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Aligned Mesoporous Architectures and Devices

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Aligned Mesoporous Architectures and Devices

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Abstract

This is the final report for the Presidential Early Career Award for Science and Engineering - PECASE (LDRD projects 93369 and 118841) awarded to Professor Yunfeng Lu (Tulane University and University of California-Los Angeles).

During the last decade, mesoporous materials with tunable periodic pores have been synthesized using surfactant liquid crystalline as templates, opening a new avenue for a wide spectrum of applications. However, the applications are somewhat limited by the unfavorable pore orientation of these materials. Although substantial effort has been devoted to align the pore channels, fabrication of mesoporous materials with perpendicular pore channels remains challenging. This project focused on fabrication of mesoporous materials with perpendicularly aligned pore channels.

We demonstrated structures for use in water purification, separation, sensors, templated synthesis, microelectronics, optics, controlled release, and highly selective catalysts.

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1. Introduction

From the Stone Age to the Age of Silicon, thousands of years of human ingenuity have brought us the life we enjoy today. Although an infinite number of materials have been found or created, making materials with life-like qualities is still a dream. For comparison, biological materials naturally possess an astonishing variety of sophisticated structures and functions. Researchers have long attempted to integrate biological materials with synthetic ones - as an alternative route to endow these inanimate materials with biological functions. This effort has created a large family of bio-composites with synergic properties. In spite of the great advances that have been made, the unprecedented opportunities offered by such integrating approaches, however, are constrained by an unsolved obstacle - the loss of activity and stability of the materials when utilized within the non-biological conditions under which most of the synthetic materials are utilized.

We hypothesized that mesoporous channels can be aligned using capillary forces. Conceptually, by contacting a lyotropic liquid crystalline fluid that contains inorganic or organic building blocks (e.g., silicate) and surfactant molecules with anodized porous alumina membranes, the capillary force generated by the curvature of the fluid meniscus causes capillary rise of the complex fluid, gradually filling the alumina pore channels with aligned liquid crystalline templates. Subsequent removal of the templates creates mesoporous silica membranes with perpendicular pore channels.

In addition to purely chemical approaches, we also developed a unique approach to synthesize highly robust protein nanocapsules that consist of a single-protein core and a thin polymer shell anchored covalently to the enzyme core. The polymer layers serve as artificial skins retaining the both the structure and function of the biomolecules even in a non-physiological environment; the skin layers are thin (\sim nanometers) and highly permeable, allowing effective substrate transport.

Combining our previous work in aligned mesoporous materials with our recent progress in making robust proteins, we synthesized a novel family of protein-composites, particularly, mesoporous protein-composites using the nanocapsules as building blocks. Note that traditional protein immobilization techniques generally result in composites in bulk or thin-film forms, which prevents their use as effective building blocks for the future composite synthesis. Success of this work will provide novel materials for chemical warfare sensing, medical, and other applications.

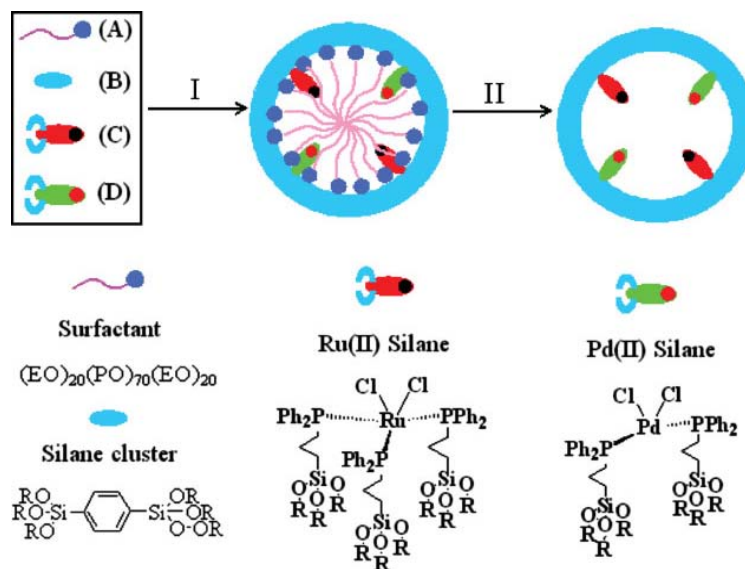
2. Experimental and Results

2.1 Mesoporous Silica with Multiple Catalytic Functionalities

Mesoporous silica containing multiple organometallic active sites is synthesized using a traditional post-synthesis complexation technique and a surfactant-directed assembly approach. Systematic spectroscopic studies and structure analysis indicate that catalytic mesoporous silica with controlled composition and pore structure can be readily synthesized. Catalytic performance examined by an aqueous medium two-step cascade reaction indicates that these materials possess excellent catalytic activity, reusability, and an interesting synergic effect. This work provides novel synthesis platforms towards multifunctional catalysts for more efficient chemical transformations.

