, but I am confident, it will be accomplished for multiple chiral nanoscale systems. Synthesis of assemblies with hybrid plasmon-exciton states is one of the routes that I can foresee to be fruitful.

1 W. Ma, H. Kuang, L. Wang, L. Xu, W.-S. Chang, H. Zhang, M. Sun, Y. Zhu, Y. Zhao, L. Liu, C. Xu, S. Link and N. A. Kotov, *Sci. Rep.*, 2013, **3**, 1934.

Ajeet Srivastav addressed Nicholas Kotov and Daan Frenkel: How should a mix of different shapes of nanoparticles in a crystallographic sense with different energies of the out-surfaces affect the kinetics of the assembly? If it favors different building blocks, as mentioned by Prof. Daan Frenkel, then how to choose those different shapes of the nanoparticles as building blocks?

Nicholas Kotov answered: The shape of the nanoparticles is not only a factor of the crystallography of the core albeit it is a big factor. The surface layer of the nanoparticles plays a big role in what effective shape the nanoparticle has. For instance a nanoparticle with a seemingly spherical core is known to behave anisotropically due to the uneven distribution of the surface ligands. Its effective shape could be quite a bit more complex than a sphere. Moreover, the shape is also a dynamic parameter. Although the dynamic reconfiguration of the crystalline particle core is not common, the reconfiguration of the particle shell is. The kinetics of the self-assembly is strongly affected by the particle shape. If we treat the particle shape as a sum of two components, static and dynamic, I can see how much faster the dynamic component of the particle shape speeds up and facilitates the self-assembly of nanoparticles.

The choice of the different shapes of nanoparticles as building blocks is governed by the symmetry relations characteristic of the assembled structures to be made. The symmetry of the static component of the nanoparticle shape and reconfigurability of its dynamic component are reflected in the resulting self-assembled structure. As a simple example, the nanoparticles with bipolar anisotropy (magnetic, electrical, *etc.*) will tend to form self-assembled systems with axial symmetry. The dynamic and entropic components can, however, change this trend dramatically and much more complex architectures with more diverse symmetry elements could be obtained. As an example, instead of the particle chain or ribbon a helix will form.

Daan Frenkel replied: The question of the shape of the building blocks is a very interesting one as it expands the degree to which interactions can be made specific. To obtain optimal interaction, one needs not only complementarity of the chemical moieties responsible for binding, but also complementarity of the shapes of the binding surfaces.

Nagaraj Shetti remarked: You have prepared a material of metallic silver on ZnO nanopillars, do you think it will act as an electrocatalyst? How will it be helpful to detect bio-active molecules in electrochemical sensors? As compared to other materials, silver has less of an electro-potential window.

Nicholas Kotov answered: I am confident that a ZnO–Ag–Ag_2O system can serve as an electrocatalyst. Chirality of the silver caps can be the key in improving the selectivity in biological compounds. Although it could be a problem to address later, I am not worried about the electropotential window of silver at the moment. Finding a "right" electrocatalytic reaction to perform on this potentially very active catalytic system would be my line of thinking for now. In case we want to expand the electrocatalytic window when it could become a problem, chiral nanocaps from gold or platinum can be created in the same way.

Priyadarshi Roy Chowdhury communicated: Please illustrate the complexity of the chiral plasmonic nanostructures, mentioned in your work.

Nicholas Kotov communicated in reply: Chiral plasmonic (or simply chiroplasmonic) nanostructures were made of great complexity using DNA bridges. For example, in collaboration with Prof. Chuanlai Xu we reported tetrahedrons made of four different nanoparticles[1] with some of them being made out of gold, silver, and semiconductor using this method. Importantly, they can be made of specific chirality not by accident but by design. It allowed us to see optical signatures of all constituent nanoparticles in mirror-image CD spectra. Most recently, propeller-like assemblies with geometries reminiscent of chiral metal complexes were made from gold nanorods and upconverting nanoparticles.

[1] W. Yan, L. Xu, C. Xu, W. Ma, H. Kuang, L. Wang and N. A. Kotov, *J. Am. Chem. Soc.*, 2012, **134**, 15114.

Priyadarshi Roy Chowdhury communicated: What type of interactions do you think play a dominant role in chiral plasmonic nanostructures?

