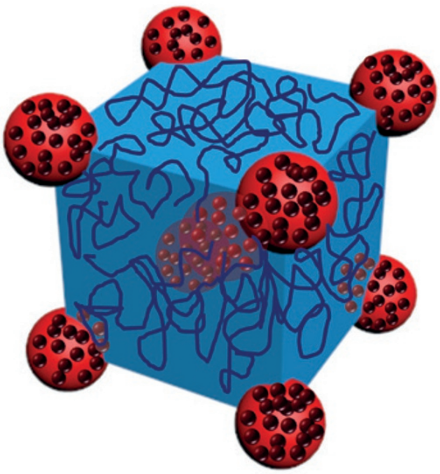
GIANT MOLECULES

Made to order

ACS Cent. Sci. **2,** 48–54 (2016)



AMERICAN CHEMICAL SOCIETY

Controlling the macroscopic properties of self-assembled structures by designing the composition of their building blocks at the atomic level is an ongoing challenge for nanoscience. Towards this goal, We-Bin Zhang, Yiwen Li, Stephen Cheng and colleagues now report preparing self-assembled polymeric nanoparticles that possess a precisely defined primary structure and also a predictable macroscopic morphology and chemical properties.

The researchers — who are based at the University of Akron, Texas State University, CNRS–Université de Strasbourg and Peking University — start with an azido-functionalized polystyrene to which they attach a silsequioxane cage bearing both an azido and an aldehyde group. Through successive click chemistry reactions, they then elongate the polymeric chain, which introduces other silsequioxane cages. Moreover, the backbone can be made either linear or branched by installing small linkers. The final, giant molecule can be as large as ~20 nm. In the bulk, the molecules self-assemble to produce a variety of ordered supramolecular structures and a variety of surface chemistries, depending on the length of the chains, the functionalization of the silsequioxane cages and the branching of the polymer backbone. *AM*

BATTERIES

Soil bacteria harmed

Chem. Mater. http://doi.org/bckw (2016)

Nickel manganese cobalt oxide (NMC) is a class of lithium intercalation compound that is widely used as a cathode material in lithium-ion batteries, which power electric cars. A single electric car with a typical 24 kWh battery pack contains >38 kg of nanoscale cathode material and it is estimated that by 2020 there will be 20 million vehicles on the road. These numbers suggest that nanoscale metal oxide could be an emerging environmental contaminant if these batteries are disposed into landfills. Christy Haynes, Robert Hamers and colleagues at the University of Wisconsin, Madison and the University of Minnesota now report that NMC can impair the growth and respiration of a soil and sediment bacterium, *Shewanella oneidensis.*

The researchers prepared thin sheets of lithium NMC and added different concentrations of the material to cultures of *S. oneidensis*, which is a gram-negative bacteria known for cycling metals in the environment. At 5 mg l^{-1} NMC, bacteria growth and respiration were inhibited. Experiments using inductively coupled plasma optical emission spectroscopy and X-ray photoelectron spectroscopy showed that NMC nanoparticles in aqueous medium preferentially released lithium, nickel and cobalt ions into solution, while leaving behind nanoparticles enriched in manganese. When nickel and cobalt ions were introduced to the bacterium culture, similar toxic effects were seen as when they were exposed to NMC nanoparticles, suggesting that toxicity is arising from the released transition metal ions rather than the remaining manganese-enriched nanoparticles. These preliminary results suggest that NMC may be a source of toxic nickel and cobalt ions, and that further efforts are needed to develop effective recycling strategies for these batteries. *ALC*

CARBON CATALYSTS

Active sites revealed

Science **351,** 361–365 (2016)

Nitrogen-doped carbon nanostructures have emerged as promising electrocatalysts for a range of important chemical reactions including the oxygen reduction reaction (ORR), which lies at the heart of proton exchange membrane fuel cells. The exact nature of the active sites in these ORR catalysts is, however, unclear, which limits the design of high-performance materials. In particular, there is debate over whether the sites involve pyridinic nitrogen (in which the nitrogen is bonded to two carbon atoms) or graphitic nitrogen (in which the nitrogen is bonded to three carbon atoms). Takahiro Kondo, Junji Nakamura and colleagues at the University of Tsukuba have now identified pyridinic nitrogen as the key species with the help of a series of graphite-based model catalysts.

The researchers tested the ORR performance of graphite catalysts that had different concentrations of pyridinic and graphitic nitrogen, using X-ray photoelectron spectroscopy (XPS) to characterize the chemical composition of the materials. The ORR activity of the catalysts was found to be dependent on the concentration of the pyridinic nitrogen. Post-reaction XPS experiments, combined with carbon dioxide adsorption measurements, ultimately suggested that the active sites are carbon atoms next to pyridinic nitrogen — sites that have Lewis basicity and that can adsorb oxygen, the initial step of the ORR. The relationship between catalytic activity and pyridinic nitrogen concentration was also found to hold for nitrogen-doped graphene nanosheet catalysts. *OV*

2D MATERIALS

Light-emitting valleys

Nano Lett. http://doi.org/bckx (2016)

Similar to the spins of electrons and holes, valleys present in the electronic band structure of some materials could potentially be used to process data. In the development of such valleytronic devices, monolayer transition metal dichalcogenides are of particular interest because of their inherent spin–valley coupling. Wei Huang, Ting Yu and colleagues have now shown that the circularly polarized light emission from valleys in transition metal dichalcogenides in a light-emitting diode (LED) can be manipulated by electrical tuning.

The researchers — who are based at Nanjing Tech University, Nanyang Technological University, Nanjing University of Posts and Telecommunications and the National University of Singapore — created a p–i–n heterostructure from monolayer WS_2. Unlike conventional approaches, where the control of the valley degree of freedom is achieved through an external magnetic field or a polarized laser light, the circularly polarized electroluminescence in this valley-LED was induced by an applied forward bias. Notably, the experimental data showed a strong correlation between the degree of circular polarization and the injection current. Although the emission mechanism was different from that of a typical LED, this valley-based optoelectronic device exhibited excellent diode-like behaviour in addition to its unique electroluminescence response, which was characterized by a tunable polarization and intensity. *OB*

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