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Effect of a pulsed electric field on the synthesis of TiO_2 and its photocatalytic performance under visible light irradiation

Bing Han [a,*], Zhi Chen [b], Marjatta Louhi-Kultanen [a]

[a] Laboratory of Separation Technology, School of Engineering Science, Lappeenranta University of Technology, P.O. Box 20, Lappeenranta FI-53851, Finland
[b] College of Materials Science and Engineering, China Jiliang University, No. 258 Xueyuan Street, Xiasha Higher Education District, Hangzhou 310018, Zhejiang Province, PR China

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ABSTRACT

Pure anatase TiO_2 nanoparticles were synthesized by sol-gel method under a pulsed electric field (PEF). The morphology and properties of the prepared materials were characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and UV–vis absorption spectra. The surface area was also analyzed by BET method. Oxalic acid and formic acid were used as model pollutants, and the degradation performance of the TiO_2 was examined using the as-prepared samples as photocatalysts. Enhanced photocatalytic activity under visible light irradiation was observed on the PEF-assisted synthesized TiO_2. Higher photocatalytic efficiency was obtained with either higher pulse frequency (949 Hz) and shorter treatment time (12 min), or lower frequency (50 Hz) and longer treatment time (24 min).

1. Introduction

Titanium dioxide nanocrystals are a widely investigated photocatalyst, and titanium dioxide plays an important role in controlling environmental pollution. The many beneficial features of TiO_2, like its high stability, nontoxicity, good corrosion resistance and low cost, have led to TiO_2 being utilized in many fields, such as toxicant degradation, antibiosis, self-cleaning and paint manufacture [1–4]. However, its large band gap (3.2 eV for the anatase phase and 3.0 eV for the rutile phase) limits the efficient use of TiO_2 nanomaterials under visible light. Consequently, many efforts have been made to improve the visible-light-driven properties of TiO_2, such as doping with metal ions [5,6] and nonmetal elements [7], sensitizing of TiO_2 with biomimetic dye [8], and modification of the TiO_2 surface with other semiconductors [9–14].

It has been reported that many chemical and physical methods have clear impacts on the thermal, structural and optical properties of TiO_2 nanomaterials. The different size, shape and structure of the crystals play a critical role in the surface properties of TiO_2 nanomaterials and the transitions between the different phases, which in turn affect the photocatalytic performance. Efforts to tune the features of TiO_2 nanomaterials to improve their photocatalytic degradation behavior have focused on changes in the synthesis method used (e.g., sol-gel, sonochemical, microwave, electrodeposition) and changes in the operational conditions (e.g., pH, temperature, initial concentration of chemicals, additives) [15]. Xu et al. [16] reported that photocatalytic degradation of methylene blue in aqueous suspensions could be accelerated by decreasing the particle size of TiO_2, especially to size below 30 nm. Luís et al. [17] found that higher photocatalytic activity can be achieved with the co-existence of the three TiO_2 polymorphs, which is strongly affected by the calcination parameters. TiO_2 nano-powders synthesized at lower pH (pH = 3) have been found to contain rutile and anatase phases, which results in higher photocatalytic degradation efficiency of methylene blue because of the lower energy band gap and higher value of the negative charge on the surface [18].

Electric fields have recently been applied in crystallization processes. Garetz et al. [19] found that an applied electric field stimulated organization of existing prenucleating clusters and promoted crystal nucleation and growth in a supersaturated aqueous urea solution. Crystallite orientation depends on the plane of polarization of the incident radiation induced by the electric field and the urea molecules thus aligned with the applied electric field. In study of thin film deposition, it was found that the surface and roughness of the film changed with the frequency of the pulsed electric field (PEF) [20]. It has been presented that an electric field decreased reduction time and quantity of crystals [21–23], and increased the number of nucleated crystals at low temperature [24]. However, Penkova et al. [25] reported that in sitting drop geometry the amount of nucleated crystals reduced or increased depending on the energy of the electric field. The influence of electric fields on titania thin films has recently been reported. Surface morphology and crystallographic orientation of titania films were affected by the applied electric field, and enhanced photocatalytic activity was observed [26,27]. These results suggest that an electric field can potentially be used to tune the microstructure of TiO_2 nanoparticles. The application of a pulsed electric field (PEF) for control of the formation

* Corresponding author.
E-mail address: bing.han@lut.fi (B. Han).

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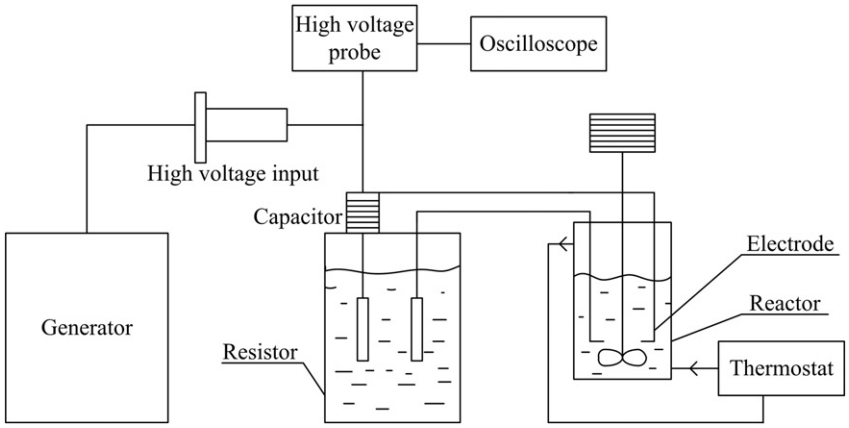

Fig. 1. Experimental set-up.

of titanium dioxide by sol-gel method has been reported by our previous study [28]. It shows that the PEF does have impact on crystal properties. To have a better understanding, the present work focuses deeply on the effect of PEF parameters on the characteristics of TiO_2 synthesized by sol-gel technique. Moreover, photocatalytic activity of the prepared TiO_2 nanoparticles under visible light irradiation is also investigated. Enhanced photocatalytic performance was observed with the PEF-assisted TiO_2 samples.