Nicholas Kotov communicated in reply: In my experience, dispersion interactions are quite strong for all plasmonic nanoparticles and need to be taken into account along with electrostatic interactions and hydrogen bonds. I see these three interactions as most universal and, to some degree, dominant for all plasmonic nanoparticles assemblies made in aqueous phase.

Himani Medhi communicated: The feasible utilization of Ag nanocaps on ZnO nanopillar arrays as an oxygen detector will really become helpful for the future as it has possibility to help people working in mines and also can help astronauts to detect the presence of oxygen in the atmosphere around them instantly. This is a nice work going to be published. I have a suggestion to try to develop a recycling method to recover the Ag nanocaps on ZnO nanopillar arrays from the oxidized one Ag_xO, which will make it more beneficial for sustainable development.

Nicholas Kotov communicated in reply: This is a very thoughtful suggestion. It is indeed necessary to think about the careful use of precious metals in chiroplasmonic materials. Recycling should be possible. I recall when I was a kid and did a lot of old school silver-based photography, the recycling of silver was possible by dissolving silver oxide with amine complexes.

Himani Medhi communicated: In your paper, it was mentioned that Ag nanocaps on ZnO nanopillar arrays with different thicknesses were prepared by spraying Ag vapour from different directions. I have some queries regarding this. Is there any chiroptical activity observed in pure ZnO nanopillars? Which directional coating did lead to better chiroptical activity and better oxygen sensitivity of Ag nanocaps on ZnO nanopillar arrays? What was the thickness of Ag nanocaps made on ZnO nanopillar arrays that led to a better oxygen sensitivity property to the material and how long can that be used as an oxygen detector?

Nicholas Kotov communicated in reply: The anisotropy of light matter interactions in thin films can come from both dichroism and birefrigence. In each case it can be linear and circular. Thin films are notorious for having all four of them at once which makes it difficult to assign CD spectra to a specific optical effect. It is difficult but not impossible. The use of Mueller matrix polarimetry (see Ref. 1 and the references therein) enables one to identify the contribution of each component. In the case of a ZnO nanowire forest, one could also expect all four components, but careful examination showed that under the same registration conditions, with incident angle and wavelength being the key ones, the ZnO nanowire forest did not have circular dichroism.

1 Y. Kim, B. Yeom, O. Arteaga, S. J. Yoo, S.-G. Lee, J.-G. Kim and N. A. Kotov, *Nature Mater.*, 2016, DOI: 10.1038/nmat4525.

Neena S. John communicated: Could you give more details regarding the “gas sensing” experiments of plasmonic silver nanocaps, particularly, what parameter one should monitor to show the sensing action? Is it the “g-factor” variation or CD intensity at a particular wavelength? In the paper, you have shown only variation with two exposure times to air. Have you done more experiments with respect to controlled oxygen flow and if so, what is the detection limit obtained using your material?

Nicholas Kotov communicated in reply: Unfortunately, Jun Li, a very diligent and hardworking student, had to go back home soon after completion of this work and I am still looking for a replacement for him. These experiments would certainly be essential for technological implementations of such gas sensors. When designing such sensors, I would measure polarization rotation at a maximum g-factor point. The optical set-up would be reminiscent of the CD spectrometer but a lot smaller in size.

Vandana Shinde communicated: 1. What is the gas sensing mechanism of metallic silver on ZnO nanopillar arrays? 2. What are the response and recovery time for this array? 3. Can you test the selectivity of this array for other gases?

Nicholas Kotov communicated in reply: Previously we showed that circular dichroism is a potent analytical tool when combined with plasmonic nanostructures.[1] The high sensitivity originates from the strong dependence of polarization rotation on the conformation of anisotropic plasmonic particles. The gas sensing mechanism for nanopillars is based on a similar effect. However, in addition to the very strong polarization rotation, we also have a wavelength shift. Both factors are synergistically combined in this system. Unfortunately, Jun Li had to go back home and we did not measure the recovery time or sensitivity to other gases. Testing hydrogen as a recovery agent and an example of a different gas would be promising.

1 M. Ma, H. Kuang, L. Xu, L. Ding, C. Xu, L. Wang and N. A. Kotov, *Nature Comm.*, 2013, **4**, 2689.

Priyadarshi Roy Chowdhury opened a discussion of the paper by Rajdip Bandyopadhyaya: In this paper, you have presented indeed a very good work on photocatalysis for degradation of a complex dye. If possible perform the Markov-Chain Monte Carlo (MCMC) simulations and co-relate the experimental and MCMC simulation results, as done by Prof. Zhao's group in his paper, published in PCCP and enlisted in Ref. 1.

