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Visible light-induced photocatalytic oxidation of 4-chlorophenol and dichloroacetate in nitrided Pt-TiO_2 aqueous suspensions

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ABSTRACT

This article reports the effect of nitridation treatment of TiO_2 and Pt-doped TiO_2 (Pt-TiO_2) photocatalyst and assesses their performance as a visible light-induced photocatalyt for the degradation of 4-chlorophenol (4-CP) and dichloroacetate (DCA). Nitridation treatment changed the physicochemical properties of TiO_2 and Pt-TiO_2. The primary particle size of nitrided samples, *n*-TiO_2 and *n*-Pt-TiO_2, was slightly smaller than that of untreated samples. Surface area was increased more than two times after nitridation treatment. Thermal phase transformation (anatase to rutile) was retarded by the nitridation treatment. The visible light absorption of *n*-Pt-TiO_2 was more extended than that of Pt-TiO_2 and Pt(II)/Pt(IV) ratio in *n*-Pt-TiO_2 was lower than that in Pt-TiO_2. Enhanced photocatalytic activities of nitrided samples were observed for 4-CP degradation under UV and visible irradiation. However, the enhancement effect of nitridation treatment was not observed under visible irradiation for DCA degradation. Photocatalytic activity was restrictively enhanced and significantly affected by the kind of substrates.

1. Introduction

TiO_2 photocatalyst has been extensively studied with regard to its application in environmental remediation processes [1,2]. However, because of the size of its band gap, TiO_2 is active only under UV irradiation, which accounts for less than 5% of solar light energy. Therefore, there have been many efforts to make a TiO_2 photocatalyst that would be active under visible irradiation. One approach is the visible light absorption by organic dye molecules adsorbed on the surface of TiO_2, which is dye sensitization method [3–5]. Another method is to prepare impurity-doped TiO_2 [6–11]. Impurity doping material would substitute the Ti^{4+} ion or O^{2-} ion in the TiO_2 lattice and form the intraband states, which could be responsible for the visible absorption of impurity-doped TiO_2. However, the highly efficient impurity-doped TiO_2 photocatalysts under visible light irradiation has not been developed yet. One of the major reasons of low activity of impurity-doped TiO_2 is increasing the recombination centers such as oxygen defects, which should be formed to keep the charge balance. Kisch and co-workers investigated the visible light-induced photocatalytic activity of TiO_2 modified with chloride complexes of platinum which is quite different from the typical metal ion-doped titania system [12]. They proposed that the surface complex of metal chloride serve as visible light absorbing sensitizer and center of charge separation and that the titania matrix functions as a charge trap.

Recently, some researchers have reported the effects of antimony or lanthanum codoping into TiO_2 and $SrTiO_3$ doped with transition metal ions or nitrogen on physicochemical properties and photocatalytic activities. Kato and Kudo showed that TiO_2 codoped with Sb^{5+} and Cr^{3+} ions was remarkably higher than that of TiO_2 doped with only Cr^{3+} ions, which was due to the keeping of the charge balance by codoping Sb^{5+} ions [13]. Miyauchi et al. have also reported that the $SrTiO_3$ codoped with nitrogen and lanthanum exhibited high photocatalytic activities under visible irradiation, which was due to the decrease in the oxygen vacancies by codoping with La^{3+} and N^{3-} ions [14].

Previously, Kim et al. investigated that Pt-ion-doped TiO_2 photocatalysts showed the efficient photocatalytic activities under visible irradiation. In that case, the Pt ions substituted in the TiO_2 lattice were present mainly in the Pt(IV) state. However, some Pt(II) state also existed on the sample surface and they seem to act as recombination center. Therefore, it is expected that the photocatalytic activities of Pt-ion-doped TiO_2 may be enhanced by inhibition of surface Pt(II) states formation.

