Aqueous synthesized mixed-phase nano-TiO_2 photocatalysts for water treatment of both organic and inorganic pollutants

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Abstract

Nano-sized mixed-phase titanium dioxide (TiO_2) particles are synthesized through aqueous hydrolytic precipitation of $TiCl_4$, in an easily-scalable continuously stirred tank reactor, CSTR. Different conditions give tunable mixed phase nanotitania particles consisting of anatase (A), rutile (R) or brookite (B) that are further characterized as photocatalysts in both oxidative and reductive roles and compared with the well-known commercial nanotitania, Evonik P25. Degradation of an organic model compound, methyl orange under UV light irradiation using the newly synthesized TiO_2 blends is first investigated. Further, the remediation of selenium inorganic species from simulated waste water is tackled. Selenium (Se) is an element of environmental concern, as it may report to natural waters via industrial effluents as those released from mining and metallurgical operations among other.

Keywords: nanoTiO_2 precipitation, photocatalytic application, effluent treatment

1. Introduction

Nano-sized mixed-phase titanium dioxide (TiO_2) particles are used for their oxidative and reductive abilities to investigate the removal of organic and inorganic pollutants from waste water. In 1972, TiO_2 excitation by light was mentioned for the decomposion of water (A. Fujishima & Honda, 1972) and since then, nanoTiO_2 have attracted a lot of attention for a variety of applications such as photocatalytic water purification using UV light. TiO_2 semiconductor has many advantages such as high specific surface area, due to its nanoscale, relatively low cost and high chemical stability in the environment.

There are several methods to synthesize TiO_2 nanoparticles, such as hydrothermal synthesis (Caramazana-González et al., 2017) and sol-gel synthesis to produce powders and films (Benehkohal, Gomez, Gauvin, & Demopoulos, 2013). In our case, we employ a new hydrolytic precipitation process of $TiCl_4$, see Eq 1 in a continuously stirred tank reactor, CSTR at steady state, that is easily scalable (Yasin, Guo, & Demopoulos, 2016). By varying process parameters, such as temperature, agitation speed, residence time, inlet Ti(IV) concentration and pH, different mixed-phase TiO_2 powders were produced to be evaluated further as photocatalyst for the two systems.

$$TiCl_4(aq) + 2H_2O \rightarrow TiO_2(s) + 4HCl(aq) \qquad \text{Eq 1}$$

There are three main types of crystallographic polymorphs: anatase (A), tetragonal, brookite (B), orthorhombic and rutile (R), tetragonal that have different morphology, particle size and semiconducting properties. All the aforementioned have an effect on the photocatalytic oxidative and reductive role of the TiO_2. Once light is illuminated on the titania with energy equal or higher than its band gap, a pair of electron (e^-) and hole (h^+) is generated. The photogenerated holes, at the valence band may be used to oxidize organic molecules, while the photogenerated electrons at the conduction band may be used to reduce inorganic pollutants (Akira Fujishima, Zhang, & Tryk, 2008). İn Figure 1 the schematic representation of the TiO_2 band gap structure is given.

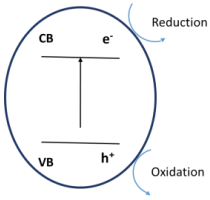

Figure 1. *Schematic representation of charge transfer after illumination of TiO_2; use of photogenerated electrons and holes for reduction and oxidation respectively*

One of the major drawbacks, which reduces the photocatalytic efficiency of TiO_2 is the recombination of the photogenerated holes and electrons. Therefore for the case of TiO_2 used as reduction photocatalyst, several organic agents, like oxalic acid and formic acid have been investigated as 'hole scavengers' to suppress and prevent the electron-hole recombination, thereby enhancing the photoreduction of inorganic pollutants like As(III,V) or Cr(VI) (Dutta, Ray, Sharma, & Millero, 2004; Tan, Beydoun, & Amal, 2003). Mixed phase nanoTiO_2 are of interest as photocatalysts in environmental applications as thanks to intrinsic heterojunction may experience less photogenerated electron-hole pair recombination. The best-known mixed phase TiO_2 photocatalyst is Evonik's

P25 that has a 3:1 ratio anatase: rutile. Its improved functionality is attributed to the rutile lattice acting like a trap for the photogenerated electrons minimizing recombination with holes thus enhancing the photocatalytic efficiency vs. that of the single phase TiO_2 (Boehme & Ensinger, 2011).

