

Transition metal doped anatase nanocrystals: Continuous-flow hydrothermal synthesis and photocatalytic activity



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ABSTRACT

Transition metal doped anatase nanoparticles have been prepared by a continuous-flow hydrothermal method. An aqueous solution containing a titanium source and appropriate amounts of cobalt or nickel nitrate is mixed in-flow with potassium hydroxide as a mineraliser before meeting a pre-heated stream of supercritical water in a counter-current mixing reactor. Mixing of the metal ion containing solution with supercritical water results in the rapid nucleation of anatase nanocrystals. Powder X-ray diffraction and electron microscopic imaging show that the dopant ions are incorporated into the anatase structure. The incorporation of dopant ions leads to reduced crystallite size and increased surface area. The doped anatase nanocrystals exhibit lower band-gap energies than the undoped material. The photocatalytic activity of the doped and undoped samples has been assessed by monitoring the degradation of methylene blue in the presence of the catalysts under UV illumination. Doping of the anatase nanoparticles significantly increases the photocatalytic activity, with nickel doping showing a pronounced improvement over both the undoped and cobalt doped catalyst nanocrystals.

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1. Introduction

Titanium dioxide (TiO₂) has been extensively studied for its photocatalytic properties [1] and is used in some well-developed applications, for example, in water splitting [2], the photochemical degradation of organic and inorganic pollutants [3,4], and self-cleaning surfaces [5]. The three commonly encountered polymorphs of titania are anatase, rutile and brookite, each consisting of TiO₆ octahedra but with different vertex-, edge- and face-sharing arrangements. Of these polymorphs, anatase is widely accepted as the most active in photochemical processes. The inherent activity of anatase may be further enhanced by various means. Confining titania to the nanoscale results in materials with very high surface areas, shorter path-lengths for electron/hole diffusion to the crystal surface as well as the capacity to control the crystallite habit, and consequently higher activity [6]. A further strategy to improve the photocatalytic behaviour of anatase is the manipulation of its electronic properties through the

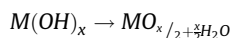
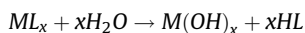
incorporation of dopant ions. The substitution of Ti⁴⁺ for alternative metal ions, typically of the transition metals or f-block elements, has been shown to introduce sub-bands to the electronic structure of anatase with the overall effect of lowering the band-gap energy, and thus enhancing photocatalytic efficiency [7,8]. Doping of titania with low levels (≤5%) of cobalt or nickel, for example, has previously been shown to improve the photochemical properties and photocatalytic performance [9,10]. The incorporation of dopant ions may have the additional effect of disrupting the crystal structure inducing disorder which can also increase photocatalytic performance.

The increasing demand for clean catalysis to mitigate environmental damage, particularly by organic contaminants, puts titania based photocatalysts in high demand. Doped anatase nanoparticles have been produced by a wide variety of methods [11], from simple co-precipitation, to sol-gel type routes [7,12], to more involved microwave assisted [13] and hydrothermal/solvothermal methods [8,14]. Each approach has its advantages and disadvantages. Precipitation and sol-gel methods are typically uncomplicated in terms of apparatus and experimental set-up, but often result in poorly crystalline materials which require additional calcination and annealing steps to promote both crystallisation

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and true doping. Hydrothermal and solvothermal routes allow the direct production of crystalline nanomaterials with atomically dispersed dopant ions without the need for additional heat-treatments. As with precipitation and sol-gel methods, however, they are typically batch processes and may be difficult to scale-up for industrial-level production. Continuous-flow hydrothermal synthesis, which was established with the goal of producing monodisperse metal oxide nanoparticles at industrially relevant scales, is ideally suited to meet the demands for anatase nanocatalysts. The continuous hydrothermal method has developed over the past 20 years as a powerful technique for the large-scale production of a range of inorganic nanomaterials [15–19]. The technique was initially conceived specifically with the continuous production of metal oxides in mind. The properties of supercritical water (scH₂O, T ≥ 374 °C, P ≥ 22 MPa) allow it to act as both a reactant and anti-solvent. Mixing scH₂O in flow with metal salt solutions permits the rapid formation of metal oxide nanocrystals via extremely fast hydrolysis and nucleation reactions:



We have used this technique to produce pure anatase as well as cobalt and nickel doped anatase nanoparticles. These materials

have been assessed for their photocatalytic activity in the degradation of methylene blue.