In this work, we have investigated that the effects of nitridation treatment on Pt-TiO_2. Nitridation treatment would inhibit the formation of Pt(II) state. We have prepared the nitrided TiO_2 and Pt-TiO_2 by simple method and investigated their physicochemical properties and photocatalytic activities for 4-chlorophenol (4-CP) and dichloroacetate (DCA) degradation.

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2. Experimental

2.1. Chemicals and materials

Chemicals used in this study include: 4-CP (Sigma), DCA ($CHCl_2CO_2Na$, Aldrich), titanium tertaisopropoxide (TTIP: $Ti(OCH(CH_3)_2)_4$, Aldrich), ethanol (Aldrich), chloroplatinic acid (H_2PtCl_6, Aldrich), nitric acid (HNO_3, Shinyo), and triethylamine (TEA, Samchun). All reagents were used as received.

Pt-TiO_2 was prepared by a sol–gel method as reported previously [11]. 2.5 ml of TTIP dissolved in 50 ml of ethanol was added dropwise to 450 ml of chloroplatinic acid solution (0.08 mM for 0.5 at.% Pt doping) whose pH was adjusted at 1.5 with nitric acid. The resulting colloidal suspension was stirred overnight. Undoped TiO_2 was prepared according to the above procedure in the absence of chloroplatinic acid. For nitridation, Pt-TiO_2 or TiO_2 nanocolloid solution was directly mixed with an excess of TEA and vigorously stirred [15]. The nanocolloid solution rapidly forms a yellowish mixture. All nanocolloid solution was evaporated at 40 °C using a rotavapor. The obtained powder was calcined at 673 K for 3 h under air atmosphere. Calcined powder was washed to remove impurities such as chlorides and nitrates and then dried. From above procedures, we obtained four types of TiO_2 photocatalyst, TiO_2, Pt-TiO_2, nitrided TiO_2 (*n*-TiO_2), and nitrided Pt-TiO_2 (*n*-Pt-TiO_2). Degussa P25 that is a mixture of anatase and rutile (8:2) was also used as a reference photocatalyst.

2.2. Characterization

BET surface area measurements were carried out by using N_2 as the adsorptive gas. Transmission electron microscopic images (TEM) were taken for the observation of the primary particles. XRD patterns were obtained with an X-ray diffractometer (Rigaku D/MAX-2500, 18 kV) using Cu-$K_{\alpha1}$ radiation. Diffuse reflectance UV–visible absorption spectra (DRS) of the powder samples were obtained using a spectrophotometer (Shimadzu UV-2401PC) equipped with a diffuse reflectance accessory. The oxidation states of the Pt atoms were determined by X-ray photoelectron spectroscopy (XPS) (Kratos XSAM 800pci) using the Mg-K_α line (1253.6 eV) as the excitation source.