1 B. Liu and X. Zhao, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22343.

Rajdip Bandyopadhyaya answered: The present paper reports only the synthesis of hybrids of a porous host-nanoparticle and its optimization to maximize the photocatalytic dye degradation rate, without any model calculation. The work done in the PCCP paper referred to in the question is indeed interesting, wherein by using a Markov-Chain Monte Carlo method, the authors have calculated both photocurrent decay and first order rate constants of photocatalysis. Although we have not yet done any MC calculations for this system, it would be possible for us to perform MC simulations in the future to correlate our experimental data, since our group has extensively worked on predicting the nanoparticle size and its aggregation behaviour by Kinetic MC simulation. In this regard, we have already published an alternative deterministic model to calculate the dye degradation kinetics of SnO_2-SBA-15 hybrids in a previous paper.[1]

1 N. R. Srinivasan, P. Majumdar, N. K. R. Eswar and R. Bandyopadhyaya, *Appl. Catal. A*, 2015, **498**, 107–116.

Madivala G. Basavaraj commented: What is the typical size of pore compared to particle diameter? Can this be tuned by the synthesis approach you follow?

Rajdip Bandyopadhyaya responded: Cylindrical pores in our mesoporous silica (SBA-15) are arranged in an ordered, hexagonal manner. The mean pore diameter for different samples (depending on whether the pores had nanoparticles or not) were between 7.5 to 9.1 nm, whereas the nanoparticles varied from 3.3 to 6.7 nm (Table 1 in our manuscript). So, the ratio of pore to particle diameter typically ranged from being slightly greater than 1, to more than 2. The diameter of the pore can be easily tuned further – it can be increased or decreased by taking amphiphilic molecules of larger or smaller tail-length than that of P123 (used in this work) during synthesis, namely F127 or CTAB, respectively. Pore diameter can also be increased by adding hydrophobic molecules (decane, octane, mesitylene, *etc.*) as a pore expander, in the conventional sol–gel synthesis step of SBA-15. In essence, we can systematically control the ratio of pore to particle diameter over small incremental steps, which is useful to examine the relative roles of pore-diffusion, adsorption and reaction on the catalyst surface. In our group, this has been one of the goals of current research in this area.

Nagaraj Shetti said: You have prepared a $Sn_xTi_{(1-x)}O_2$ solid solution nanoparticle embedded mesoporous silica (SBA-15) hybrid as a photocatalyst and used to degrade a rhodamine B dye. But, you have not discussed the degradation products, or degradation mechanism. I think it will be better if you explain the degradation mechanism and the respective products.

Rajdip Bandyopadhyaya replied: The present work reports the synthesis of hybrids of a porous host–nanoparticle system, wherein each nanoparticle was successfully embedded inside the porous host (SBA-15). The approach followed in the present work to form solid-solution nanoparticles inside a porous host without causing pore blockage, and is a promising route towards increasing reaction rates in catalytic applications. To this end, Rhodamine-B was considered as a model dye and we investigated its degradation in the presence of the photocatalyst, with possible mechanisms *via* an energy band diagram. The goal of this work was to establish the efficacy of such a hybrid system to achieve an enhanced reaction rate, rather than exploring the reaction pathway and the kinetic scheme. However, currently we are in the process of measuring the degradation products using chromatographic techniques to precisely uncover these aspects. According to the literature, the possible degradation products are pthalic acid, malonic acid, benzoic acid, maleic acid, pthalic anhydride *etc.* which we also plan to measure.

Siddharth Kulkarni asked: Will the aggregation behaviour of the particles be different if particles are dispersed in complex anisotropic medium such as liquid crystal? Will the particles still showcase predominantly repulsive forces?

Liquid crystals consists of molecules with intermediate order and mobility between perfect solids and liquids? The liquid crystal medium mediates the forces between particles which are attractive in nature.

