

Enhanced Photocatalytic Activity of Ce³⁺-TiO₂ Hydrosols in Aqueous and Gaseous Phases

Tong-xu Liu^{a,b}, Xiang-zhong Li^{a*}, Fang-bai Li^b

^a Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong, China

^b Guangdong Key Laboratory of Agricultural Environment Pollution Integrated Control, Guangdong Institute of Eco-Environment and Soil Science, Guangzhou 510650, PR China

Abstract

A series of cerium ion-doped titanium dioxide (Ce³⁺-TiO₂) hydrosols were prepared by a coprecipitation-peptization method and characterized by UV-Vis transmittance spectroscopy (T%), particle size distribution (PSD), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halender methods (BJH), respectively. The results demonstrated that as the doped Ce³⁺ content increased, the crystalline size, BET surface area and transmittance decreased significantly, but the particle size increased gradually. The photocatalytic activity of Ce³⁺-TiO₂ hydrosols was evaluated in aqueous solution for methylene blue (MB) and 2,3-dichlorophenol (2,3-DCP) degradations, and also in gaseous phase for benzene degradation. The results showed that the overall photocatalytic activity of Ce³⁺-TiO₂ hydrosols in aqueous and gaseous phases under UVA and visible illumination was significantly higher than pure TiO₂ hydrosol due to its better separation of electron-hole pairs and visible light response. Additionally, the formation surface-complex of TiO₂ and 2,3-DCP with visible-light-response is also contributed to the 2,3-DCP degradation, and the relevant possible reaction mechanisms were discussed with details. The kinetic data demonstrated that the Ce³⁺-TiO₂ hydrosols with the content of Ce³⁺ doping between 0.5-1% achieved the best performance in both the aqueous and gaseous phases. This study provided the comprehensive understanding of the Ce³⁺-TiO₂ hydrosol characteristics and reaction mechanisms, and the results indicate that these Ce³⁺-TiO₂ hydrosols may have good potential for pollutant degradation either in aqueous phase or gaseous phase.

Keywords: Ce³⁺-TiO₂, Environmental Application, Hydrosols, Preparation, Photocatalytic Activity

* To whom correspondence should be addressed. Tel.: +852-27666016. Fax: +852-23346389. E-mail: cexzli@polyu.edu.hk

1 **1. Introduction**

2 TiO₂ photocatalysis has become a promising technique for degrading aqueous or gaseous toxic
3 organic pollutants in water and wastewater treatment, and air purification owing to its
4 environmental benign [1, 2]. So far, a variety of physical and chemical approaches have succeeded
5 in synthesizing crystalline TiO₂ catalysts by calcinations methods [3-5], while Xie et al. [6]
6 synthesized the crystallized TiO₂ hydrosol at low temperature of < 100 °C by a hydrothermal
7 method to avoid the serious aggregation by the calcinations methods. In comparison with the
8 conventional TiO₂ powder catalysts, TiO₂ hydrosol is a colloidal solution with much finer TiO₂
9 particles and much better colloidal stability and homogeneity, and it can utilize the light more
10 efficiently compared to those aqueous TiO₂ powder suspensions. Additionally, a key technique of
11 using TiO₂ for indoor air purification is how to coat the catalysts such as P-25 powder onto walls,
12 windows, or furniture easily and durably, without any blights such as color change and transparency
13 decay of the substrates after coating, while using TiO₂ hydrosol can solve these problems because it
14 is transparent and easy for coating on these substrates. Recently, only a few reports [7, 8] have
15 directly used TiO₂ hydrosol to eliminate the air pollution under UV illumination, but there is still
16 lack of the studies on the TiO₂ hydrosol for air purification under visible light illumination.

17
18 To further enhance the photocatalytic performance of TiO₂ hydrosols, some literatures have proved
19 that the incorporation of lanthanide ion doping could improve the photochemical properties by
20 increasing the photocurrent response and the separation of electron-hole pairs under UV
21 illumination [9-13]. Some reports [14] showed the overall photocatalytic activity for 2-
22 mercaptobenzothiazole degradation under UV or visible light irradiation was significantly enhanced
23 by doping with the cerium ions with a special 4*f* electron configuration because the higher
24 adsorption equilibrium constant and the higher separation efficiency of electron-hole pairs were
25 obtained simultaneously for Ce³⁺-TiO₂ powder catalysts and the introduction of Ce 4*f* level led to
26 the optical absorption band between 400 and 500 nm, resulting its visible-induced photocatalytic
27 activity. Xie et al. [15] reported Ce⁴⁺-TiO₂ sol catalysts had photocatalytic activity for X-3B
28 degradation under visible light irradiation, and they speculated the possible mechanisms. However,
29 the photocatalytic activity of Ce³⁺-TiO₂ hydrosol catalyst has only been studied with very limited
30 data about dye degradation in aqueous solution. Especially, there is a lack of studies about its
31 photocatalytic activity for degrading pollutants in gaseous phase. Recently, the development of non-

