



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