



# Preparation of porous metal-ion-doped titanium dioxide and the photocatalytic degradation of 4-chlorophenol under visible light irradiation

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## ABSTRACT

Aiming at developing a highly active photocatalyst to decompose organic compounds under visible light irradiation, we have prepared metal ion doped TiO<sub>2</sub> (M-TiO<sub>2</sub>) by conducting dialysis in sol-gel method. Dialysis leads to the formation of mesoporous materials with surface area larger than 200 m<sup>2</sup> g<sup>-1</sup> but the metal ions should be added into the TiO<sub>2</sub> sol at pH 3 in order to avoid their losses during dialysis. Among seven metal ions tested as dopants, Pt-TiO<sub>2</sub> and Cr-TiO<sub>2</sub> showed higher photocatalytic activity for the degradation of 4-chlorophenol under visible light irradiation. The photocatalytic activity of Cr-TiO<sub>2</sub> was strongly affected by the doping amount of Cr ion and the optimal value was evaluated to be 0.68–1.30 atom%. X-ray photoelectron spectroscopy analyses showed the Cr ion was present mainly in Cr(III). The Cr-TiO<sub>2</sub> can be used safely for a practical application to remediate environmental contamination instead of expensive Pt-TiO<sub>2</sub>.

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## 1. Introduction

Titanium dioxide has been widely studied as a photocatalyst for applications to environmental remediation since it is stable, harmless and inexpensive and has a high reactivity for decomposition of harmful compounds [1–6]. However, TiO<sub>2</sub> is active only under ultraviolet (UV) irradiation ( $\lambda < 388$  nm) due to its large band gap energy of 3.0–3.2 eV, resulting in a low efficiency to utilize solar radiation. Many attempts have been devoted to extend the spectral response of TiO<sub>2</sub> to visible light [7]. Doping of transition metal ion is one of the most reported approaches and believed to achieve the band gap narrowing by forming impurity energy levels in the TiO<sub>2</sub> band gap [8–14]. Doping has been attempted physically by metal ion implantation and vapor deposition or chemically by co-precipitation and sol-gel method. Anpo and co-workers demonstrated Cr or V ions implanted TiO<sub>2</sub> is active under visible light irradiation ( $\lambda > 450$  nm) and the ions are present in a highly dispersed and isolated state in octahedral coordination, suggesting that the ions are incorporated into the lattice positions of the TiO<sub>2</sub> in place of the Ti ions [15,16]. They also described that the photocatalytic reaction did not proceed on the chemically doped TiO<sub>2</sub>

under visible light irradiation ( $\lambda > 450$  nm), in which the metal ions were present as oxide aggregates. Although metal ion implantation is able to result in atomic level doping, it requires expensive equipment. Shen et al. achieved vanadium doping of TiO<sub>2</sub> at the atomic level by a new facile liquid phase atomic layer deposition method to improve the photocatalytic activity under visible light [17]. On the other hand, by using a simple sol-gel method, Kim et al. synthesized Pt ion doped TiO<sub>2</sub> and demonstrated its visible light photocatalytic activities for the oxidative and reductive degradation of chlorinated organic compounds [18]. Choi et al. adopted the similar sol-gel method to synthesize TiO<sub>2</sub> doped with 13 different metal ions and compared the effects of individual dopants on the resulting physicochemical properties [19]. They mentioned that Pt- and Cr-doped TiO<sub>2</sub>, which had relatively high percentage of rutile, showed significantly enhanced visible light photocatalytic activity, suggesting that the presence of the rutile structure in the doped TiO<sub>2</sub> may affect photocatalytic activities. Wang et al. prepared indium-doped TiO<sub>2</sub> by the sol-gel method and showed improved photocatalytic activity due to the existence of a unique chemical species, O-In-Cl<sub>x</sub> on the surface under visible light irradiation [20].

Specific surface area of photocatalysts is one of the important factors for improving the activity in heterogeneous photocatalytic decomposition of organic compounds. A large number of efforts has been made to prepare mesoporous TiO<sub>2</sub> with high surface area and uniform pore size [21]. Xu and Anderson reported that

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specific surface area and porosity of TiO<sub>2</sub> xerogel prepared by sol–gel method increased with an increase in pH of the sol by dialysis [22]. Most metal oxide particles are charged at low pH and thus, they repel each other upon approach, forming a stable colloidal suspension. However, when the pH is increased by gradually removing protons from the suspension through dialysis, the particles tend to undergo aggregation, leading to the formation of large pores. We synthesized porous Pt–TiO<sub>2</sub> with pores of ca. 4 nm in diameter and BET surface area higher than 200 m<sup>2</sup> g<sup>-1</sup> by using only water as the solvent and conducting dialysis in the sol–gel method and demonstrated to have superior photocatalytic activity for the photodegradation of 4-chlorophenol (4-CP) under both ultraviolet and VL irradiation [23]. However, platinum is highly expensive and the use of less expensive metal ions is more favorable. In this study, we prepared porous TiO<sub>2</sub> doped with various metal ions by using our synthetic method having dialysis procedures and examined the photocatalytic activity for the degradation of 4-CP in aqueous solutions under visible light irradiation.