1 TiO₂ photocatalysts (such as β-Ga₂O₃, InOOH, and Zn₂GeO₄) [16] is one of the alternative
2 approaches for treating gaseous benzene at ambient conditions, but these semiconductors usually
3 have wide bandgap which should be excited by the light with the wavelength less than 300 nm.
4 Comparatively, the Ce³⁺-TiO₂ hydrosols with the ability of benzene degradation under UVA or
5 visible light, is more suitable for the practical application, especially for the indoor air purification.

6
7 In this study, Ce³⁺-TiO₂ hydrosol was prepared by using a chemical coprecipitation-peptization
8 method and its colloidal properties and nanoparticle properties were characterized with details. The
9 degradations of methyl blue (MB) and 2,3-dichlorophenol (2,3-DCP) with the Ce³⁺-TiO₂ hydrosols
10 in aqueous solution were first investigated and the degradations of benzene (C₆H₆) with the Ce³⁺-
11 TiO₂ hydrosols in gaseous phase were then conducted to evaluate its photocatalytic activity under
12 UV or visible illumination. This study was aimed at investigating the enhanced photoactivity of
13 Ce³⁺-TiO₂ hydrosol photocatalyst for its environmental applications in aqueous and gaseous phases.

15 **2. Experimental**

16 **2.1 Materials**

17 Metatitanic acid (TiO₂·2.5H₂O·0.3SO₄), a precursor of titania powder, was supplied from
18 Panzhihua Iron & Steel Research Institute, China. While the MB and 2,3-DCP chemicals were
19 obtained from BDH and Aldrich Chemical Company, respectively, NH₄OH, HNO₃, Ce(NO₃)₃ and
20 other chemicals with analytical grade were obtained from Shanghai Reagent Ltd. The benzene gas
21 with a certified concentration of 1,000 ppm/v in air was purchased from Foshan Kedi Gas Ltd. in
22 China. Deionized distilled water (DDW) was used for preparation of all solutions.

24 **2.2 Preparation of Ce³⁺-TiO₂ hydrosols**

25 The Ce³⁺-doped TiO₂ hydrosols were prepared by a chemical coprecipitation-peptization method,
26 in which 90 g of metatitanic acid was added into DDW and stirred continuously until a uniform
27 metatitanate suspension was obtained. 2.3 g of Ce(NO₃)₃ was dissolved into DDW to obtain cerium
28 nitrate solution, which was then added into the metatitanate suspension and uniformly mixed.
29 Excessive amount of ammonia was dropped therein to adjust the pH value to be above 9. The
30 resulting suspension was stirred continuously for 3 h and heated at the temperature of below 40 °C,
31 and then filtered to get filter cake. The filter cake was washed repeatedly for several times until no

1 sulfate ion was detected by titration using a 0.5 mol L⁻¹ barium chloride solution. Finally, the filter
2 cake was uniformly mixed with water to form uniform suspension. 190 mL of nitric acid (10%) was
3 dropped therein to adjust the pH value to be 1.5. The resulting suspension was stirred continuously
4 for 2 h at room temperature, followed by stirring and heating at the higher temperature of 65 °C.
5 The suspension was peptized for 24 h to eventually obtain a Ce³⁺-TiO₂ hydrosol solution in slight
6 yellowish colour with a doped amount of cerium at 1.0% (mol/mol). This hydrosol sample was
7 named “1.0%Ce³⁺-TiO₂”. With the same procedure, 0.5%Ce³⁺, 1.5%Ce³⁺, 2.0%Ce³⁺, and 2.5%Ce³⁺
8 doping TiO₂ hydrosol samples were also prepared and named “0.5%Ce³⁺-TiO₂”, “1.0%Ce³⁺-TiO₂”,
9 “1.5%Ce³⁺-TiO₂”, “2.0%Ce³⁺-TiO₂”, and “2.5%Ce³⁺-TiO₂”, respectively.

