

Synthesis of Novel Thermo-responsive Glycopolymers Achieved through Click Chemistry

Click chemistry is a relatively new synthetic approach toward the development of novel polymers with well controlled network formations. Click reactions spontaneously occur through relatively simple chemical conversions that induce irreversible bond formations between preformed polymeric building blocks. This reaction has garnered great attention toward the development of unique biomaterials by providing an efficient and extremely adaptable alternative method to traditional techniques, such as living polymerizations, to prepare existing materials classes.

The most commonly utilized type of click reaction takes advantage of orthogonal directed chemistry through a copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC), which eliminates key reaction parameters involving functional group protection, and requires no further purification procedures. A recent development in the click strategy has emerged through

the addition of thiols to alkenes, commonly known as a thiol-ene coupling or thiol-ene click reaction. The coupling nature, complete specificity, and ability to obtain nearly perfect quantitative yields, makes the application of this polymerization ideal when the chemical synthesis must occur in the presence of a wide variety of functional groups under physiological conditions. To further investigate the use of thiol-ene click mediated polymers *in vivo*, post functionalized, pre-formed, thermo-responsive polymeric micelles containing sugar moieties have been developed by G. Chen, S. Amajjahe, and M.H. Stenzel of the Center for Advanced Macromolecular Design (CAMD), The University of New South Wales, as reported in a recent issue of *Chemical Communications* (issue 10; DOI: 10.1039/b900215d; p. 1198).

Homopolymers and block copolymers bearing carbohydrate side chain functionality were obtained by grafting unprotected glucosamine onto alkene functional scaffolds through a thiol-ene click reaction and the resulting copolymer was used to form thermo-responsive micelles

as a potential drug carrier. These novel thiol-linked glycopolymers have the potential to mimic natural glycoproteins for investigating bioprocesses or as multivalent ligands for drug delivery vehicles. The robust nature of click chemistry allows reactions to occur in the harshest of environments, even wine, and directs network formation under mild conditions in the presence of a variety of additives which would normally hinder or terminate polymerization under traditional radical or photochemical conditions. Thus, using click chemistry produces polymers that are environmentally stable, tolerant to various additives, and maintain excellent performance capabilities.

The researchers said that they have devised "a simple and nontoxic method to produce complex glycosylated macromolecular constructs" with application potential toward "targeted drug delivery systems," which may have a significant influence in this area of materials research.

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Ternary Nanocrystals Used as Building Blocks for Solar Cells

Semiconductor nanocrystals have low production costs, are easy to process in solution, and have a reasonably high photoactivity. They should be, in principle, ideal candidates for photovoltaic applications. But the quantum confinement effect, which improves the nanocrystals' optical absorption, can hinder charge transport and limit the efficiency of the photovoltaic device. This phenomenon has been observed in various binary semiconductor nanoparticles, and compositional tuning has been suggested as an alternative to overcome this problem. Ternary compositions for nanocrystals might improve the photovoltaics performance. In the March 12 issue of *Nano Letters* (DOI: 10.1021/nl900388a; p. 1699), W. Ma, J.M. Luther, H. Zheng, Y. Wu, and A.P. Alivisatos from

the University of California and the Lawrence Berkley National Laboratory in Berkeley, California, report their exploration of the compositional tuning alternative, presenting and characterizing photovoltaic devices made using ternary $\text{PbS}_{(x)}\text{Se}_{(1-x)}$ nanocrystals.

These nanocrystals were synthesized using a one-pot hot injection reaction, and their crystalline structure and composition were subsequently characterized using Rutherford back scattering (RBS) and energy-filtered transmission electron microscopy (EF-TEM). Analysis of the TEM measurements suggested that the $\text{PbS}_{(x)}\text{Se}_{(1-x)}$ nanocrystals were made of alloyed composites with a uniform lattice structure. The RBS measurements demonstrated that the anion ratio ($S/(S+Se)$) was nonlinear with the S content of the precursor solution, but that the


concentration of each could be controlled. RBS measurements also showed that, for this synthesis method, all nanocrystals were rich in Pb, regardless of whether Pb was in excess during the synthesis.

Further characterization of the nanocrystals included optical absorbance measurements, which helped identify a linear relationship between the $\text{PbS}_{(x)}\text{Se}_{(1-x)}$ nanocrystals bandgaps and their PbS/PbSe ratio, and photoluminescence measurements, which confirmed that the nanocrystals were monodisperse.

The $\text{PbS}_{(x)}\text{Se}_{(1-x)}$ nanocrystals were then used to fabricate back contact Schottky devices that spanned the range of anion ratios. The photovoltaic properties of these devices were measured. The ternary nanocrystal devices achieved higher efficiency than devices made of pure PbS and PbSe with the best performance observed for devices with an anion ratio of approximately 0.7.

The research demonstrated that ternary nanocrystals, obtained through alloying of binary precursors, can improve photovoltaic properties. The alloying of binary lead chalcogenides—PbS and PbSe—tunes the nanocrystals' bandgap and improves their charge transport properties while maintaining the advantages of the binary compound counterparts.

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