Here we report the synthesis of a novel class of multifunctional catalysts: mesoporous silica-based organometallic catalysts (MOCs). Mesoporous silica represents a family of novel materials prepared by surfactant-directed assembly of silicate building clusters. Such materials contain tunable pore structures, chemistries, and functionalities, which make them ideal platforms latter approach involves chelating metal ions or complexes with the ligands covalently linked on the silica scaffold.

We have synthesized catalytic mesoporous silica containing two-type active organometallic centers through a post-synthesis complexation and an assembling technique (summarized in Scheme 1). The composition was studied using various spectroscopic techniques while the pore structure of these materials was investigated using XRD, nitrogen sorption, and TEM. These studies indicate that catalytic mesoporous silica with multiple catalytic centers and controlled pore structure can be readily fabricated. The catalytic activity, synergic effect of the active sites, and reusability of these materials were systematically investigated using an aqueous-medium two-step cascade reaction. Activity and reusability of these materials synthesized from the assembly approach are better than those prepared from the post-synthesis complexation approach. NMR studies indicate that the reduced activity in a post-synthesis complexation catalyst is attributed to their inability to retain the original active-site chemical environment upon chelating to the rigid silica framework. For comparison, the assembly approach affords a better approach in retaining the active-site chemical environment, as well as better composition and spatial control of the active sites. This work provides novel synthesis approaches towards the synthesis of multifunctional catalysts for more efficient chemical transformations.



Scheme 1. Schematic synthesis approach towards the assembled MOC through reacting organosilicate (B), Ru-containing organometallic silane (C), and Pd-containing organometallic silane (D) in the presence of surfactant (A).

Reference: Zhang F, Liu G, He W, Yin H, Yang X, Li H, Zhu J, Li H, Lu Y. 2008. Mesoporous Silica with Multiple Catalytic Functionalities. *Advanced Functional Materials* 18: 3590-7

2.2 Alloyed Semiconductor Nanocrystals with Broad Tunable Band Gaps

Semiconductors with tunable band gaps are of great interest for various applications, such as light-emitting diodes¹ and photovoltaics. In general, band gaps of semiconductor nanocrystals may be controlled by the size or composition of the nanocrystals. The size-dependent band gap of quantum dots has been extensively studied; however, such size-dependent property will disappear once the nanocrystals are deposited and converted into a dense film in solar cell applications. In this context, composition control is a more feasible route to fabricate semiconductor thin films with tunable band gaps. To date, various semiconductor alloyed nanocrystals with tunable band gaps have been reported, such as $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (3.7–2.4 eV), $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ (2.7–1.7 eV), $\text{CuGa}_x\text{In}_{1-x}\text{S}_2$ (2.4–1.5 eV), and $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$ (1.7–1.0 eV). These nanocrystals, however, were synthesized by alloying two cationic elements from the same group and generally exhibit narrow ranges of band gap.