2. Experimental

2.1. Materials

Titanium bis(ammonium lactato) dihydroxide (TiBALD) (50 wt% in water), cobalt nitrate hexahydrate, Co(NO₃)₂·6H₂O (reagent grade 98%), nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O (purity ≥ 98.5%) and potassium hydroxide, KOH (reagent grade ≥ 85%) were purchased from Sigma-Aldrich and used as received.

2.2. Reactor design

The reactor used in this work is the counter-current nozzle reactor designed at the University of Nottingham [20,21]. Briefly, the reactor, constructed from stainless steel 316 Swagelok[®] components, is comprised of a preheater section which feeds supercritical water downwards through an inner tube into a vertically aligned outer tube through which room temperature reagent streams flow. The supercritical and reagent streams mix thoroughly at the outlet of the inner tube before immediately passing through a heat exchanger to cool down. The product stream exits through a back pressure regulator which maintains pressure within the system. Both preheated water and the reagent

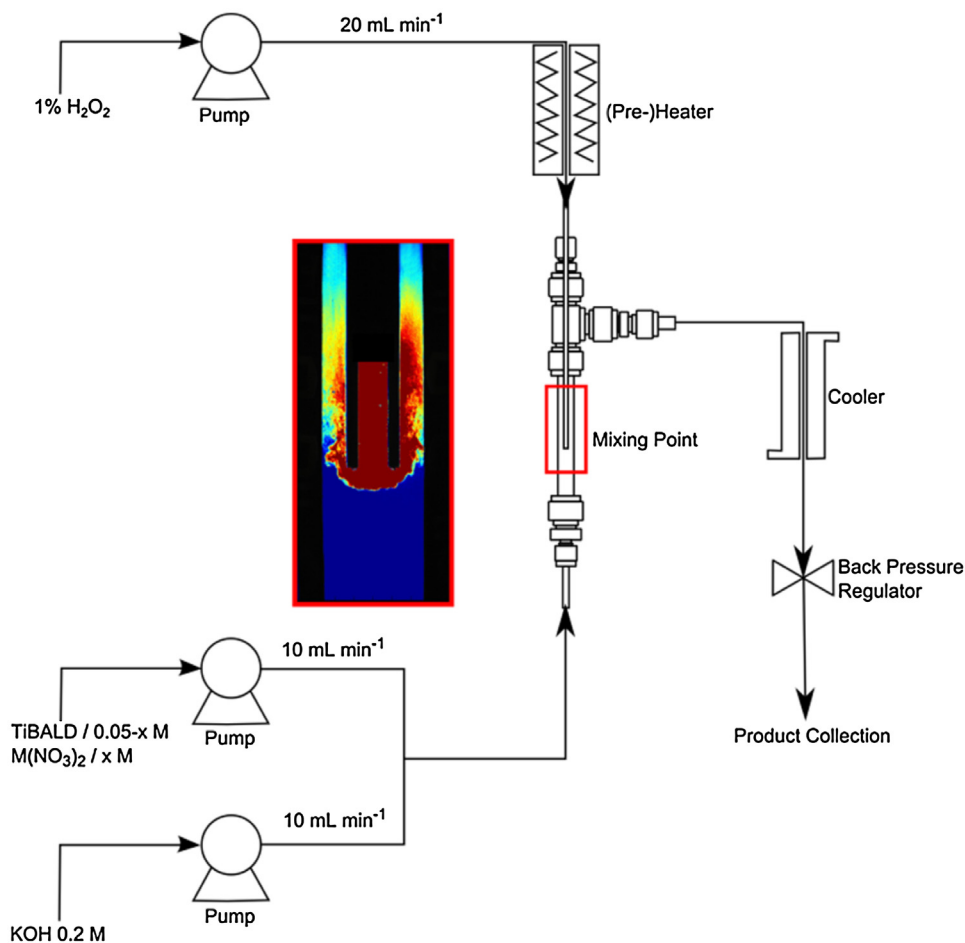


Fig. 1. A simplified schematic of the reactor used for the continuous production of transition metal doped anatase nanocrystals.

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