10

11 **2.3 Characterization of Ce³⁺-TiO₂ hydrosols**

12 The as-prepared hydrosol samples were first scanned using a TU-1801 UV-visible
13 spectrophotometer (UV-Vis TU-1800, Purkinje General, Beijing) in the wavelength range of 200-
14 600 nm to determine their UV-visible transmittance spectra. The particle size distributions (PSD) of
15 the hydrosols were directly determined by a light-scattering size analyzer (Beckman N5, USA). To
16 characterize the crystalline and adsorption properties of the hydrosols, the titania xerogel powder
17 was obtained through gelation treatment at 65 °C for 24 h. The X-ray powder diffraction (XRD)
18 patterns were recorded using a Rigaku D/Max-III A diffractometer at room temperature with 30 kV
19 and 30 mA under a Cu K α radiation ($\lambda = 0.15418$ nm). The crystal sizes were calculated using the
20 Scherrer’s formula [17]. The specific surface area and total pore volume of hydrosol samples were
21 measured by the Brunauer-Emmett-Teller (BET) method, in which the N₂ adsorption at 77 K using
22 an ASAP 2020 Sorptometer was applied. The xerogel sample was degassed at 90 °C prior to
23 nitrogen adsorption measurements. The pore size distribution was determined by the Barret-Joyner-
24 Halender (BJH) method according to their desorption isotherm [18]. The nitrogen adsorption
25 volume at the relative pressure (P/P_0) of 0.9733 was used to determine the pore volume and average
26 pore sizes.

27

28 **2.4 Photoreaction experiments**

29 MB and 2,3-DCP chemicals were used as two model pollutants to evaluate the photocatalytic
30 activity of the hydrosols in aqueous solution, while benzene was also tested to determine the
31 photocatalytic activity of the hydrosols in gaseous phase.

1 *Aqueous Phase Experiments.* The photocatalytic reactions of MB/2,3-DCP degradation in aqueous
2 solution were conducted in a Pyrex cylindrical photoreactor surrounded by a circulation water
3 jacket to control the temperature during reaction. A medium-pressure mercury lamp (Philips, 8 W,
4 365 nm) was used as a UVA light source ($I = 1.28 \text{ mW cm}^{-2}$), and a 300 W Xeon lamp (PLS-
5 SXE300UV, Beijing Trusttech Ltd., China) with a UV cutoff filter at 420 nm was applied as a
6 visible light source. The reaction mixture was prepared by adding hydrosol or P-25 powder into 250
7 mL of aqueous MB/2,3-DCP solution as colloid solution or powder suspension. In all experiments,
8 the initial concentration of MB/2,3-DCP was 10 mg L^{-1} and the solid content of TiO_2 was 1.0 g L^{-1} .
9 Prior to the photoreaction, the colloid solution/powder suspension was magnetically stirred in the
10 dark for 30 min to establish adsorption/desorption equilibrium. During the photoreaction, the
11 colloid solution or suspension was irradiated by UVA or visible light with air blowing and
12 magnetically stirring. At the given time intervals, the samples were taken from the colloid solution
13 or suspension and stored in the dark before analysis. The MB concentration was determined by a
14 UV-Vis spectrophotometer at the wavelength of 665 nm. The 2,3-DCP concentration was
15 determined by HPLC (Finnigan SpectraSYSTEM P4000) with a Pinnacle II C18 reverse-phase
16 column (5 mm, 4.6 mm \times 250 mm) and a UV detector (UV 6000LP) using all wavelength, in which
17 a mobile phase was composed of acetonitrile and water (v:v = 3:2) and flowed at 1.0 mL min^{-1} .

18
19 *Gaseous Phase Experiments.* Gaseous benzene degradation was conducted in a stainless steel
20 column reactor with an effective volume of 100 L (46 cm (D) \times 60 cm (H)), which inner surface
21 was coated with a Teflon film for eliminating adsorption. The reactor was placed in a small air
22 chamber where temperature and humidity were well controlled. Inside of the reactor, three medium-
23 pressure mercury lamps (Philips, 8 W) with the main emission at 365 nm or three fluorescent lamps
24 (Philips, 8 W) with the main emissions at 405 nm, 430 nm, 540 nm, and 580 nm were equipped at
25 the upper level as a UVA or visible light source and a TiO_2 -coated sheet was placed on a Teflon
26 film at the lower level horizontally about 1.5 cm below the lamps ($I = 1.42 \text{ mW cm}^{-2}$ for UV light,
27 and 1.12 mW cm^{-2} for visible light). The TiO_2 -coated sheet was prepared by spraying the hydrosol
28 solution containing 0.5 g of TiO_2 onto a piece of filter paper (18 cm \times 26 cm) to form a catalyst
29 loading of 1.07 mg cm^{-2} and was then dried at $60 \text{ }^\circ\text{C}$ for 24 h before use. A synthetic benzene gas
30 was prepared by mixing the certified benzene gas with zero air from cylinders with an initial
31 benzene concentration of $5.5 \pm 0.2 \text{ ppm/v}$. All the experiments were carried out at $25 \pm 1 \text{ }^\circ\text{C}$. The

1 humidity was controlled at $52 \pm 2\%$ by passing through a humidifier before photoreaction. The
2 gaseous benzene concentration was determined using a benzene monitor (Ultra RAE, PGM-7200,
3 USA), which has a measurement range of 0-10 ppm/v with a detection limit of 0.01 ppm/v.