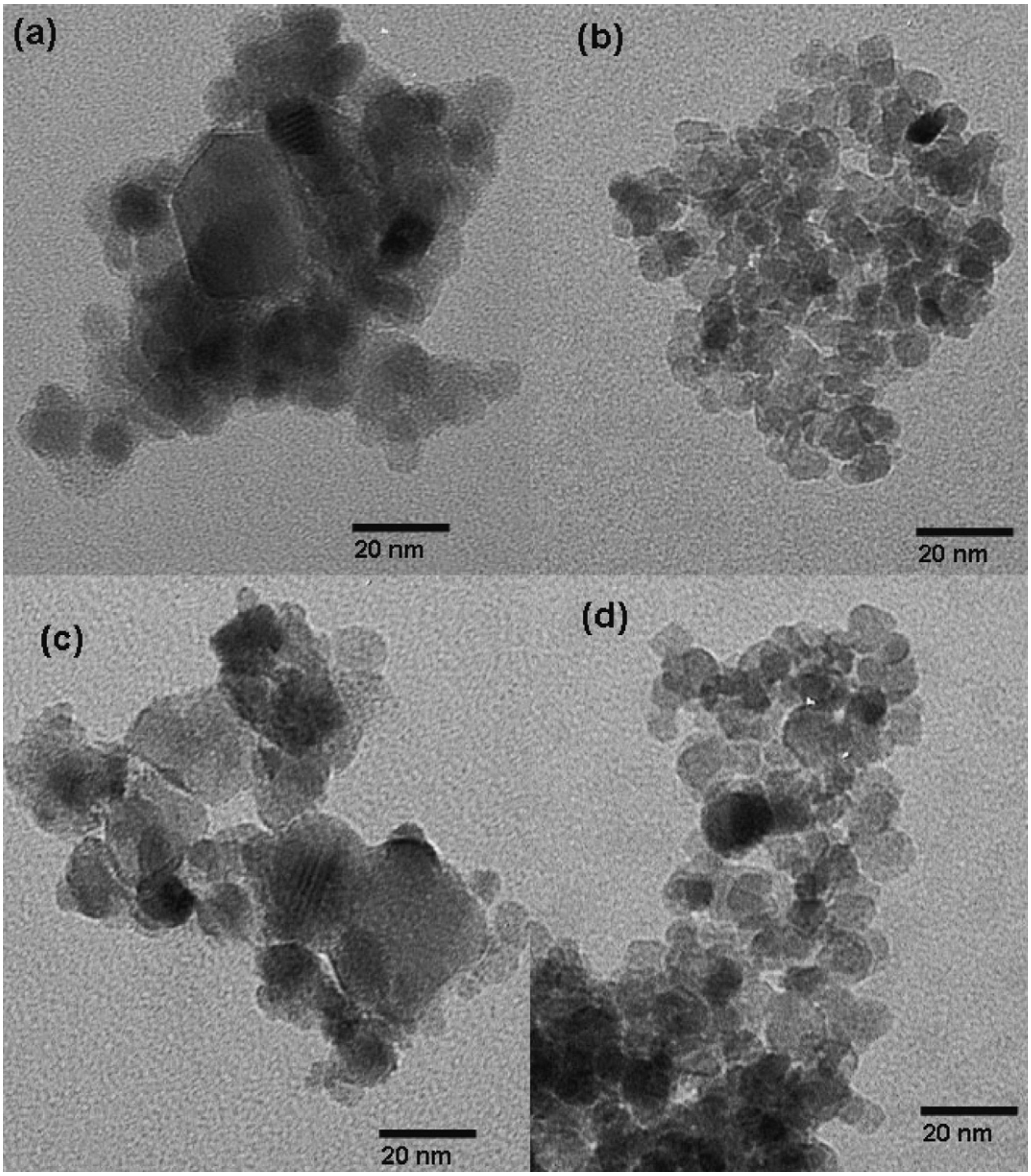

Fig. 1. TEM images of various TiO_2 samples. (a) TiO_2, (b) *n*-TiO_2, (c) Pt-TiO_2, and (d) *n*-Pt-TiO_2.

2.3. Photocatalytic activities measurements

The photocatalytic activities were evaluated for the photocatalytic degradation of 4-CP and DCA. TiO_2 was dispersed in distilled water (0.5 g/L) by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. An aliquot of the substrate stock solution (1 mM) was subsequently added to the suspension to give a desired substrate concentration, and then the pH of the suspension was adjusted at pH 3 with $HClO_4$ standard solution.

Photoirradiation employed a 300-W Xe arc lamp (Oriel) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 295$ nm for UV irradiation or $\lambda > 420$ nm for visible irradiation), then the filtered light was focused onto a 30-mL Pyrex reactor with a quartz window. The reactor was filled with minimized headspace and stirred magnetically. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45-μm PTFE syringe filter (Millipore).