Rajdip Bandyopadhyaya responded: In the present work, pluronic block copolymer (P123) molecules form a hexagonal, liquid crystalline mesophase in solution. The hexagonal array of cylinders act as a template-structure, on which mesoporous silica (SBA-15) was formed, by sol–gel reaction and subsequent calcination to remove the P123 molecules. Finally, $Sn_xTi_{(1-x)}O_2$ photocatalyst nanoparticles were synthesized *in situ* within the pores of SBA-15 to obtain the hybrid nanomaterial. In our synthesis scheme, the liquid crystalline phase acted only as a template for nanoparticle formation, not as a medium for dispersion of nanoparticles. Therefore, being formed *in situ* within the pores, the particles were mostly separated from each other by the few nm thick, silica-walls of SBA-15 (intertwining between two pores), thereby preventing interparticle aggregation of the nanoparticles. On the other hand, if pre-formed nanoparticles are attempted to be impregnated into the pores, there is a much greater possibility of the particles becoming aggregated, either outside or inside the pores, which is not desirable. In general, dispersion of nanoparticles in liquid crystals can be understood in detail in the paper by Hegmann *et al.*[1]

[1] T. Hegmann, H. Qi and M. V. Marx, *J. Inorganic and Organometallic Polymers and Mater.*, 2007, **17**, 483–508.

Ajeet Srivastav commented: How reliable is the localized elemental mapping with such a large length scale and poor statistical measures? The mapping should be done at smaller length scale with a reduced number of frames per second for a longer period of time.

Rajdip Bandyopadhyaya responded: Elemental mapping is a useful technique to get insight into both composition and spatial dispersion of different elements (Sn and Ti) in our sample. Area mapping was chosen instead of point mapping as the mesoporous silica (SBA-15) particle is relatively large, with a mean diameter of 630 nm and a standard deviation of 85 nm. Thus, elemental mapping using SEM for a large area (several tens of micron-square containing many SBA-15 particles, Fig. 4 in our paper) was done, to identify whether $Sn_xTi_{(1-x)}O_2$ solid solution nanoparticles were present with the correct ratio of Sn and Ti within SBA-15. Data of Sn/(Sn+Ti) in Table 1, in our paper, indeed validate the composition in the actual samples, in line with the intended stoichiometric ratios of reactants. For this, a high dwell time (40 s) was maintained to reduce any statistical errors. On the other hand, a well-dispersed state and small size of the nanoparticles (3–7 nm, Table 1 in our manuscript) in the porous hosts have both been ascertained from the bright field TEM images (Fig. 1 in our paper) of $Sn_xTi_{(1-x)}O_2$ solid solution nanoparticle-SBA-15. During the actual presentation of this paper in the Faraday Discussions meeting, elemental mapping using SEM of a single SBA-15 particle was additionally shown (with a much higher magnification than in the printed-version of the paper) to prove that in the local scale too, the hybrid consists of both Sn and Ti, throughout the solid solution nanoparticle.

Priyadarshi Roy Chowdhury communicated: From the photoluminescence analysis of the hybrid photocatalyst, what type of defect states could be evident?

Rajdip Bandyopadhyaya communicated in reply: Photoluminescence spectroscopy is an efficient technique to explore the defect state emission. The origin of defect state emission in the hybrid are oxygen vacancies and self-trapped charges. In the PL spectra (Fig. S2, supplementary information of our manuscript) the peaks around 410, 460 and 520 nm are ascribed to intrinsic state transitions of anatase phase TiO_2, trapped charges and oxygen vacancies, respectively. This information and its implication has already been elaborated in the supplementary information of this paper.

Priyadarshi Roy Chowdhury communicated: What is the thickness of the hybrid photocatalyst along the *c*-axis, mentioned in this work?

Rajdip Bandyopadhyaya communicated in reply: Both the photocatalyst ($Sn_xTi_{(1-x)}O_2$ nanoparticle) in the hybrid, as also the SBA-15 host particle (of the hybrid), is basically isotropic, mostly spherical/polygonal in shape (Fig. 4 in our paper). As a result there is no thickness to be reported. Typically, the estimated mean diameter of the nanoparticles is 3–7 nm (Table 1 in our paper).

Himani Medhi communicated: As I have gone through your paper, I have found that the material $Sn_{0.15}Ti_{0.85}O_2$-SBA-15 showed better characterization results like a comparatively higher specific surface area, pore size and volume and lower band gap compared to that of $Sn_{0.05}Ti_{0.95}O_2$-SBA-15, but $Sn_{0.05}Ti_{0.95}O_2$-SBA-15 showed better photocatalytic degradation. Will you please explain this anomaly?

