

Template Synthesis of Semiconductor and Metal-Semiconductor Composites for Photoelectrochemical Applications

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Nanostructured semiconductor materials and composites are especially of interest in photoelectrochemical devices such as solar cells, photoelectrochromic systems, and nanosensors.

Here we report the preparation and characterization of semiconductor and metal-semiconductor nanostructures using a template-directed growth. Two contrasting template structures were used for our purpose: anodized alumina films with self-organized cylindrical holes, and ordered monolayer arrays of polystyrene spheres.

Cuprous thiocyanate semiconductor nanorods were fabricated on gold nanowires using the following procedure: (1) electrodeposition of gold nanowires of desired length into the alumina nanoholes, (2) electrodeposition of copper nanorods on top of gold wires, and (3) partial electrooxidation of the copper nanorods in thiocyanate solution. The final nanostructure is compared in its photoelectrochemical behavior with that of a continuous p-type CuSCN film prepared by electrooxidation of a macro-sized copper electrode in a thiocyanate media.

Titanium dioxide and metal - titanium dioxide nanotubes with different lengths and diameters were also prepared into the alumina templates. The TiO₂ nanotubes were sol-gel deposited either directly into the alumina nanoholes or into a modified alumina template by previous deposition of nickel (or other metal) in its walls. The resultant metal/TiO₂ nanostructures possess an orderly distribution of metals sites and semiconductor sites in close proximity, and were tested in their photooxidation efficiency and contrasted with those of TiO₂ nanocomposites films prepared by the occlusion electrodeposition method.^(1,2)

A contrasting template consisting of a monolayer of polystyrene spheres was used for the electrodeposition of compound semiconductor nanocrystal arrays, such as cadmium selenide and indium sulfide. These polystyrene templates (PST) with two-dimensional periodical arrays were electrophoretically deposited on gold or ITO surfaces. Cadmium selenide nanocrystal arrays were prepared using a new strategy involving two steps: (1) selenium dots were first electrochemically grown in the PST void lattices, and (2) the Se dots were then cathodically stripped as Se²⁻ in a Se(IV)-free electrolyte medium dosed with the requisite amount of Cd²⁺ ions, thus generating CdSe nanocrystals arranged in an orderly fashion on the gold substrate.

Thus, by combining our present approach for the electrosynthesis of cadmium selenide⁽³⁾ with the procedure for electrophoretic self-assembly of colloidal polystyrene spheres,⁽⁴⁾ high purity CdSe nanocrystals (no Se admixed) can be obtained. Extensions to other systems such as the electrosynthesis of In₂S₃ nanocrystals following an adaptation of our reported In₂S₃ thin film electrosynthesis⁽⁵⁾ to a template-directed deposition are under current investigation.

References

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