The degradation of 4-CP was monitored using a high performance liquid chromatograph (HPLC: Agilent 1100 series) equipped with a UV detector and a ZORBAX 300SB C18 column (4.6 mm × 150 mm). The eluent was a binary mixture of water containing 0.1% phosphoric acid and acetonitrile (80:20 by volume). Identification and quantification of DCA and chloride ions were performed by using an ion chromatograph (IC, Dionex DX-120) which was equipped with a Dionex IonPac AS 14 (4 mm × 250 mm) column and a conductivity detector. The eluent solution was 3.5 mM Na_2CO_3/1 mM $NaHCO_3$.

3. Results and discussion

3.1. Characterization of nitrided Pt-TiO_2

Fig. 1 shows TEM images of TiO_2, n-TiO_2, Pt-TiO_2, and n-Pt-TiO_2. The spherical particles were agglomerated. Although there were little differences in primary particle size distribution, which was in the range of 5–12 nm, the particle size of nitrided samples, n-TiO_2 and n-Pt-TiO_2, have smaller than that of unnitrided samples, TiO_2 and Pt-TiO_2. The surface areas of nitrided samples have larger than that of unnitrided samples as shown in Table 1.

In Fig. 2, XRD results showed that crystalline phase of all samples were almost anatase and in both TiO_2 and Pt-TiO_2 rutile phase was also detected. These results indicated that the nitridation treatment inhibited the anatase to rutile phase transformation, which seems to be closely related to the crystallite size of anatase phase. Compared with the TEM images in Fig. 1, it might be estimated that the reduction of the particle size by nitridation affected to the rutile formation which occurs by coalescence of the anatase particles. The stabilization of TiO_2 in the anatase phase can usually be achieved by changing its bulk or surface composition [16]. Nitridation treatment may stabilize the anatase phase by changing its surface composition.

DRS results are shown in Fig. 3. Although after treatment of triethylamine the nanocolloid solution forms a yellowish mixture, the particles prepared by evaporation and subsequent calcination of the yellowish nanocolloid solution did not show any absorption in the visible region. This result indicated that the nitrogen could not substitute the oxygen in TiO_2 bulk phase but change the TiO_2 surface site. Therefore, we could not expect the visible light-induced reaction initiated by visible light absorption of n-TiO_2. On the other hand, Pt-TiO_2 could absorb the visible light. Band gap energy of Pt-TiO_2 is estimated as 2.7 eV from DRS spectrum data. The redox energy states of many transition metal ions fall in the band gap region of TiO_2, and the substitution of Pt ions into the TiO_2 lattice should create defect sites in the band gap. The electronic transition between the defect energy states and the band edge (CB or VB) should be responsible for the visible light absorption of Pt-TiO_2. Kim et al. [11] previously reported that the Pt ions are incorporated into the oxide lattice. The DRS spectrum of n-Pt-TiO_2 is clearly distinguished from that of Pt-TiO_2 and the nitridation of Pt-TiO_2 extended the absorption in the visible region. However, absorbance of n-Pt-TiO_2 in the region between 300 and 450 nm drastically decreased compared to that of Pt-TiO_2. Therefore, we could expect the decrease in the activity of the visible light-induced degradation of organic pollutants.

Table 1
BET surface areas (m^2/g).

