



Synthesis of TiO₂ nanoparticles using novel titanium oxalate complex towards visible light-driven photocatalytic reduction of CO₂ to CH₃OH

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ABSTRACT

TiO₂ nanoparticles (NPs) with controlled crystalline structure and morphology were synthesized by a facile hydrothermal method using a novel titanium oxalate complex. The structure, morphology, and spectral properties of the synthesized TiO₂ NPs were characterized by X-ray diffraction, Raman spectroscopy, scanning/transmission electron microscopy, and UV–vis diffuse reflectance spectroscopy. The titania phases of anatase, rutile, or brookite can be easily tuned by tailoring the solution pH during reaction. Highly ordered flower-like rutile could be obtained with oxalic acid additive. The synthesized TiO₂ catalysts showed excellent visible light absorption and remarkable photocatalytic activity for CO₂ reduction to CH₃OH under both UV–vis and visible light irradiation, mainly due to doped carbon and nitrogen. Bicrystalline anatase–brookite composite afforded maximum CH₃OH yield, attributed mainly to the unique electrical band structures and efficient charge transfer between the two crystalline phases.

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1. Introduction

The foreseen shortage of fossil fuels is of global concern. The development of alternative and renewable energy sources has gained increased attention. Since the pioneering work of water splitting using a TiO₂ electrode by Honda and Fujishima in early 1970s, the conversion of solar energy into chemical energy has been intensively studied [1]. Typical examples include transformation of solar energy into hydrogen via photocatalytic water splitting [2] and solar-driven photocatalytic conversion of CO₂ into chemical fuels. The latter approach provides intriguing opportunity for economic utilization and simultaneous reduction of CO₂, which is beneficial to tackle global warming. Considerable efforts have been devoted to explore the photoreduction of CO₂ into chemical fuel such as CO, CH₄, or CH₃OH [3–13]. A variety of catalysts such as metal oxides [3–6], InTaO₄ [7], ZnGa₂O₄ [8], Zn₂GeO₄ [9,10], and Ti-based materials [11–13] have been explored for CO₂ conversion in either liquid or gas phase. Among them, titanium oxide (TiO₂) is one of the most promising candidates, presumably owing to its powerful oxidation properties, stability, efficiency, and long-term durability [13–23]. To improve the TiO₂ application efficacy, current research has focused on the development of light-harvesting

strategy [18–20] and extended its photo-response to visible light region [13–17,21,22]. Indeed, a great deal of effort on investigating TiO₂ doped with metal [13–20] or nonmetal elements [21,22] has been reported. By comparison, the effect of TiO₂ crystalline structure, i.e. brookite phase, and morphology on the CO₂ photoreduction has not been considered appreciably.

Kakihana et al. recently proposed a novel route using water-soluble compounds formed by coordinating small organic molecules with metals, facilitating the control of nucleation and assembly to afford desired nanostructures by bottom-up approach [24–27]. A new series of water-soluble titanium complexes were developed as precursors for the selective synthesis and morphological control of TiO₂ polymorphs [24–28]. The synthesized TiO₂ were usually doped with nonmetal elements during the nucleation and crystallization stage, providing increased photoactivity under visible light irradiation [25].

We recently adopted this approach for the synthesis of FeTiO₃/TiO₂ with increased photocatalytic performance [29]. Herein, we report the controlled synthesis of TiO₂ NPs with various phases and morphologies for photocatalytic reduction of CO₂ to CH₃OH. Particularly, we propose a hydrothermal method using a novel titanium oxalate complex to synthesize TiO₂ catalysts with tunable crystalline structure and morphology. The oxalic acid ligand possess unique symmetry structure and rich coordination properties, assisting the control of nucleation and morphology to yield TiO₂ catalysts containing anatase, rutile, or brookite phase. The size and morphology effect on TiO₂ catalyst photocatalytic reduction of CO₂ to CH₃OH was investigated in detail.

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