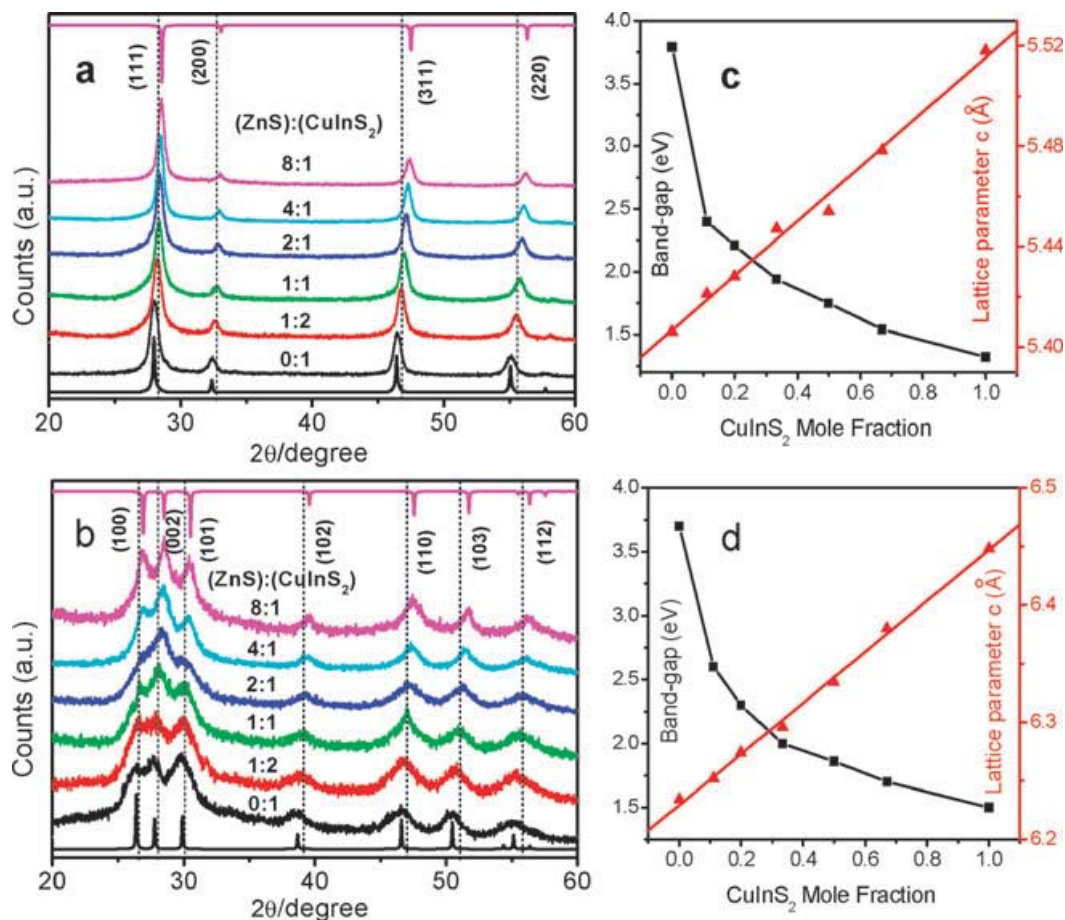


Figure 1. X-Ray diffraction patterns of the cubic (a) and hexagonal (b) structured alloy nanocrystals with various compositions (molar ratio); lattice parameters c and optical band gaps of the cubic (c) and hexagonal (d) alloy nanocrystals as a function of CuInS_2 molar fraction. For comparison purposes, XRD patterns of the cubic (a) and hexagonal (b) ZnS crystals (top patterns) and the simulated CuInS_2 pattern (bottom patterns) are also provided.

We synthesized semiconductor nanocrystals with band gaps tunable within the whole visible light region. This was achieved by alloying ZnS (3.7 eV band gap) with CuInS_2 (1.5 eV band gap) to create a family of nanocrystals with band gaps broadly adjustable from 3.7 to 1.5 eV (see Figure 1c and 1d). Note that formation of homogeneously alloyed nanocrystals requires crystalline-structure matching of the constituents. However, ZnS generally exhibits a cubic or hexagonal phase whereas CuInS_2 possesses a tetragonal phase. Although cubic-phase CuInS_2 does exist, it is generally formed by a phase transition at temperatures higher than 980 °C. As a result, the alloyed $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$ materials reported, are limited to heterogeneous crystals consisting of tetragonal phase CuInS_2 -rich regions and cubic-phase ZnS -rich regions; the synthesis of homogenous $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$ alloys over the entire composition range has not been reported yet.