Selenium, Se is an essential element for living species, which occurs naturally and exist in Earth's crust, though may be hazardous and toxic in high levels as a by-product from a wide variety or mining and metallurgical industries. The maximum acceptable concentration (MAC) for Se in drinking water is based on chronic selenosis symptoms 50 µg/L (Canada, 2014). Se exist in several inorganic and organic species; the removal of which depends on their oxdation states. Se exists in four different oxidation states; selenide, Se(-II), elemental selenium, Se^0, selenite Se(IV) and selenate, Se(VI), as well as other organic forms (Canada, 2014). Both Se(VI) and Se(IV) are the predominant soluble species in contaminated surface waters.

2. Results

In this work, we primarily focus on a novel synthesis process for mixed phase TiO_2 nanoparticles (Ab, Ba, Rb, caps indicate the major phase), by regulating operating conditions; namely pH, concentration and residence time and compare them with the commercial mixed phase, P25. The paper will present highlights from this research and in particular on (1) the synthesis of the nanoparticles, (2) their effectiveness as oxidation photocatalysts in degrading a model organic pollutant, methyl orange, (3) their effectiveness in photocatalytic reduction of Se (IV, VI) species and finally, (4) discuss the mechanism of Se(VI) species adsorptive reduction on the surface of TiO_2 via multitude characterization techniques.

The investigation reveals some interesting contrasting photocatalytic performance when switching from oxidative to reductive processes. Thus in the case of photo-oxidative degradation of methyl orange under UV irradiation (refer to kinetic plots of Figure 2(a)) it is the predominantly anatase nano TiO_2 photocatalyst (P25 vs. Ab) that offers the best performance. Note that the heterojunction in the case of P25 is A/R while in our material is A/B. When however we consider the case of inorganic Se(VI) photo-reduction (refer to kinetic plots in Figure 2(b)) P25 proves the worst photocatalyst. It is the predominantly rutile (minor phase brookite, Rb) nanoTiO_2 that delivers the best performance.

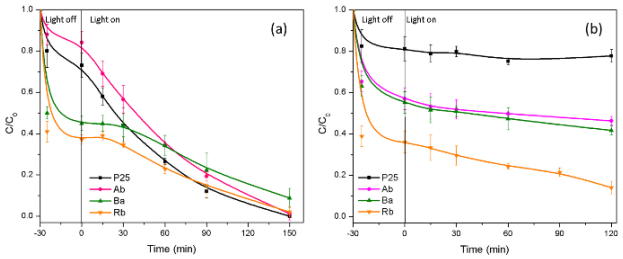

Figure 2. *Comparison of synthesized mixed phase TiO_2 and P25 versus time; (a) Photo-decomposition of methyl orange (1 g/L catalyst, C_0: 25 mg/L) and (b) Photo-reduction of Se(VI) (1.5 g/L catalyst, C_{Se}: 30 mg/L, C_{HCOOH}: 300 mg/L)*

Work is underway focusing on elucidating the underlying photocatalyst properties responsible for this contrasting behavior. This work includes Prior- and Post-photocatalytic experiment characterization of the Se-decorated TiO_2 by XRD, XPS, Raman, SEM and TEM.

3. Conclusion

Synthesized mixed phase of the TiO_2 blends were evaluated for organic pullutants, methyl orange and inorganic pollutants, Se species under UV irradiation. Synthesized TiO_2 mixed phases show equivalent photocatalytic activity to commercial, P25 in terms of organic pollutant degradation, but superior reducing performance in terms of selenate removal.

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