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## Adsorption and photo-catalytic properties of layered lepidocrocite-like quasi-amorphous compounds based on modified potassium polytitanates

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### ABSTRACT

TiO<sub>2</sub> compounds possess relatively high adsorption abilities and exhibit high photocatalytic activities that exhibit potential for the destruction of organic pollutants in natural and waste waters. Nanostructured potassium polytitanates modified using transition metals and their oxides/hydroxides generate new nanomaterials that operate in the visible spectral range.

This study presents the synthesis and investigation of the structure, composition and photocatalytic activity of powdered nanoscale quasi-amorphous potassium polytitanates particles modified with iron, zinc, copper, cobalt and nickel sulfate in aqueous solutions. All of the powders investigated in this work exhibit a high adsorption capacity for methylene blue dye (15–20 mg/g) related to the well-developed surface of the layered potassium polytitanate particles. Introducing transition metals and their oxides/hydroxides influences the electronic structure of the obtained systems. A high photocatalytic activity was observed for systems containing iron, zinc, nickel and their oxides/hydroxides in the ultraviolet and visible ranges.

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### 1. Introduction

The photocatalytic destruction of organic pollutants is a promising method for natural water purification and waste water treatment. Photocatalysis over titania (TiO<sub>2</sub>) has been extensively investigated for destroying various organic pollutants contaminating natural and technological waters (Akpan & Hameed, 2009; Gaya & Abdullah, 2008; Han, Kambala, Srinivasan, Rajarathnam, & Naidu, 2009; Shan, Ghazi, & Rashid, 2010). Although TiO<sub>2</sub> has several drawbacks, such as a low efficiency and a restrictive short-wavelength excitation in the UV range, considerable effort has been expended to enhance the photocatalytic efficiency and utility of visible light by doping the TiO<sub>2</sub> particles with metals and/or non-metals to modify energy bands of the TiO<sub>2</sub>. This procedure extends the photo-responsiveness of these materials into the visible-light (vis) region and intensifies the separation of the electron–hole pairs in the TiO<sub>2</sub> particles (Bettinelli et al., 2007; Chen, Wang, et al., 2008; Chen, Huang, & Tsai, 2007; Devi, Kottam, Murthy, & Kumar, 2010; Li, Duan, Liu, & Li, 2008; Xu, Gao, & Liu, 2002; Zhu, Chen, Zhang, Chen,

& Anpo, 2006). However, establishing an optimal content of the doping elements is difficult; an excess of the dopant promotes the recombination of electrons and holes, hindering their participation in the redox reactions (Wong, Feng, Hu, & Yue, 2004).

The photocatalytic activity of the TiO<sub>2</sub> powders might be enhanced by formation of different p–n junctions. Semiconductor oxides loaded with TiO<sub>2</sub> have been extensively investigated for various applications, including nano-p–n junction photocatalysts (Chen, Zhao, Liu, & Zhang, 2008; Ku, Lin, & Hou, 2011; Lee & Lai, 2009; Lin et al., 2011; Liu, Wang, Yang, Cheng, & Lu, 2010; Rawal, Chakraborty, & Lee, 2009; Tristão, Magalhães, Corio, & Sansiviero, 2006). Coupling a wide band gap semiconductor TiO<sub>2</sub> or titanate and a narrow band gap semiconductor transition metal oxide/hydroxide might create photocatalysts that are active under visible light.