Rajdip Bandyopadhyaya communicated in reply: The $Sn_{0.15}Ti_{0.85}O_2$-SBA-15 sample has a slightly higher pore volume and surface area (Table 1 in our paper), with little less band gap, compared to $Sn_{0.05}Ti_{0.95}O_2$-SBA-15. The reason for these differences is due to the introduction of strain in the $Sn_{0.15}Ti_{0.85}O_2$ sample during the replacement of Ti^{4+} with Sn^{4+}. The strain decreases the particle size (from 5.6 nm in $Sn_{0.05}Ti_{0.95}O_2$ to 4.3 nm in $Sn_{0.15}Ti_{0.85}O_2$, Table 1) and thereby increases pore volume and surface area. Now, to explain enhanced photocatalytic activity, it is important to look at various aspects – crystallinity of the nanoparticle, mobility of the charge carriers, pore surface area, nanoparticle size and band gap values, *etc.* It can be seen from the XRD curves (Fig. 2 in our paper) that the gradual loss of the anatase phase in TiO_2 (which is observed for nanoparticle samples with a high Sn fraction of 0.50 to 0.15) is not seen in $Sn_{0.05}Ti_{0.95}O_2$, as the 0.95 fraction of it is Ti, with very little (0.05 fraction) Sn. As a result, $Sn_{0.05}Ti_{0.95}O_2$-SBA-15 provides better photocatalytic activity than that of $Sn_{0.15}Ti_{0.85}O_2$-SBA-15. This has already been discussed in the paper in the Conclusions section.

Himani Medhi communicated: In the Table 1 on page no. 6 of your paper, it has been reported that the band gap of $Sn_{0.05}Ti_{0.95}O_2$-SBA-15 is 3.23 eV, $Sn_{0.15}Ti_{0.85}O_2$-SBA-15 is 3.19 eV and $Sn_{0.25}Ti_{0.75}O_2$-SBA-15 is 3.25 eV. But in the 3rd line of page no. 9, it has been mentioned, for $Sn_xTi_{(1-x)}O_2$-sphere like SBA-15, to be 3.23, 3.19 and 3.25 eV for $x = 0.05$, 0.10 and 0.15, respectively. Is it correct as it appears in the paper?

Rajdip Bandyopadhyaya communicated in reply: The band gap values reported in Table 1 (page no. 6 of the paper) are correct. However, there is a small mistake in page no. 9. It should be read as, $x = 0.05$, 0.15 and 0.25, respectively, instead of $x = 0.05$, 0.10 and 0.15. Otherwise, the numerical values of band gaps (given in eV) are correct in both pages, hence the ensuing conclusions remaining in the paper are valid.

Vandana Shinde communicated: On what basis did you fit the electrochemical circuit? Is the circuit really fitted properly to all impedance spectra? For SBA-SnO_2, the Nyquist plot shows a nearly straight line, while the others show a slightly arc type behavior. What is its meaning?

Rajdip Bandyopadhyaya communicated in reply: Separation and transport properties of charge carriers are crucial factors in determining photocatalytic activity. Electrochemical impedance spectroscopy (EIS) is a useful method to get physical insights into interfacial electron transfer at the electrode, during the photocatalytic process. The impedance spectra are plotted in terms of Zreal and Zimg, which comes from the resistance and capacitance elements of the electrochemical cell. The most common method of analyzing EIS spectra is the equivalent circuit model; the simplest model in the literature includes a solution resistance, a double layer capacitor and a charge transfer resistance. Moreover, this model is the starting point for more complex models, including the Warburg diffusion element. However, since our EIS spectra could be fitted properly with the simplest model itself, it was not required to add more elements in the equivalent circuit. The chi-square value for all samples is in the order of 10^{-3}.

In general, a semicircular arc in the EIS corresponds to effective separation of charge carriers and a faster interfacial charge transfer rate. In contrast, the straight line behaviour seen in SnO_2-SBA-15 (Fig. 6a in our paper) could be due to a diffusion-limited charge transport process, which resulted in a lower charge transfer rate. The smaller arc seen for the $Sn_xTi_{(1-x)}O_2$-SBA-15 hybrids (Fig. 6a), compared to SnO_2-SBA-15 indicated a faster interfacial charge transfer rate at the photocatalyst surface. These results show that replacing Ti^{4+} with Sn^{4+} ions enhances the separation and charge transfer efficiency of charge carriers, leading to a superior photocatalytic material. This was already discussed in the paper, under the Results and discussion section.