



Nano Focus

Copolymerization of nanorods generates one-dimensional plasmonic heterostructures

Structures generated from the assembly of metallic nanoparticles (NPs) have garnered significant attention due to their potential technological applications. Now, an international research group has developed strategies which can generate linear assemblies of anisotropic gold nanorods (NRs). Linkage of nanorods with different dimensions led to random and block copolymer structures. The group's approach was further extended to the co-assembly of random copolymers of gold and palladium NRs.

Eugenia Kumacheva of the University of Toronto, Kun Liu of Jilin University, China, Michael Rubenstein of the University of North Carolina, and their colleagues describe their copolymerization methodologies in the March 3 issue of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.201309718; p. 2648). Gold NRs with mean diameter

of 12 nm and lengths of 99 nm were etched to fine-tune their lengths, and were then functionalized with thiol-terminated polystyrene (PS) molecules. End-to-end association of NRs, which behave as monomers, is initiated when the quality of the solvent for the PS tethers is reduced by adding water to the solution of PS-functionalized NRs in dimethylformamide (DMF). When the process is repeated with a mixture of *short* 50-nm in length NRs (SNRs) and 80-nm *long* NRs (LNRs), co-assembly into linear copolymer structures with limited extent branching is revealed in scanning transmission electron microscopy (STEM) images.

The researchers also used strategies commonly employed in the synthesis of molecular block copolymers to co-assemble block copolymer structures from gold SNRs and LNRs. In the two-prepolymer approach, homopolymer structures from SNRs and LNRs are separately prepared in DMF/water mixture. Upon mixing the solutions of the homopolymers, the chains of SNRs and LNRs copolymerize to give large

fractions of diblock and triblock copolymers. In the one-prepolymer approach, individual SNRs are introduced right after the assembly of LNR homopolymer in a water/DMF mixture. Analysis of STEM images reveal that the SNR monomers primarily attach to the ends of the LNR blocks or to each other.

Palladium NRs with mean lengths and diameters of 270 nm and 20 nm, respectively, assemble in an end-to-end manner when homopolymerized by adding water to the NR solution in DMF. However, when the co-assembly is initiated from mixtures of individual solutions of gold and palladium NRs in DMF, STEM images reveal copolymer structures where the palladium NRs can be clearly distinguished from the gold NRs due to their rougher surface and lower electron density.

The ability to visualize the assembly of these one-dimensional plasmonic heterostructures at different stages of copolymerization is very useful for mechanistic interpretations, according to the researchers.

Soma Chattopadhyay

Energy Focus

Polymer series enables all-polymer solar cells

Organic photovoltaics have captured much attention because they are lightweight and mechanically flexible, allowing them to occupy new niches for solar power like integration with clothing and building materials. They are also manufactured using a low-cost, roll-to-roll process, which is key if they are to successfully compete with silicon-based PV. However, one limitation is the current requirement for relatively costly fullerenes as the electron acceptor material. Now, H. Huang and colleagues at Northwestern University, the University of the Chinese Academy of Sciences, the University of Málaga, and Polyera Corporation have synthesized and characterized a new series of alkoxy-functionalized, π -conjugated polymers that show significant promise for use as electron

acceptors, enabling an all-polymer solar cell with power conversion efficiency of 1.70%. They recently reported their results in *Advanced Functional Materials* (DOI: 10.1002/adfm.201303219).

Typical organic photovoltaic cells (OPVs) are based on an active organic layer sandwiched between electrodes (usually indium tin oxide and aluminum). Since this system can be built on a plastic substrate, the resulting devices are lightweight and mechanically flexible, opening a wide range of potential applications. Of particular interest are bulk heterojunction (BHJ) architectures, in which the active layer is a blend of a *p*-type polymer electron donor and a small-molecule fullerene electron acceptor. These materials are co-dissolved in a solvent and then printed, enabling low-cost, roll-to-roll manufacturing. However, OPV efficiencies remain below that of silicon PV. Replacing the fullerenes with a polymer—thus creating all-polymer solar cells—would have

several advantages, including cost reductions, increased spectral sensitivity in the red and infrared range, and enhanced polymer mechanical properties.

In pursuit of this goal, the Northwestern team had previously developed a new bithienyl-vinylene polymer building block; when this was copolymerized with (1) benzodithiophene (BDT) as an electron donor, and (2) naphthalenediimide (NDI) as an in-chain electron acceptor, the resulting *p*- and *n*-type polymers show high electron mobility and excellent ambient stability.

In the current work, the researchers built on these prior results to investigate variations of the polymer architecture, including the effects of different alkyl and alkoxy side chains, in order to develop a new series of polymers for optoelectronic applications. Tobin Marks, one of the co-authors, said, "Alkoxy groups have a wonderful ability to weakly bond with nearby sulfur groups; the interaction is sufficiently weak to give



good processability in solution, but in films, is strong enough to lock the polymer backbone into place and planarize the structure in the active layer.”