2. Experimental method

2.1. Synthesis of TiO_2 nanoparticles

In synthesis of the particles, 7 ml titanium isopropoxide (purity 97%, Aldrich) was used as a precursor and mixed with 120 ml analytical ethanol (purity 99.8%, VWR) in a 250 ml jacketed glass reactor with inner diameter of 65 mm for 15 min. The stirring speed was maintained at 800 rpm with a pitch blade turbine (4 blades). The diameter of the impeller is 20 mm. The temperature of the mixed solution was maintained at a constant 20 °C with a thermostat in order to avoid temperature change caused by the pulsed electric field. Two electrodes were immersed into the mixed solution. The voltage across the two electrodes was supplied by a 130 W DC pulsed generator with a capacitor and a water resistor. Then 30 ml acid water adjusted to pH 3.2 by deionized water and nitric acid was added into the mixed solution and the pulsed generator was simultaneously turned on. The PEF was then applied in the hydrolysis reaction process. Two pulse duration times (12 min and 24 min) and three pulse frequencies (50 Hz, 294 Hz and 949 Hz) were used. After application of the pulsed electric field, the mixer was removed from the reactor and the sol-gel solution was aged for 24 h. Following ageing, the sol-gel solution was transferred to Petri dishes and dried in an oven at 80 °C for 4 h. The dried solid product was then annealed at 500 °C for 2 h to obtain the crystalline phase. The experimental schematic diagram is shown in Fig. 1. A sample prepared in the same way but without PEF was used as a reference.

2.2. Characterization

Raman spectra were collected with a LabRam 300 Raman spectrometer from Horiba Jobin Yvon using a 785 nm laser operating at 150 mW. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 powder diffractometer using Cu-Kα as the radiation source. A Micromeritics Gemini 23850 surface area analyzer was used for BET analysis of the surface area of the TiO_2 nanoparticles. Transmission electron microscopy (TEM) images were acquired with a JEM-2010 TEM instrument with an accelerating voltage of 200 kV. UV–vis absorption spectra were collected on a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere using $BaSO_4$ as the reference.

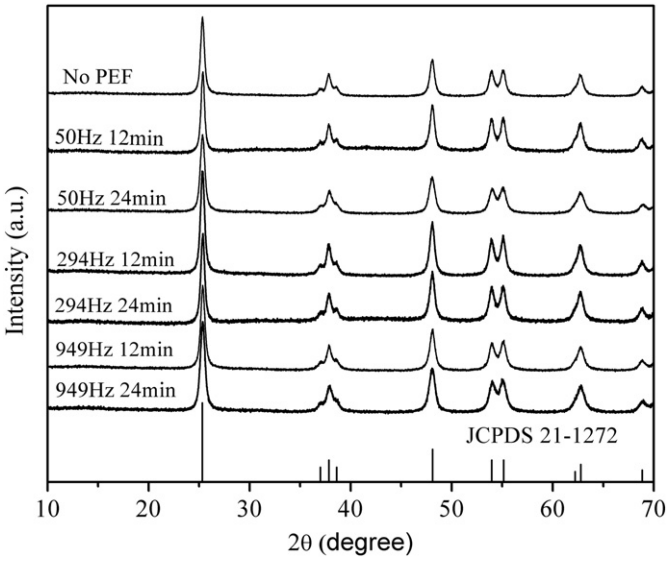

Fig. 2. XRD patterns of the as-prepared TiO_2 nanoparticles.

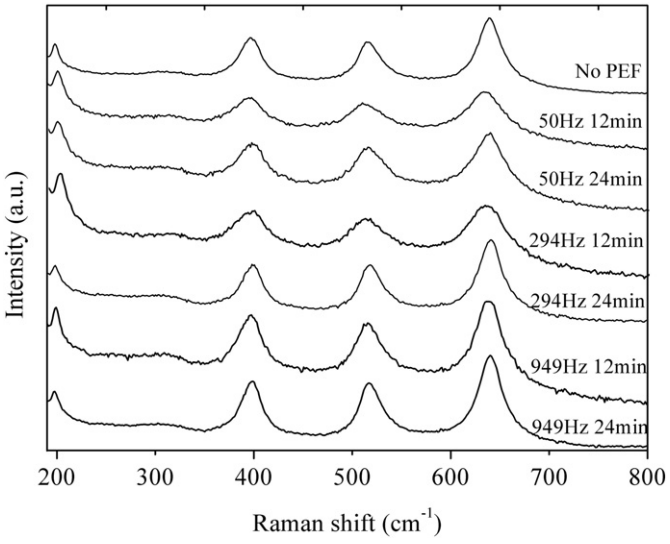

Fig. 3. Raman spectra of prepared TiO_2 nanoparticles.