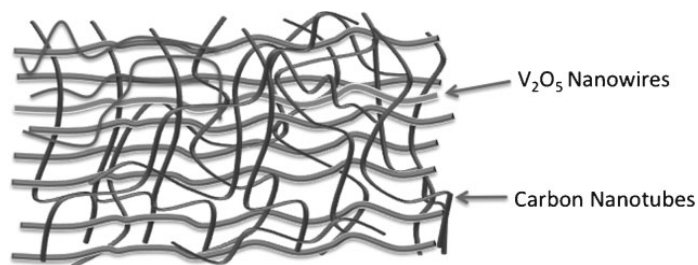
In summary, nearly monodisperse $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$ alloyed nanocrystals with tunable compositions and crystalline structures were synthesized using a simple wet-chemical approach. The band gaps of these nanocrystals can be broadly tuned from 1.5 to 3.7 eV simply by controlling ratios of the co-precursors used. To the best of our knowledge, this is the first report of homogeneous $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$ alloy nanocrystals over the entire composition range, providing new materials for photovoltaic and photocatalytic applications.

Reference: Pan D, Weng D, Wang X, Xiao Q, Chen W, Xu C, Yang Z, Lu Y. 2009. Alloyed semiconductor nanocrystals with broad tunable band gaps. *Chemical Communications*: 4221-3

2.3 Design and Synthesis of Hierarchical Nanowire Composites for Electrochemical Energy Storage

Nanocomposites of interpenetrating carbon nanotubes and vanadium pentoxide (V_2O_5) nanowires networks are synthesized via a simple in situ hydrothermal process. These fibrous nanocomposites are hierarchically porous with high surface area and good electric conductivity, which makes them excellent material candidates for supercapacitors with high energy density and power density. Nanocomposites with a capacitance up to 440 and 200 F g^{-1} are achieved at current densities of 0.25 and 10 A g^{-1} , respectively. Asymmetric devices based on these nanocomposites and aqueous electrolyte exhibit an excellent charge/discharge capability, and high energy densities of 16 Wh kg^{-1} at a power density of 75 W kg^{-1} and 5.5 Wh kg^{-1} at a high power density of 3750 W kg^{-1} . This performance is a significant improvement over current electrochemical capacitors and is highly competitive with Ni-MH batteries. This work provides a new platform for high-density electrical-energy storage for electric vehicles and other applications.

We synthesized novel supercapacitor materials based on composites of low-cost, interpenetrating CNTs and V_2O_5 nanowires, as illustrated in Scheme 2. This unique architecture provides several major advantages: i) the small dimension of the CNTs and the nanowires provide high surface areas, leading to a high EDLC and better utilization of the V_2O_5 active sites (i.e., higher specific pseudocapacitance); ii) the interpenetrating nanotubes/ nanowire structure creates hierarchical porous channels, enabling effective electrolyte transport and active-site accessibility; iii) the nanowires are intimately intertwined with highly conductive CNTs, facilitating faster electron transport and more efficient current collection.



Scheme 2. Schematic of method to form supercapacitor material based on interpenetrating networks of CNTs and V₂O₅ nanowire.

Figure 2A and B show, respectively, representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the CNTs, revealing a porous network of entangled CNTs with diameters of around 20–30nm and lengths up to the micrometer scale. Similarly, the diameter of the V₂O₅ nanowires is around 20–50nm with lengths up to tens of micrometers (SEM image, Fig. 2C). A high-resolution TEM image (Fig. 2D) indicates that the nanowires contain an ordered layered structure; the selective area electron diffraction (SAED) pattern (inset, Fig. 2D) suggests that they are single crystalline. In situ growth of the V₂O₅ nanowires within the porous CNT networks led to the formation of flexible, dark-brown nanocomposites, in which the V₂O₅ loading can be readily controlled by tuning the ratio of CNTs to the V₂O₅ precursor. Figure 2E shows an SEM image of a representative composite with 33 wt% CNTs (CVC-2), showing a continuous fibrous structure with pores up to micrometers in diameter.