## 2. Experimental

### 2.1. Preparation and characterization of M–TiO<sub>2</sub>

Method A, as shown in Scheme 1 indicates the synthetic method for porous M–TiO<sub>2</sub> photocatalysts which is the same sol–gel method as in our previous paper for Pt–TiO<sub>2</sub> [23]. As the metal ion precursors, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, K<sub>2</sub>RuCl<sub>6</sub> or RuCl<sub>3</sub>·nH<sub>2</sub>O were used. After peptization in an aqueous solution at pH ≤ 1 for 6 days, the highly dispersed TiO<sub>2</sub> sol containing the metal ions was dialyzed in 2750 ml of water using a molecularly porous dialysis tube (molecular weight cut-off: 3500) for 3 days

until approximately pH 4 was obtained. The water was exchanged once a day and the concentration of the metal ions removed out of the TiO<sub>2</sub> sol through the dialysis tube was determined by inductively coupled plasma spectroscopy (Varian, ICP-AES Liberty Series II). Then, the sol was dried in an oven at 40 °C for 3 days and the resulting gel was sintered at 100–500 °C (ramping rate at 3 °C min<sup>-1</sup> and keeping the desired temperature for 2 h). The obtained xerogel was crushed into powders by using mortar and pestle. In this paper, the contents of metal ions in the samples are denoted as the nominal atomic percentage (atom%) against all

metal ions (M and Ti). The value of atom% was calculated on the basis of the ICP-AES measurement which determined the concentration of M<sup>n+</sup> removed from the TiO<sub>2</sub> sol. Undoped TiO<sub>2</sub> powder was prepared according to the above procedures without the metal ion precursors.

Crystal structure of the M–TiO<sub>2</sub> was examined by X-ray diffraction (XRD, Rikagaku RINT-2500) analysis with Cu Kα radiation (40 kV, 100 mA) at 2θ angles from 10° to 90° with a scan speed of 4° min<sup>-1</sup>. The Brunauer–Emmett–Teller (BET) surface area was measured with nitrogen as the adsorptive gas by automatic surface area analyzer (Shimadzu, Trister II 3020). Diffuse reflectance UV–vis spectra of the M–TiO<sub>2</sub> were obtained using a spectrophotometer (Nippon Bunko, V-670). X-ray photoelectron spectroscopy (XPS) analysis was carried out through KRATOS ESCA-3400 system. The Cr–TiO<sub>2</sub> powder was compressed into a pellet for the XPS measurements. The number of data accumulation was 120 for Cr 2p and 10 for other elements.

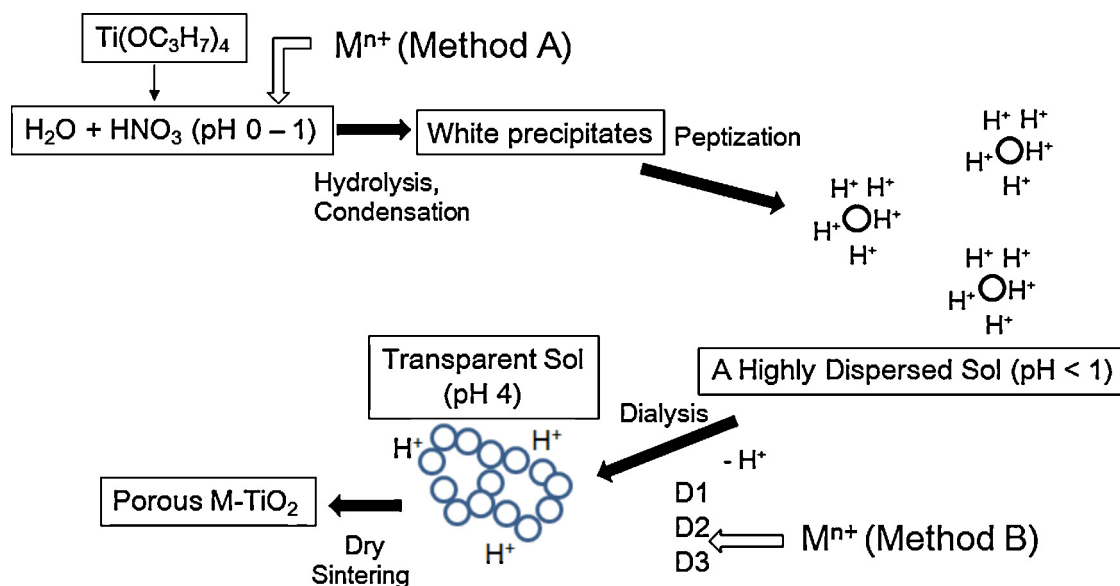
### 2.2. Determination of photocatalytic activity

Photocatalytic activity was evaluated at 30 °C by the degradation of 4-CP in aqueous solutions suspended with M–TiO<sub>2</sub> powders. After air was purged through the suspension for 30 min under vigorously stirring, a 150 W halogen lamp was ignited. The light intensity through a long pass filter (Edmund, cut-on wavelength: 400 nm) was measured to be 63 mW cm<sup>-2</sup> (Koito, Memory Sensor MES-101 with IKS-37). Aliquots of the suspension were withdrawn at appropriate times and centrifuged at 2000 rpm for 15 min. The supernatant liquid was filtrated through a 0.45 μm filter and then analyzed by a high performance liquid chromatograph (HPLC, Shimadzu) equipped with a UV–vis detector and a C18 column (Shim-pack, VP-ODS 4.6 mm × 25 cm).

## 3. Results and discussion

### 3.1. Loss of metal ions during dialysis

Fig. 1 indicates the absorption spectra of the TiO<sub>2</sub> sol and M–TiO<sub>2</sub> sol (M = Pt, Cr, Fe, Ru(IV), and Ru(III)) just before the dialysis. The broken lines in Fig. 1 show the values calculated by adding the spectra of the TiO<sub>2</sub> sol to those of an aqueous solution containing each metal ion at pH 1. All absorption spectra of the M–TiO<sub>2</sub> sol



Scheme 1. Synthetic method for porous M–TiO<sub>2</sub> photocatalysts.

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