TiO_2	83
n-TiO_2	194
Pt-TiO_2	87
n-Pt-TiO_2	161

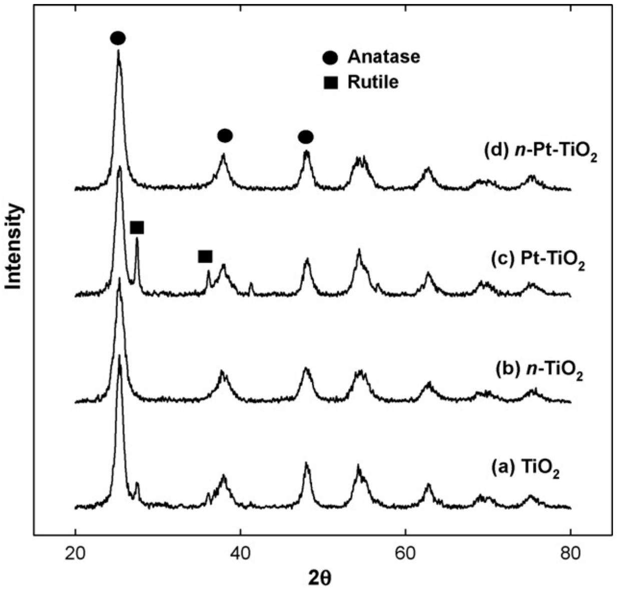

Fig. 2. X-ray diffractograms of various TiO_2 samples. (a) TiO_2, (b) n-TiO_2, (c) Pt-TiO_2, and (d) n-Pt-TiO_2.

Fig. 4 compares the XPS spectra of Pt-TiO_2 and n-Pt-TiO_2 for the Pt 4f band. The oxidation states of Pt species are clearly different between them. The Pt 4f signals for n-Pt-TiO_2 seem to be

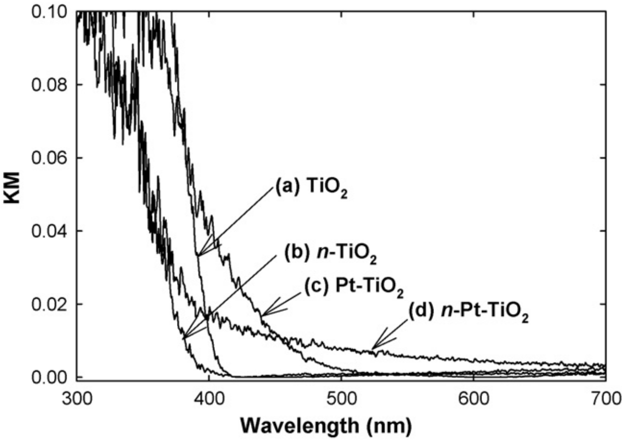

Fig. 3. Diffuse reflectance UV/vis spectra of various TiO_2 samples. (a) TiO_2, (b) n-TiO_2, (c) Pt-TiO_2, and (d) n-Pt-TiO_2.

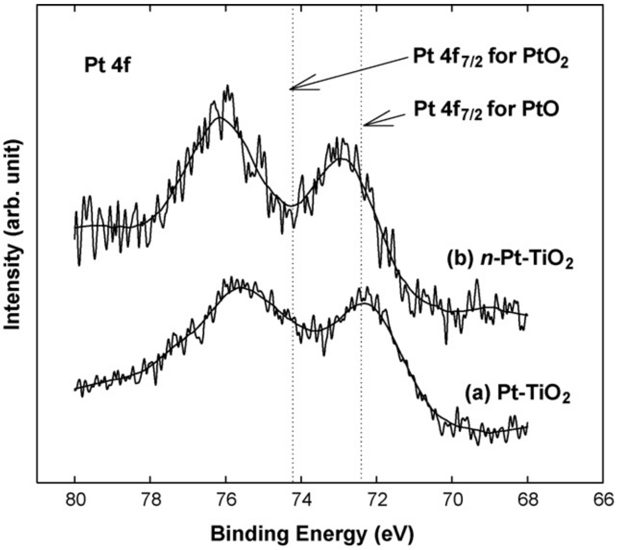

Fig. 4. XPS spectra of (a) Pt-TiO_2 and (b) *n*-Pt-TiO_2 for the Pt 4f band.