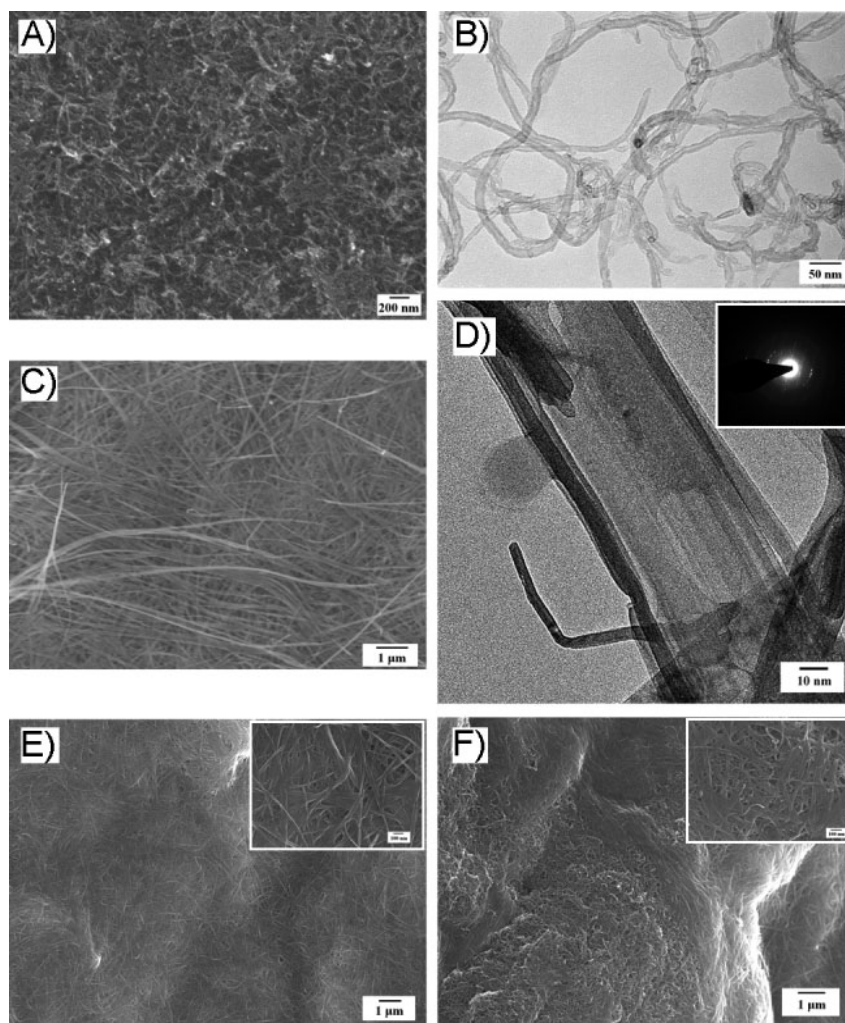


Figure 2. A) SEM and B) TEM images of the modified CNTs. C) SEM and D) TEM images and selective area electron diffraction (SAED, inset) of the V_2O_5 nanowires. SEM images of CVC-2 E) before and F) after etching showing an interpenetrating structure.

In summary, we have developed a class of supercapacitor composites based on confined growth of V_2O_5 nanowires within a conductive porous CNT scaffold. The hierarchically porous, interpenetrating network structure provides the composites with high capacitance and excellent rate performance. This design concept can be generalized towards other capacitor composites containing other low-dimensional metal oxides, such as MnO_2 , Co_3O_4 and NiO , opening a new avenue for a large spectrum of device applications.

Reference: Chen Z, Qin Y, Weng D, Xiao Q, Peng Y, Wang X, Li H, Wei F, Lu Y. 2009. Design and Synthesis of Hierarchical Nanowire Composites for Electrochemical Energy Storage. *Advanced Functional Materials* 19: 3420-6.

2.4 Quaternary Semiconductor Nanocrystals with Tunable Band Gaps

Dispersible quaternary $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ and $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ nanocrystals were successfully prepared by a toluene-thermal and a hot-injection approach and characterized using UV-vis spectroscopy, X-ray powder diffraction (XRD), and transmission electron microscopy (TEM). UV-vis absorption spectra of $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ nanocrystals revealed that the band gaps of alloyed nanocrystals can be precisely adjusted in the range of 1.43 to 2.42 eV by increasing the indium content. From XRD analysis, the lattice parameters of $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ nanocrystals decreased linearly with an increase in the Ga/(Ga+ In) ratio in accordance with Vegard's law, which confirmed that alloyed nanocrystals have a homogeneous structure. Alloyed $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ and $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ nanocrystals have a narrow size distribution according to TEM analysis results. Moreover, it was found that oleylamine played an important role in the formation quaternary homogeneous $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ and $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ nanocrystals due to eliminating the reactivity difference of copper, gallium, and indium as well as thallium precursors.