After synthesizing the polymers through Stille polycondensation, the researchers found them to be thermally stable up to 280°C and to have optical absorption spectra with peaks in regions consistent with DFT calculations. One *n*-type NDI-containing copolymer with branched alkyl side chains was envisioned to be particularly suitable as an OPV acceptor material; encouragingly, when it was blended with the polymer donor PTB7, the system displayed almost completely quenched photoluminescence, a signature of good charge transfer from donor to acceptor and thus good photovoltaic response. The researchers tested solar cells based on this blend and found them to have a power conversion efficiency of 1.70%, the highest reported to date with NDI as an electron acceptor. To better understand the

potential of the polymer series, a thin-film transistor based on this same blend was also constructed and was found to have a high electron (hole) mobility of 5.1 (3.9) $\times 10^{-3}$ cm²/V/s.

One important remaining issue in all-polymer OPV device performance is the optimal morphology of the organic thin film. This can be difficult to control with polymer–polymer blends, which tend to phase separate. As Rafael Verduzco of Rice University notes, the ideal microstructure is still unclear: “You probably want well-defined domains of about 10 nanometers, but recent polymers like PTB7 are challenging this thinking.” Verduzco’s group is investigating an approach in which donor and acceptor monomers are block copolymerized, and self-assemble into block lamellar microdomains approximately 9 nm in size. Using this technique, they have demonstrated an all-polymer OPV device with an efficiency of 3.1%.

Organic electronics are increasingly entering commercial use, and the results of this research are obviously of great interest to Polyera, an Illinois-based company whose markets include wearable electronics, flexible mobile displays, and disposable electronics for supply-chain tracking (one co-author, Antonio Facchetti, is a co-founder and Chief Scientific Officer; Tobin Marks is the other co-founder). Massachusetts-based Konarka was commercializing fullerene-based OPV cells until its bankruptcy in 2012, a fact that has certainly been noted by other aspiring organic electronics companies.

While organic electronics are still not competitive with silicon-based systems for most commercial applications, it is clear that they offer some unique properties and are making good progress in closing the gap. It may not be long until OPV throws the solar market a curve—literally.

Colin McCormick

Nano Focus

Grain size determines nanoscale grain rotation

Controlling the texture of materials is a crucial element in improving the strength and in extending the lifetime of materials. Plastic deformation of coarse-grained (>100 nm in grain size) metals has been well-described as a process in which the application of shear stress causes crystallites to rotate within the lattice structure until they achieve a preferred texture. It has proven challenging to determine if the same process occurs in nanomaterials due to the challenges associated with observing the rotation of ultrafine crystals.

As reported in the March 4 issue of *PNAS* (DOI:0.1073/pnas.1324184111), an international team of scientists from six different institutions have now succeeded in observing nanoscale plastic deformation by collecting x-ray diffraction (XRD) on polycrystalline metal samples under high pressure in a radial diamond-anvil cell (rDAC). For the series of experiments, the samples consisted of spherical platinum particles (~1 μ m) within a medium

of spherical nickel particles (500 nm, 20 nm, or 3 nm in diameter). According to Bin Chen, lead author and director of the Shanghai Laboratory of HPSTAR (Center for High Pressure and Technology Advanced Research), “We chose platinum and nickel, because both have fcc structures, and both are relatively easy for performing texture analysis. We also had several sizes of nickel to work with.”

Much to the surprise of the research team, the texture strength of platinum dropped significantly as the particle size of the nickel media was reduced, even though the same-sized platinum particles were used throughout the experiments. Texture was obvious when 500-nm nickel was used, but a considerable loss in texture was observed with the 20-nm nickel. With 3-nm nickel, almost all of the texture disappears. One possible theory was a lack of sufficient shear stress, but this was ruled out both mathematically and by the observation of curved diffraction lines because the curvatures of the unrolled two-dimensional diffraction lines demonstrate the existence of differential/shear stress.

Once the first theory was excluded, said the researchers, it became obvious that an enhanced grain rotation of the large platinum particles within the finer nickel medium caused the reduction in texture. The dislocation of particles under high pressure is an attempt to minimize system energy and to establish equilibria between neighboring grains. A mixture of coarser grains thus requires high energy and torque to rotate the particles, and rotation occurs at a slow rate. However, for a system with fine particles, dislocation has little to do with equilibrating the system. Instead, grain rotation is the system’s attempt to minimize the increase in compression-induced energy, which results in a high rotation rate of the fine particles and a loss in texture of the coarse particles.

Chen said, “The degree of grain rotation in other metals may be different, but the observed size-dependence of grain rotation should be similar. Since this report was qualitative, our future plans are to directly measure the degree of rotation of the nanocrystals.”

Anthony S. Stender