Recently, TiO<sub>2</sub> derivatives, particularly layered titanates, have exhibited high photocatalytic activity (Amano, Yasumoto, Shibayama, Uchida, & Ohtani, 2009; Bao, Shen, & Yanagisawa, 2004; Kim, Kim, Im, Ha, & Hwang, 2009; Tawkaew, Chareonpanich, & Supothina, 2008; Xu, Ding, Chen, & Peng, 2007). These crystalline layered titanate compounds, including H<sub>1.5</sub>Na<sub>0.5</sub>Ti<sub>3</sub>O<sub>7</sub>, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>, K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>, Cs<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>, are characterized by their high adsorption properties relative to the parent TiO<sub>2</sub> powder;

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moreover, these materials can be produced using hydrothermal, solid-phase or sol-gel syntheses. The main disadvantage of the layered titanates as photocatalytic materials remains similar to that of the titanium oxide: their low activity in the visible spectral range. Due to their structural features, the layered titanates might be very convenient alternative host materials for synthesizing heterostructured nanomaterials. For example, the potassium polytitanates (PPT) (Sanchez-Monjaras, Gorokhovskiy, & Escalante-Garcia, 2008) described by  $K_2O \cdot nTiO_2$  ( $n = 2-6$ ) are promising new materials for photocatalytic applications; they feature a lepidocrocite-like ( $\gamma$ -FeOOH) layered structure and a high adsorption activity related to their large interlayer distance (Gorokhovskiy et al., 2011).

Previously we showed (Gorokhovskiy, Tretyachenko, Escalante-Garcia, Yurkov, & Goffman, 2014) a possible method for modifying amorphous PPT powders via treatment in aqueous transition metal salt solutions. The obtained heterostructured particles exhibited layered nanosheets containing potassium titanates decorated by nano-scale particles of transition metal oxide/hydroxides; concurrently, the interlayer space of the PPT sheets was filled with  $Me^{y+}$  ions,  $K^+$  and  $H_3O^+$ . This structure was typical of the particles (powders) obtained at pH = 5–7. However, no reports have detailed the photocatalytic activity of these compounds. In this work, we studied the synthesis, adsorption and photocatalytic properties of semiconductor materials based on amorphous PPT powders modified with transition metal oxides/hydroxides.

## 2. Materials and methods

The PPT powder was produced using a molten salt synthesis route adding  $TiO_2$  (10 wt%) powder (anatase 99%, ALDRICH, average particle size of 7  $\mu m$ ) in a molten mixture of KOH (10 wt%) and  $KNO_3$  (80 wt%) at 500 °C for 2 h in an alumina crucible, as previously described by Sanchez-Monjaras et al. (2008). The product was washed with distilled water until a  $TiO_2$ -to- $K_2O$  molar ratio of 3.92 for potassium polytitanate was obtained.

To produce heterostructured nanoparticles based on modified PPT, an aqueous solution of copper (II), zinc, cobalt, iron (III), or nickel sulfate was added to the aqueous PPT dispersion (i.e., 10 g of PPT powder in  $10^{-3}$  M sulfate solution) and stirred for 12 h. The pH was adjusted with  $H_2SO_4$  and maintained at 5–6. The obtained products were filtered over filter paper (Wathman-42) and dried at 140 °C for 4 h in the oven. The temperature of the thermal treatment was selected based on the high stability of the amorphous PPT demonstrated by our previous studies (Sanchez-Monjaras et al., 2008).

The X-ray diffraction (XRD) patterns of the products were obtained at room temperature using an X-ray diffractometer (Philips X'Pert-MPD) with  $Cu-K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The morphology of the heterostructured particles was investigated with a transmission electron microscope (TEM, JEOL JEM-1011) operated at 80 kV. The general and local chemical composition of the modified PPT powders was studied using energy dispersive X-ray spectroscopy (EDS), with a scanning electron microscope (Philips XL30ESEM) equipped with an EDS EDAX Pegasus analyzer operated at 20 kV. The specific surface area of the samples was investigated using the  $N_2$  sorption (Brunauer–Emmett–Teller (BET) method) measured with a Micrometrics ASAP2020C apparatus.