We recently reported the synthesis of high quality Cu-In-S nanocrystals with a cubic and hexagonal structure and tunable copper to indium ratio. Copper diethyldithiocarbamate ($\text{Cu}(\text{dedc})_2$) and $\text{In}(\text{dedc})_3$ were used as precursors, and oleylamine was used as an activation agent that can expedite the precursor decomposition process. The use of oleylamine helps to eliminate the reactivity difference of the precursors and benefits the formation of the homogeneous ternary $\text{Cu}_x\text{In}_y\text{S}_{0.5x+1.5y}$ nanocrystals. The band gaps of the $\text{Cu}_x\text{In}_y\text{S}_{0.5x+1.5y}$ nanocrystals, however, were almost the same when the ratios of Cu to In were changed from 1:3 to 3:1. In this work, band gap sensitive elements, gallium and thallium, were introduced into the $\text{Cu}_{1.0}\text{In}_{2.0}\text{S}_{3.5}$ nanocrystals to form homogeneous quaternary $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ and $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ ($0 \leq x \leq 2$) nanocrystals. The influence of the gallium and thallium on their band gaps and lattice parameters was also discussed. It was found that the introduction of gallium and thallium enables precise tuning of the band gaps from 1.37 to 2.42 eV. Such tunable-bandgap materials may allow precise control over the emission and absorption wavelengths, which is of interest for applications for photovoltaics, light-emitting diodes (LEDs), and other applications.

In summary, multiple component $\text{Cu}_{1.0}\text{Ga}_x\text{In}_{2-x}\text{S}_{3.5}$ and $\text{Cu}_{1.0}\text{In}_x\text{Tl}_{2-x}\text{S}_{3.5}$ ($0 \leq x \leq 2$) semiconductor nanocrystals with a tunable band gap were synthesized using generic chemicals by toluene-thermal and a hot-injection approaches. Equivalent gallium or thallium were introduced into the $\text{Cu}_{1.0}\text{In}_{2.0}\text{S}_{3.5}$ nanocrystals to partly replace the indium, forming multicomponent nanocrystals with broad compositional ranges.

The optical band gaps and lattice parameters of the alloyed nanocrystals are composition-dependent, following the bowing equation and Vegard's law. These nanocrystals have good solubility in common solvents and may be potentially used as absorber and window materials in multijunction photovoltaic cells and other applications.

Reference: Pan D, Wang X, Zhou ZH, Chen W, Xu C, Lu Y. 2009. Synthesis of Quaternary Semiconductor Nanocrystals with Tunable Band Gaps. *Chemistry of Materials* 21: 2489-93

2.5 A Novel Intracellular Protein Delivery Platform Based on Single-Protein Nanocapsules

An average cell contains thousands of proteins that participate in normal cellular functions, and most diseases are somehow related to the malfunctioning of one or more of these proteins. Protein therapy, which delivers proteins into the cell to replace the dysfunctional protein, is considered the most direct and safe approach for treating disease. However, the effectiveness of this method has been limited by its low delivery efficiency and poor stability against proteases in the cell, which digest the protein. Here, we show a novel delivery platform based on nanocapsules consisting of a protein core and a thin permeable polymeric shell that can be engineered to either degrade or remain stable at different pHs. Non-degradable capsules show long-term stability, whereas the degradable ones break down their shells, enabling the core protein to be active once inside the cells. Multiple proteins can be delivered to cells with high efficiency while maintaining low toxicity, suggesting potential applications in imaging, therapy and cosmetics fields.

We report a novel intracellular delivery platform based on nanocapsules that consist of a single-protein core and thin polymer shell anchored covalently to the protein core. As illustrated in Fig. 1a, polymerizable vinyl groups are covalently linked to the protein (I). Subsequent polymerization in an aqueous solution containing monomers (1, 2) and crosslinker (3, 4) results in each protein core being wrapped in a thin polymer shell. This scheme enables the synthesis of protein nanocapsules with a non-degradable (II) or degradable (III) skin by using non-degradable (3) or degradable (4) crosslinkers, respectively. Appropriate choice of the monomer, such as the cationic (2) or neutral (1) monomers, allows precise control of surface charge. The protein cores can be chosen from a vast library of proteins, including enhanced green fluorescent protein (EGFP), horseradish peroxidase (HRP), bovine serum albumin (BSA), superoxide dismutase (SOD) and caspase-3 (CAS).