shifted to higher binding energy, which indicates the presence of more oxidized Pt states. Pt $4f_{7/2}$ peaks in PtO and PtO_2 are located at binding energies of 72.4 and 74.2, respectively [17]. Therefore, the oxidation state of Pt in Pt-TiO_2 and *n*-Pt-TiO_2 might comprise a mixture of Pt(II) and Pt(IV) states and the ratio Pt(II)/Pt(IV) could be lower in *n*-Pt-TiO_2 than Pt-TiO_2. The reason for changing the ratio of Pt(II)/Pt(IV) by nitridation treatment is not clear at this moment. We assume that the nitridation treatment partly inhibited the formation of Pt(II) state in lattice of TiO_2, which could be responsible for the electron–hole recombination. Therefore, the fact that *n*-Pt-TiO_2 had higher oxidation state of Pt ion than Pt-TiO_2 could be a reason for the enhancement of photoactivities of *n*-Pt-TiO_2. Kato and Kudo [13] reported that when Cr^{3+} ion were partly substituted for Ti^{4+} ion in TiO_2, oxygen defects and/or Cr^{6+} should be formed to keep the charge balance, and they cause the increase in the recombination centers between photogenereated electrons and holes. And they showed that the activity of TiO_2 codoped with chromium and antimony was remarkably higher than that of TiO_2 doped with only chromium, due to the keeping of charge balance.

3.2. *Photocatalytic activities*

Fig. 5 showed the photocatalytic degradation of 4-CP and production of chloride on various TiO_2 under UV or visible irradiation. Under UV irradiation P25 was the most efficient for the photocatalytic degradation of 4-CP and *n*-Pt-TiO_2 was comparable with P25. Under visible irradiation, however, 4-CP was not degraded on P25 and TiO_2 at all because both P25 and TiO_2 cannot absorb the visible light. On the other hand, *n*-TiO_2, Pt-TiO_2, and *n*-Pt-TiO_2 have degraded 4-CP under visible irradiation and *n*-Pt-TiO_2 showed the most effective visible light-induced photocatalytic activity for the 4-CP degradation. Although *n*-TiO_2 did not absorb the visible light as shown in Fig. 3, it could also degrade the 4-CP under visible irradiation. This result seems to be due the interactions between 4-CP and *n*-TiO_2 surface. Kim and Choi [18] reported that phenolic compounds such 4-CP could degrade on the visible-illuminated TiO_2, which could not absorb the visible light, through the complex formation between phenolic compounds and TiO_2 and their activities could be affected by the surface area of TiO_2. And Orlov et al. [19] showed the interaction of 4-CP with TiO_2 by NEXAFS, XPS, and UPS and they suggested that the 4-CP could degrade on TiO_2 under visible irradiation through the photosensitization mechanisms. Surface area of *n*-TiO_2 was more than twice that of TiO_2 as shown in Table 1.

