II.K.14 Protein-Templated Synthesis and Assembly of Nanostructuctures for Hydrogen Production

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Objectives

Photocatalysis using solar radiation represents a significant opportunity for the development of renewable energy sources (H_2 production). In general, the visible-light-driven photocatalysis reactions that have been explored thus far exhibit low quantum efficiency for solar energy conversion, which limits their practical utility. The goal of the project is to develop protein-templated approaches for the synthesis and directed assembly of semiconductor nanomaterials that are efficient for H_2 production from water under visible light irradiation.

Technical Barriers

The low quantum efficiency for visible-light-driven photocatalysis is primarily because of materials-related issues and limitations, such as the control of the band gap, band structure, photochemical stability, and available reactive surface area of the photocatalyst. Synthesis of multicomponent hierarchical nano-architectures using biomimetic approaches, consisting of semiconductor nanoparticles with desired optical properties fabricated to maximize spatial proximity for optimum electron and energy transfer, represents an attractive route for addressing the problem.

Abstract

A variety of sulfide nanomaterials with controlled size, phase structure, and three-dimensional architectures have been synthesized using *E. Coli* bacteria and genetically engineered virus (P22) as affinity bio-templates. Photoelectrodes fabricated using the *E. Coli* templated synthesis of hollow CdS nanostructures exhibit excellent performance for photocatalytic hydrogen production with a photoconversion efficiency of 4.2 % under global AM 1.5 illumination in the presence of a sacrificial electron-donor of mixed S^{2-} and SO_3^{2-}. This is significantly better than the 1.34% efficiency obtained using CdS nanoparticles synthesized utilizing the same procedure in the absence of *E. Coli*. The potential of utilizing the P22 virus architecture to improve efficiency and durability of the IrO_2-Zn Porphyrin system for the water splitting reaction is also being explored. Moreover, the ability of the icosahedral P22 structures to act as scaffolds for energy harvesting via Förster resonance energy transfer (FRET) is being investigated.

Progress Report

(a) Bacterial syntheses of quantum dots, nanocrystals, and hollow nanostructures: Sulfide semiconductors have a wide variety of optical, electrical, and photoelectric applications. CdS has a narrow band gap and a valence band at relatively negative potentials, which offer them good visible-light-active photocatalysts. Nanoporous hollow nanostructures are one of the best architectures since they avoid agglomeration of the NCs and reduce bulk/interface electron/hole recombinations. However, it is challenging to assemble NCs into highly ordered hollow nanostructures. We have developed a general biotemplate synthesis approach to prepare hollow CdS nanostructrures by taking advantage of the natural morphology of the common bacteria *E. coli*. The CdS nanostructures are prepared with high yield under mild ambient conditions with the assistance of sonochemistry using cadmium acetate dehydrate and thioacetamide as reactants. The CdS coating on the *E.coli* can be controlled in the form of monodisperse quantum dots (1-2 nm), near monodisperse NCs (7-8 nm), discontinuous CdS NC agglomerates, and uniform porous coating of NCs. Both the band gap and crystal structure of these CdS NCs can be tuned by simply adjusting the synthetic conditions, such as reaction time and the concentration of precursors (Figure 1 a-c). The photoelectrodes fabricated using the synthesized hollow CdS nanostructures exhibit excellent performance for photocatalytic hydrogen production with a photoconversion efficiency of 4.2 % under global AM 1.5 illumination in the presence of a sacrificial electron-donor of mixed S^{2-} and SO_3^{2-} (Figure 1d). The method has been extended to the synthesis of other sulfides including ZnS, PbS, AgS, etc., with controlled size, structure, and optical adsorption properties.

(b) Virus protein-templated three-dimensional sulfide nanoarchitectures: We have successfully developed a facile bioinspired approach for the synthesis of ordered 3D nanostructures of sulfide NC assemblies over genetically engineered P22 viral capsids (Figure 2a-e). The assembly procedure consists of (1) the self-assembly of spherical protein templates from genetically engineered P22 coat protein, and (2) the nucleation and growth of NCs on the self-assembled protein templates (Figure 2c). We