4 5 **3. Results and Discussion**

6 **3.1 The colloidal properties of Ce^{3+} - TiO_2 hydrosols**

7 In this study, a pure TiO_2 hydrosol and a series of Ce^{3+} - TiO_2 hydrosols (0.5% Ce^{3+} - TiO_2 , 1.0% Ce^{3+} -
8 TiO_2 , 1.5% Ce^{3+} - TiO_2 , 2.0% Ce^{3+} - TiO_2 , and 2.5% Ce^{3+} - TiO_2) were prepared, respectively, but it was
9 found that not all samples were formed as good colloid solution. The detailed results are shown in
10 Table 1.

11 12 **[Table 1]**

13
14 It can be seen that some stable hydrosols with a Ce^{3+} content up to 1.0% were obtained without any
15 precipitates, while other hydrosols with a Ce^{3+} content at 1.5% or above contained some precipitates.
16 The results showed that the higher content of Ce^{3+} doped into the TiO_2 hydrosols resulted in more
17 precipitates and less sols in the sol solution. When the Ce^{3+} content reached 2.5%, no colloid
18 solution could be formed at all. Furthermore, the transmittance spectra of hydrosols samples in Fig.
19 1 showed that the light transmittance decreased sharply as the Ce^{3+} content increased from 0% to
20 1.5%. Therefore, only four hydrosols (pure TiO_2 , 0.5% Ce^{3+} - TiO_2 , 1.0% Ce^{3+} - TiO_2 , and 1.5% Ce^{3+} -
21 TiO_2) were used in the following experiments.

22 23 **[Fig. 1]**

24
25 The PSD of the four hydrosols are presented in Fig. 2. The results demonstrated that all the
26 hydrosol samples had a single-modal distribution characteristic with their PSD in the range of 15-50
27 nm. Furthermore, it was found that as the Ce^{3+} content increased, the PSD curves shifted to the right
28 side, indicating that the main particle sizes of hydrosols became larger and the average particle sizes
29 increased from 26.3 to 32.8 nm (Table 2). This could be the reason causing the decrease of light
30 transmittance in the hydrosol solution with a high Ce^{3+} content.

1 **[Fig. 2]**

2

3 **3.2 The structural properties of Ce³⁺-TiO₂ hydrosols**

4 The structural properties of the obtained Ce³⁺-TiO₂ hydrosols were examined by the analyses of
5 XRD, BET, and pore size distributions and the results are shown in Figs. 3 and 4.

6

7 *XRD analysis.* The XRD patterns of the TiO₂ and Ce³⁺-TiO₂ hydrosols in Fig. 3 showed five
8 distinctive TiO₂ peaks at 25.38°, 37.98°, 48.08°, 54.68° and 62.88°, corresponding to anatase (101),
9 (004), (200), (105) and (204) crystal planes (JCPDS 21-1272), respectively. These results indicated
10 that all the samples had anatase structure. The height of A (101) in Fig. 3 can denote the degree of
11 the crystalline of various hydrosols, which was decreased gradually as the Ce³⁺ content increased
12 from 0 to 1.5%. This decrease might indicate that the cerium ion doping inhibited the TiO₂ phase
13 transfer from amorphous structure to anatase, and that Ce³⁺-TiO₂ had higher thermal stability than
14 pure TiO₂. Additionally, no cerium oxides peaks were found in the XRD grams because of a low
15 cerium content [14].

16

17 **[Fig. 3]**

18

19 *BET-BJH analysis.* The effects of Ce³⁺ doping on the pore structure and adsorption ability of the
20 TiO₂ catalyst were examined by the BET method, in which a set of N₂ adsorption/desorption
21 isotherm tests was carried out and the experimental results are presented in Fig. 4a. The pore-size
22 distribution of different catalysts was also determined by the BJH method and the results are shown
23 in Fig. 4b. The adsorption isotherms in Fig. 4a showed the hysteresis loops of the Ce³⁺-TiO₂
24 demonstrated a curve pattern between Type IV (BDDT classification) which exhibit hysteresis
25 loops mostly of type H3 [18]. This indicates that the powders contain mesopores (2 - 50 nm) with
26 narrow slit-like shapes or plate-like particles. It can be seen that all the adsorption capacity
27 decreased gradually with the increase of Ce³⁺ content. The results in Fig. 4b demonstrated that the
28 pore sizes of most catalysts were distributed in the range of 4 - 24 nm. But the peak of pore size
29 distribution curves decreased sharply with the increase of Ce³⁺ content from 0 to 1.5%.
30 Simultaneously, the data in Table 2 showed that both the BET surface area and pore volume
31 decreased due to the increase of Ce³⁺ content, indicating the Ce³⁺ doping might occupy the porous