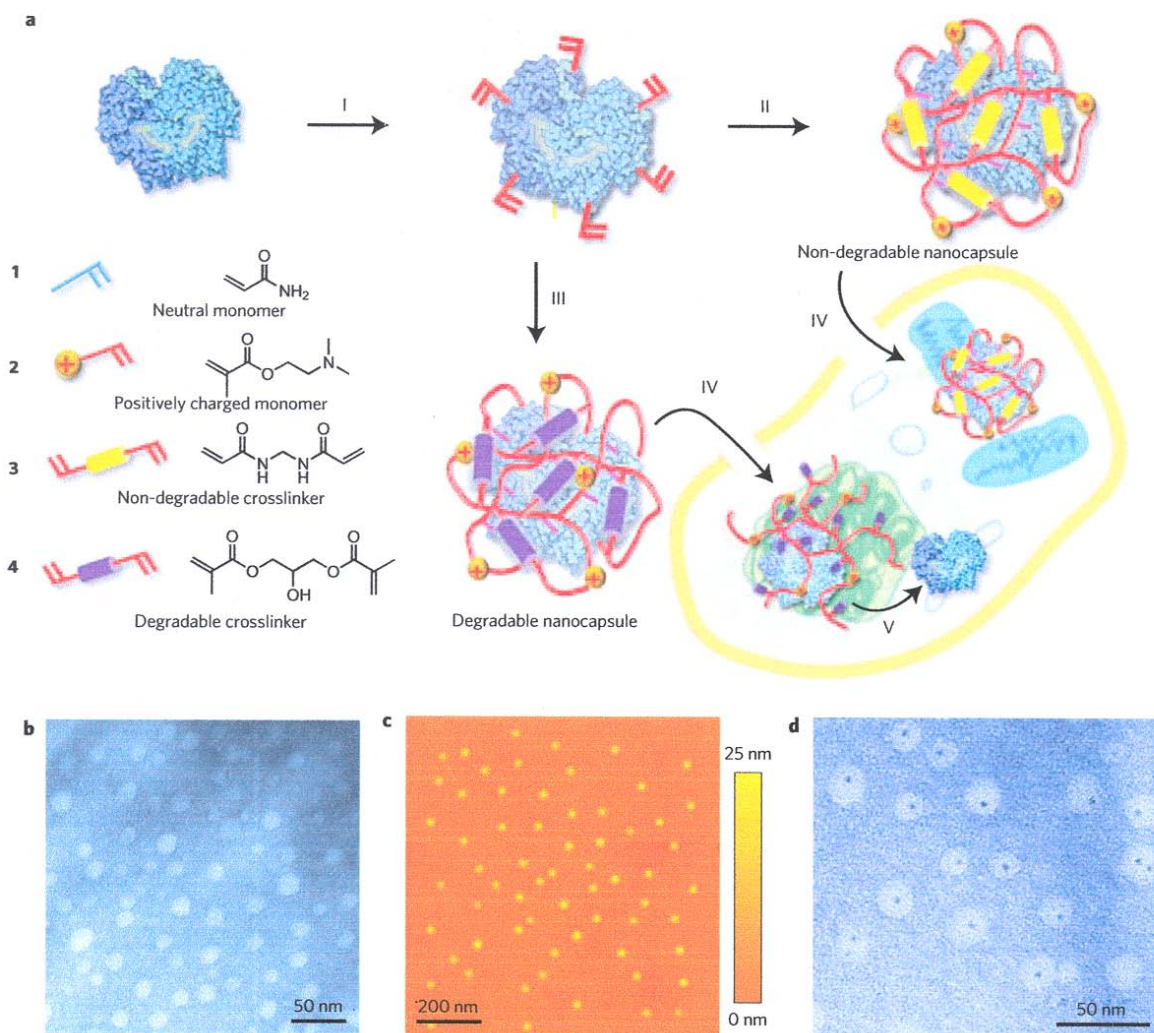


Figure 3 Protein nanocapsules. a, Schematic showing the synthesis and cellular uptake of cationic single-protein nanocapsules with degradable and non-degradable polymeric shells prepared by in situ co-polymerization of acrylamide 1, 2-dimethylaminoethyl methacrylate 2 and non-degradable crosslinker methylenebisacrylamide 3 or acid-degradable glycerol dimethacrylate 4: I, formation of polymerizable proteins by conjugating polymerizable acryl groups to the protein surface; II, formation of non-degradable nanocapsules from 1, 2 and 3; III, formation of degradable nanocapsules from 1, 2 and 4; IV, cellular uptake of the degradable or non-degradable nanocapsules via endocytosis; V, shells of degradable nanocapsules break down after internalization to release the protein cargoes, allowing them to interact with large molecular substrates. b, c, Representative TEM(b) and AFM (c) images of the HRP nanocapsules. d, TEM image of nanocapsules containing a single 1.4-nm gold-quantum-dot-labelled HRP core confirms the formation of a single-core nanoscale architecture.