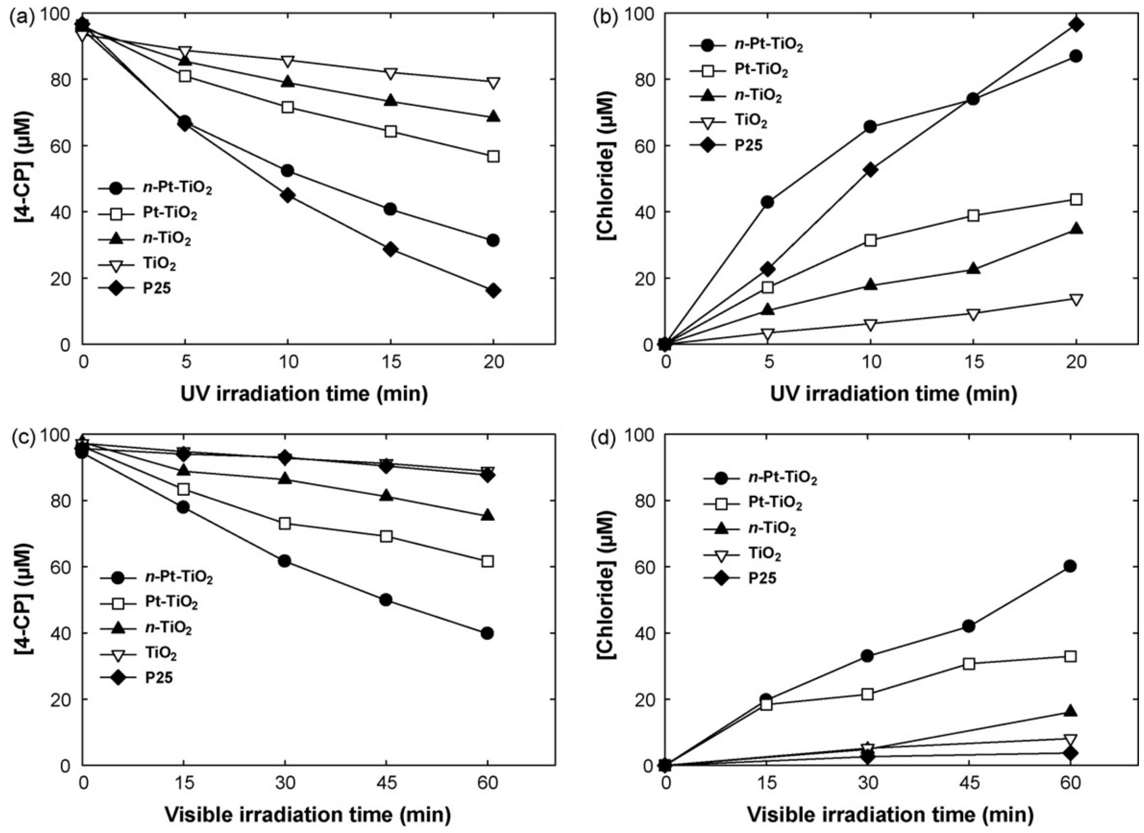

Fig. 5. Photocatalytic degradation of 4-CP (a and c) and chloride production (b and d) under UV (a and b) or visible (c and d) irradiation.