The evolution of the band structure of the PPT particles after  $Me^{y+}$  intercalation and  $Me_xO_y/Me(OH)_y$  decoration was investigated using diffuse reflectance ultraviolet–visible (UV–vis) spectroscopy (a Shimadzu UV-2550PC UV/Vis spectrophotometer, equipped with an ISR-2200 integrating sphere). The photocatalytic activity of the modified PPT powders was determined by degrading methylene blue (MB) dye under solar irradiation simulated by

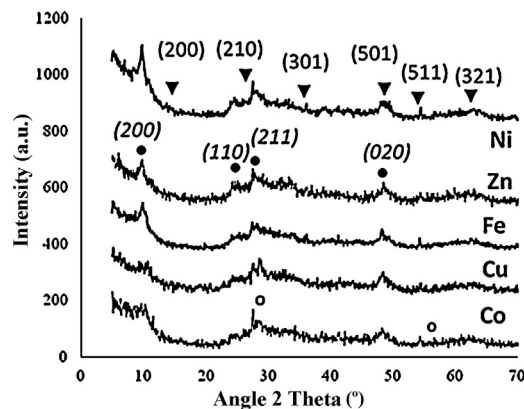


Fig. 1. XRD patterns of the PPT powders modified in aqueous solutions containing different transition metal salts: (●) reflections of the pattern of lepidocrocite-like PPT powder, (▼) reflections related to the lepidocrocite (AMCSD database #0017984), (○) reflections of  $TiO_2$  (rutile) (AMCSD database #0001735).

a DRL-250W T40 light source (intensity of 284  $mW/cm^2$  at the distance of photoreactor location). The photocatalyst (200 mg) was added to a Pyrex glass beaker (photoreactor) containing 250 mL of the MB aqueous solution (40 mg/L). Before irradiation, the suspension was stirred in the dark for 1 h to reach the adsorption equilibrium. At each stage (1 h), a 5-mL aliquot of the aqueous suspension was taken and centrifuged at 6000 rpm for 20 min, removing any suspended catalyst particles. The filtrates were analyzed with a spectrophotometer (Evolution-3000) at its maximum absorption wavelength (665 nm).

## 3. Results and discussion

### 3.1. Structure and composition of the modified PPT powders

The XRD patterns of the modified PPT powders treated in various transition metal sulfate aqueous solutions are presented in Fig. 1. All of the products are quasi-amorphous, and their structures can be characterized using the four broad diffraction lines usually assigned to the potassium polytitanate precursor: the first diffraction line (2 0 0) at  $10^\circ$  ( $2\theta$ ) is related to the interlayer distance and the other three ( $25^\circ$ ,  $28^\circ$ , and  $48^\circ$ ) are typical lines for the layered titanate nanomaterials that are characterized with a lepidocrocite-like structure (Chen, Du, Zhang, & Peng, 2002; Morgado et al., 2006; Yoshida, Suzuki, & Yoshikawa, 2005). The reflections remain at the angles typical of crystalline lepidocrocite ( $\gamma$ -FeOOH) with peaks at approximately  $9^\circ$ ,  $15^\circ$ ,  $27^\circ$ ,  $36^\circ$ ,  $47^\circ$ ,  $52^\circ$ , and  $60^\circ$  (Lin, Wei, & Sun, 2012; Sanchez-Monjaras et al., 2008). The decreased intensity and broadening of the first peak indicate a distortion in the layered structure after treating the PPT particles in the aqueous solutions.

Fig. 2 shows the TEM images of the modified PPT particles obtained after treatment. Independent of the transition metal salt used for the treatment, the products are plate-like PPT particles 150–600 nm in diameter that are decorated with nanoscale (5–90 nm) particles. The size of the particles decorating the surface of the PPT substrate can be grouped according to the added metal salts: zinc (5–10 nm), cobalt (10–30 nm), nickel (20–40 nm), copper (20–50 nm) and iron (40–90 nm).

The chemical compositions of the heterostructured nanopowders obtained after modifying the PPT particles with the aqueous solutions of various transition metal salts are presented in Table 1. Representative EDS spectra for the unmodified PPT and zinc-modified PPT particles are provided in Fig. 3. The presence of  $Al_2O_3$  in the PPT particles likely results from contamination during the potassium polytitanate synthesis in alumina crucibles.

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