In this project, we synthesized mesoporous protein/ceramic composites. There has been extensive interest in making ceramic/protein composites for many applications. Traditional synthesis approaches generally involve the direct addition of protein to the media, which has resulted in significantly reduced activity.

Mesoporous silica composites were synthesized using surfactant, silicate, and the protein nanocapsules as building blocks. Lipase, organophosphorus hydrolase (OPH) and other proteins were used as model proteins. Particularly, OPH is an organophosphotriester (OP)-hydrolyzing enzyme that can effectively hydrolyze a series of chemical warfare agents, such as sarin and soman. Thus, we synthesized the nanocapsules and compared their activities with native enzymes. Various silicate precursors with different functional groups were used and the structure of the resulting composites was studied by TEM and nitrogen sorption experiments. Activity and stability of the composites at different temperatures, pHs, and solvents was determined and compared with those prepared from naked enzymes.

We have demonstrated a general, effective, low-toxicity intracellular protein delivery system based on single-protein nanocapsules. This work opens a new direction for cellular imaging, cancer therapies, anti-aging, cosmetics and many other applications. Further work on more robust, non-degradable nanocapsules for large molecular substrates is under way.

Reference: Yan M, Du J, Gu Z, Liang M, Hu Y, Zhang W, Priceman S, Wu L, Zhou ZH, Liu Z, Segura T, Tang Y, Lu Y. 2010. A novel intracellular protein delivery platform based on single-protein nanocapsules. *Nat Nano* 5: 48-53

Summary

Our work has demonstrated that pore channels of mesoporous silica can be aligned by exploiting capillary forces. We optimized the synthesis conditions and successfully aligned mesostructures by optimizing the pH, temperature and aging time, which allowed us to minimize the polymerization reaction kinetics and maximize the mobility of the building blocks. We conducted both fluidic mechanical calculations and experimental studies to understand the aligning mechanism. Viscoelastic properties and contact angle of the nanocomposite were measured and used to calculate the capillary force and shearing force. A mechanism was proposed based on these studies. We investigated the alignment of mesostructures within different-size alumina pore channels. Alumina membranes with different pore diameters were used as the template to allow an investigation of the assembly of the mesostructure within this confined environment.

We achieved the following major milestones:

- 1) We synthesized catalytic mesoporous silica containing two-type active organometallic centers through a post-synthesis complexation and an assembling technique.
- 2) We demonstrated the first homogenous $(\text{CuInS}_2)_x(\text{ZnS})_{1-x}$ alloy nanocrystals over the entire composition range, providing new materials for photovoltaic and photocatalytic applications. We synthesized semiconductor nanocrystals with

band gaps tunable within the whole visible light region.

- 3) We synthesized novel supercapacitor materials based on composites of low-cost, interpenetrating nanowires based on confined growth of V_2O_5 nanowires within a conductive porous CNT scaffold.
- 4) We synthesized multiple component semiconductor nanocrystals with a tunable band gap were synthesized using generic chemicals by toluene-thermal and a hot-injection approaches. The resulting nanocrystals have good solubility in common solvents and may be potentially used as absorber and window materials in multijunction photovoltaic cells and other applications.
- 5) We have demonstrated a general, effective, low-toxicity intracellular protein delivery system based on single-protein nanocapsules. This work opens a new direction for cellular imaging, cancer therapies, anti-aging, cosmetics and many other applications.

This work may provide a new technique to fabricate controlled structure materials and devices for water purification, separation, sensors, templated synthesis, microelectronics, optics, controlled release, highly selective catalyst, and other applications. For example, such aligned mesoporous materials can be further functionalized with responsive or recognizable components, leading the fabrication of smart devices, such as intelligent artificial membranes and highly sensitive sensors.

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