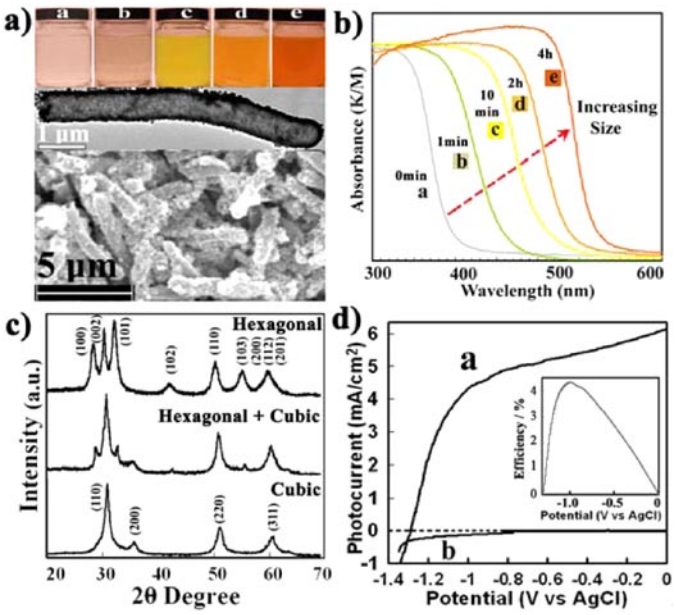

FIGURE 1. (a) SEM and optical images, (b) reaction time-dependent UV-vis spectra, (c) XRD patterns of *E. coli*-templated nanoporous hollow CdS microrods. (d) Photocurrent density (a) and dark current (b), and photoconversion efficiency (the inset) of a photoelectrode fabricated using nanoporous CdS hollow microrods.

have used ZnS and CdS grown on the engineered P22 coat protein assembly as a model system since binding peptides with strong affinity for these sulfides have been identified. Furthermore, the structure and assembly of the P22 coat proteins is reasonably well understood. By changing the reaction time and reactant concentration, the final protein-directed sulfide growth is expected to exhibit different structures, such as well ordered spherical NC assemblies (Figure 2d) during the early stage of growth that eventually develop into spherical hollow nanostructures for longer growth periods (Figure 2e). Both the diameter and configuration of the self-assembled P22 coat protein template can be controlled over a specific range by heating in solution at temperatures of up to 70 °C. This offers some degree of control over the size and shape of the synthesized inorganic nanostructures. Additionally, the crystallite size of the NCs can be varied by changing the reactant concentration and the reaction time. The synthetic strategy is quite general and can be extended to the fabrication of a variety of other nanostructures.

(c) Synthesis of IrO_2-Zn porphyrin labeled phage capsids: Filamentous viruses carrying Zn porphyrins which act as a photosensitizer and IrO_2 oxide hydrosol clusters which act as a catalyst have been demonstrated to effect photocatalytic water splitting, although immobilization of the viruses in a microgel was required to improve the structural durability. To evaluate the potential of spherical virus architecture to improve efficiency and durability we have inserted an IrO_2 binding peptide into the exterior surface of the bacteriophage P22 capsid and have taken advantage of a internal uniquely chemically reactive site (engineered in section 1.4 below) to conjugate a Zn porphyrin to the interior of the particle. A commercially available Zn porphyrin starting material was modified by the laboratory of Trevor Douglas by the introduction of a maleimide group which in turn is capable of efficient conjugation to the thiol group of the amino acid cysteine. Preliminary experiments suggest a modest level of conjugation of the porphyrin to the interior of the capsid at natural pH and optimization of the reaction is currently underway.