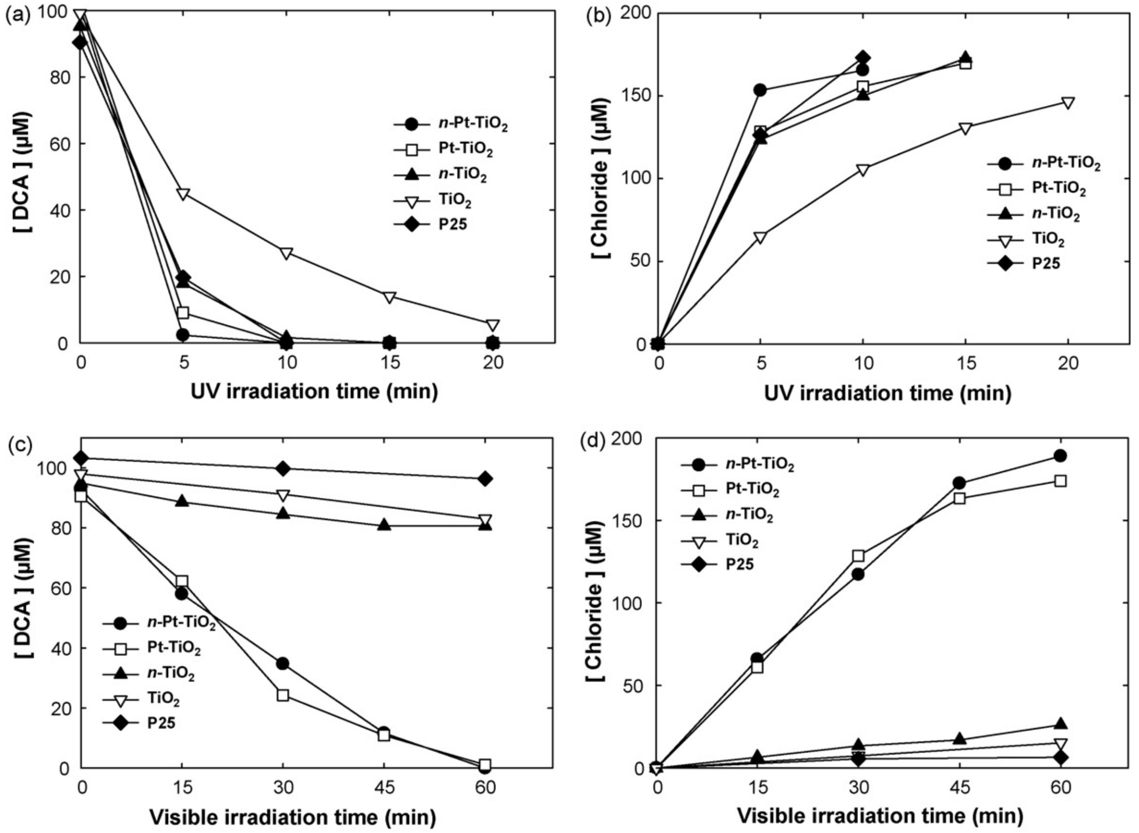

Fig. 6. Photocatalytic degradation of DCA (a and c) and chloride production (b and d) under UV (a and b) or visible (c and d) irradiation.

Therefore, the nitridation increase the surface area of TiO_2 and high surface area positively affected the visible light-induced 4-CP degradation.

Photocatalytic degradation of DCA and production of chloride was shown in Fig. 6. DCA was drastically degraded under UV irradiation and *n*-Pt-TiO_2 slightly enhanced the degradation rate of DCA. However, under visible irradiation, DCA degraded only on Pt-TiO_2 and *n*-Pt-TiO_2 and its degradation rates on Pt-TiO_2 and *n*-Pt-TiO_2 was similar. Synergetic effects of nitridation treatment for DCA degradation were not observed at all.

Above observations indicate that photocatalytic degradation activities of photocatalysts are depended on the kind of substrate as reported by Ryu and Choi [20]. Although they compared the photocatalytic activities under UV irradiation their conclusions could apply to the photocatalytic activities under visible irradiation. In our case, the synergetic effect of *n*-Pt-TiO_2 was showed in 4-CP degradation but it was not observed in DCA degradation. The synergetic effects of *n*-Pt-TiO_2 for 4-CP degradation under visible irradiation seem to be due to enhancement of surface area by nitriding. For DCA degradation, surface area enhancement of TiO_2 might not affect on the visible activity of TiO_2. Although nitridation treatment significantly affected the physiochemical properties of Pt-TiO_2 and we expected the enhanced visible activities for the degradation of organic substances, as previously discussed, its positive effects were limited to the degradation of 4-CP.

4. Conclusions

We have investigated the effects of nitridation treatment of TiO_2 and Pt-TiO_2 for the visible light-induced photocatalytic activities of 4-CP and DCA degradation. Nitridation treatment changed the physicochemical properties of TiO_2 and Pt-TiO_2. The primary particle size of nitrided samples was slightly smaller than that of unnitrided samples and the anatase to rutile phase transformation seem to be retarded by the nitridation treatment. The visible light absorption of *n*-Pt-TiO_2 was more extended than that of Pt-TiO_2 and Pt ion state of *n*-Pt-TiO_2 was higher than that of Pt-TiO_2. Furthermore, surface area of nitrided samples was more than twice that of unnitrided samples. From these changes of physicochemical properties, we expected the enhanced photocatalytic activities of nitrided samples. However, their photocatalytic activities were restrictively enhanced and significantly affected by the kind of substrates. For 4-CP degradation, both *n*-TiO_2 and *n*-Pt-TiO_2 showed the enhanced photocatalytic activity under UV and visible irradiation. For DCA degradation, although the photocatalytic degradation of DCA on *n*-TiO_2 and *n*-Pt-TiO_2 were more efficient than that on TiO_2 and Pt-TiO_2, respectively, under UV irradiation, the enhancement effect of nitridation treatment was not observed under visible irradiation.

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