Controlling the shape of anatase nanocrystals for enhanced photocatalytic reduction of CO2 to methanol

Quang Duc Truong, Huu Thu Hoa, Dai-Viet Vo and Thanh Son Le

Herein, we report a simple thermal-induced synthesis of pyramidal anatase TiO2 nanocrystals with exposed (101) and (001) facets with controlled shapes and truncated particles. Anatase phase of rod-like structures or truncated bipyramidal nanocrystals was prepared by tailoring the temperature or treatment time in a hydrothermal method using peroxotitanic acid as a precursor without using any shape-controlling reagent. The presence of both (101) and (001) facets in the synthesized nanocrystals enhances the separation of electrons and holes and improves the photocatalytic reduction of CO2 to methanol.

1. Introduction

The foreseen shortage of natural energy resources such as fossil fuels, for example, coal, gas, etc., and the pollution caused by the combustion of these fuels have raised much attention worldwide. The search for sustainable approaches for generating renewable energy, therefore, has gained extensive attention. The photocatalytic reduction of carbon dioxide to methanol using semiconductor photocatalysts that convert solar energy into chemical fuels has attracted widespread interest as a promising strategy for the production of clean fuels. Numerous photocatalysts have been developed: carbon nitride, copper, BiVO4, CdS, WO3, etc. Among these, titanium dioxide (TiO2) is a promising photocatalyst owing to its chemical inertness, non-toxicity, low-cost, and long-term stability against corrosion. Current research has been focused on the improvement of photocatalytic efficiency via the investigation of the chemistry and physics of photocatalyst materials. The photocatalytic activity of TiO2 is heavily dependent on various physicochemical properties such as particle size and shape, surface area, crystalinity and geometry, which has triggered considerable efforts in the development of controllable synthesis to enable enhanced photocactivity. Among these factors, structural properties, including the surface atomic configuration and coordination on different crystal facets of TiO2, are significant in a heterogeneous catalytic system. In particular, the different energy levels of the conduction and valence bands, which are determined by the configuration and coordination of the constituent atoms, drive electrons and positive holes to different exposed crystal facets, which results in a decrease in the back-reaction rate owing to the predominance of reduction or oxidation on each crystal facet. Therefore, the control of the shape and surface structure of titania is a critical step forward for optimizing the activity of these semiconductor particles in catalytic reactions.

Anatase TiO2 nanocrystals with controlled shapes and exposed surfaces have drawn considerable attention owing to their shape-dependent photocatalytic properties. For instance, anatase nanocrystals with exposed {101} facets and/or exposed {001} facets have attracted an extraordinary amount of research interest because their synergetic effect is attributed to the efficient separation of photogenerated charges. It was reported that the presence of both {101} and {001} exposed crystal facets will drive photoexcited electrons and positive holes to different exposed crystal facets, which results in a decrease in recombination of the generated electrons and holes and forces the reduction and oxidation processes to occur on different crystal facets. There have been many synthetic routes for preparing TiO2 particles with controlled shapes and exposed facets. Inorganic mineral or organic shape-controlling reagents such as polymeric surfactants, long-chain carboxylic acids and amines have been effectively used to induce the growth of shape-controlled nanocrystals. In particular, much work has been devoted to the hydrothermal synthesis of single crystals with a high percentage of reactive {001} facets using hydrofluoric acid as a capping reagent. Hydrophilic polymers, such as polyvinyl alcohol and polyvinylpyrrolidone, and...