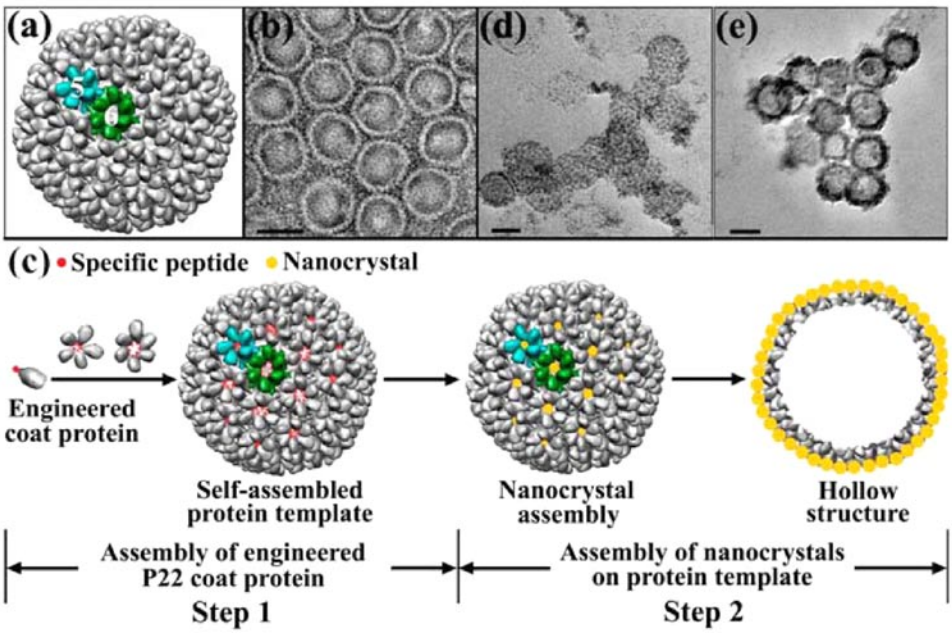

FIGURE 2. (a) Three-dimensional surface representation of P22 procapsid viewed along a 3-fold axis; (b) TEM image of stained protein assemblies of genetically engineered P22 coat protein; (c) Schematic illustration of the formation of ordered NC assemblies over self-assembled genetically engineered P22 coat proteins. Step 1: assembly of P22 coat proteins (gray) genetically engineered with specific peptide (red). Step 2: protein-directed nucleation and growth of NCs (yellow) on the protein assembly. (d and e) TEM images of sulfide NC assemblies grown on the self-assembled protein templates shown in Figure 1b. All scale bars represent 50 nm.

(d) Antenna effect studies using spherical P22 capsids: The antenna effect is the ability

of an ensemble of chromophores with similar absorbance bands to transfer energy to a common acceptor, hence to act as photon collecting antennas. We have analyzed the antenna effect displayed by chromophores on the exterior of the 60 nm spherical P22 capsid particle over a range of photon acceptor and donor densities. Our data indicated that the degree of donor emission increased with increasing fraction of labeled subunits up to a value of approximately 10% (~50 subunits) after which it decreased. The decrease was due to donor/donor collisional quenching. Under the most favorable conditions the antenna effect was limited to value of approximately 2 (meaning two donors could transfer to an acceptor). By mapping the site of the modification onto the capsid lattice it became evident that rather than being uniformly distributed on the capsid surface, as a result of the capsid architecture, the sites are locally clustered. It is the local clustering that result in the donor quenching and limited antenna effect. In collaboration with Reidun Twarock of the York Center for Complex Systems Analysis, an alternative site for modification which would result in a more uniform distribution of chromophores was identified.

(e) Construction of P22 phage capsids with internal chemically reactive sites: We have constructed a set of plasmids whose expression results in the production of P22 procapsids with chemically reactive amino acid residues located on the interior face of the capsid wall. Cysteine residues were inserted into a long a-helical region of the coat protein and the protein was tested for its ability to assemble into procapsids and the chemical reactivity of the cysteine residue in the various states of the procapsid was determined. Substitution of a cysteine at residue 110 of the capsid protein results in the formation of a properly dimensioned capsid in which the cysteine is reactive in the unexpanded procapsid form but unreactive in the expanded "wiffle ball" form. In contrast, substitution of residue 118 with cysteine results in a capsid in which the cysteine is reactive in the "wiffle ball" form but relatively unreactive in the procapsid form.

Future Directions

During the last phase of the current project, we are focusing on the fabrication of multicomponent inorganic nano-architectures over genetically engineered P22 capsids. The specific peptide sequences responsible for binding to different materials, including PbS, CdS, Fe_2O_3, and TiO_2, will be fused into the scaffolding protein of P22. The genetically engineered P22 capsids with the specific affinity for binding to PbS, CdS, Fe_2O_3, and TiO_2 will then be used to prepare porous hollow nanoballs, possibly consisting of multiple components. We will optimize synthetic conditions for control of the shell structure, the size of NC subunits, and the assembly of heterogeneous components. The physical and chemical properties of the products will be studied in detail. Photocatalytic activity and photoconversion efficiency of the obtained heterogeneous nanoarchitectures will be evaluated.

Publication list acknowledging the DOE grant

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