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Synthesis of Titania Nanocrystals: Application for Dye-Sensitized Solar Cells

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2.1. Formation of Titania Nanocrystals by Surfactant-Assisted Methods

2.1.1. Introduction: How to Control Morphology and Functionalize Ceramic Materials

Titania nanocrystals, which have a large surface area with controlled surface structure and high electron transport properties, are essentially important for high-efficiency dye-sensitized solar cells. Morphological control and high crystallinity are the key properties needed in titanium oxide materials for dye-sensitized solar cells. In this section, we first review morphological control and functionalization of nanosize ceramic materials from a wide point of view.

One of the most active trends in modern materials chemistry is the development of synthetic methods to obtain size- and shape-controlled inorganic nanocrystals. The shape and size of inorganic nanocrystals determine their widely varying electrical and optical properties. For example, quantum dots exhibit strongly size-dependent optical and electrical properties. Magnetic studies of nanocrystals show that the blocking temperature, saturation, and remnant magnetization of nanocrystals are solely determined by the size, regardless of the shape. However, the shape of the nanocrystals is the dominant factor in their coercivity.

Morphological control of nanosize materials is essential for their functionalization, as shown by the above examples. Investigators have recently shown keen interest in controlling the morphology of nanomaterials and clarifying the correlations between a material’s properties and its morphology. Until now, a number of methods have been developed to control the shape of nanocrystals.

In the case of CdSe, the shape of the nanocrystals is controlled by a mixture of surfactants that differently bind to the crystallographic faces, utilizing the interaction between the surfactant and the nanocrystal surface. The organic surfactants cannot coat one face of the nanocrystals, which raises the energy of this face relative to others, allowing it to grow quickly and form a rod shape. In the formation of CdSe nanocrystals, the monomer concentration in the growth solution is also a determining factor in shape control and shape evolution. If the remaining
monomer concentration in the growth solution is extremely high, the solution can supply a sufficient amount of monomers for each seed to fully grow arms on the four (111) facets of the zinc-blende structure of the tetrahedral seeds, yielding tetrapoles. A moderately high monomer concentration can only support the growth of a single arm in its one-dimensional (1D) growth stage, generating rod-shaped nanocrystals. At low monomer concentrations, these elongated nanocrystals are not compatible with the low chemical potential environment. Consequently, the system can only generate dots. On the other hand, ligand influence on the monomer is also important. In general, a relatively small number of nuclei are desired for the growth of elongated nanocrystals because the change of the monomer concentration in the solution caused by the nucleation process and the subsequent growth process should be relatively small. This should result in a relatively stable monomer concentration in the solution, suitable for the growth of a given shape.

How to control the growth rate of the nanocrystal is another method for shape control. In the formation of the CoFe$_2$O$_4$ nanocrystal, the growth rate of the nanocrystal is the key in shape control. A slow heating rate kept a low concentration of available metal cations from the decomposition of precursors, which, combined with the low growth temperature, gave a slow rate of crystal growth. The growth of cubic CoFe$_2$O$_4$ nanocrystals was terminated at $\{100\}$ planes, which were predicted to have the lowest surface energy. When a much faster heating rate was employed, a high concentration of metal cations was present. A faster growth rate at a high temperature with abundant metal cations available resulted in crystal growth with much less selectivity in direction and, hence, produced spherical CoFe$_2$O$_4$ nanocrystals.

The biological route is a developing and attractive method for the shape control of nanocrystals. Metal alloy ferromagnetic nanostructures FePt were successfully synthesized by biological methods. A phage display methodology was adopted to identify peptide sequences that both specifically bind to the ferromagnetic L1$_0$ phase of FePt and control the crystallization of FePt nanoparticles using a modified arrested precipitation technique. Transmission electron microscopy (TEM), electron diffraction, scanning transmission electron microscopy (STEM), and X-ray diffraction all indicated that these nanoparticles were composed of an FePt alloy with some degree of chemical ordering, and super quantum interface device (SQUID) analysis showed that these nanostructures are ferromagnetic at room temperature, possessing coercivities up to 1000 Oe.

Controlled removal of the stabilizing organic molecules from the surface of nanoparticles induces fusion of nanoparticles, which produces a simple method to synthesize 1D nanocrystals using self-assembly. Nanoparticles of CdTe were found to spontaneously reorganize into crystalline nanowires upon controlled removal of the protective shell of an organic stabilizer, thioglycolic acid. In an early stage of the nanowire formation, “pearl necklace” agglomerates composed of nanoparticles were observed in the TEM image. The “pearl-necklace” shape of fused gold metal was successfully synthesized by controlling the concentration of the capping reagent. A template approach is an effective way to make nanorods and nanotubes. To date, the oxide nanotubes and nanorods such as TiO$_2$, MnO$_2$, Co$_3$O$_4$, WO$_3$, and