1 sites on the TiO₂ and result in lower surface area and smaller pore volume. These results seem to be
2 matched with the PSD results but inconsistent with the XRD results. In fact, the ionic radii of Ce³⁺
3 and Ce⁴⁺ (1.03 and 1.02 Å) are much bigger than that of Ti⁴⁺ (0.64 Å). So it is difficult for
4 Ce³⁺/Ce⁴⁺ to enter the lattice of TiO₂ structure. These results showed that the amount of cerium ion
5 on the surface of the Ce³⁺-TiO₂ catalysts is higher than that in the bulk [19]. Hence, the cerium ion
6 covered on the TiO₂ surface can inhibit the crystal growth of anatase to decrease crystal size, but
7 can enhance the aggregation of colloidal particles to increase particle sizes.

8

9 **[Fig. 4]**

10 **[Table 2]**

11

12 **3.3 Photocatalytic activity in aqueous phase**

13 To evaluate the effects of Ce³⁺ content on the photocatalytic activity of Ce³⁺-TiO₂ hydrosols in
14 aqueous phase, two sets of tests for degradation of MB and 2,3-DCP in aqueous solutions under UV
15 or visible illumination were conducted. The experimental results of MB and 2,3-DCP degradation
16 with different catalysts under UVA illumination and visible illumination are shown in Figs. 5 and 6,
17 respectively. To study the kinetics of MB and 2,3-DCP degradation in the aqueous phase, the
18 pseudo-first-order model was applied to fit the experimental data and the kinetic reaction rate
19 constants, k , versus cerium ion content are shown in Figs. 5c and 6c, respectively. The experimental
20 results showed that the MB and 2,3-DCP degradations were considerably affected by the Ce³⁺
21 content. While the 0.5%Ce³⁺-TiO₂ and 1.0%Ce³⁺-TiO₂ hydrosols achieved the best performance in
22 the MB and 2,3-DCP degradations under UVA illumination, 1.0% Ce³⁺-TiO₂ and 0.5% Ce³⁺-TiO₂
23 hydrosols achieved the best performance in the MB and 2,3-DCP degradations under visible
24 illumination, respectively.

25

26 **[Fig. 5]**

27 **[Fig. 6]**

28

29 Under UVA illumination, our previous investigation [14] had proved that Ce³⁺ doping can
30 accelerate the separation efficiency of charge carriers according to the photoluminescence emission

1 analysis. The Ce 4*f* level plays an important role in interfacial charge transfer and elimination of
2 electron-hole recombination. Ce³⁺ ion could act as an effective electron scavenger to trap the
3 conduction band electrons of TiO₂ and then photogenerated electrons were transferred efficiently.
4 Hence, the enhanced activity of TiO₂ hydrosols under UVA illumination can be mainly attributed to
5 the Ce³⁺-induced higher separation efficiency of charge carriers. Under visible illumination,
6 electron-hole pairs could be generated on either Ce³⁺-TiO₂ or surface Ce₂O₃ as two approaches.
7 Under visible light irradiation with the photon energy higher than ($E_{\text{Ce}4f} - E_v$), the electrons can be
8 excited from the valence band of TiO₂ or the ground state of Ce₂O₃ into Ce 4*f* level to successfully
9 separate the electron-hole pairs.

10
11 Furthermore, the visible response of Ce³⁺-TiO₂ hydrosol was not just attributed to the above-
12 mentioned reason. For dye degradation by cerium ion-doped TiO₂ hydrosol under visible
13 illumination, Xie and Yuan [15] pointed out the four proposed mechanisms: (I) photolysis
14 mechanism; (II) photosensitization mechanism for TiO₂ nanocrystallites system; (III)
15 photosensitization mechanism for cerium ion-doped TiO₂ hydrosol system; and (IV) interband
16 photocatalysis mechanism for cerium ion-doped TiO₂ nanocrystallites. In this study, the MB
17 degradation with pure TiO₂ hydrosol under visible illumination should obey the mechanisms (I) and
18 (II). The “Blank” (without catalyst) and “Pure TiO₂” in Fig. 5b may represent the photolysis and
19 photosensitization, respectively. However, since these two reaction rates were very slow, the
20 photolysis (I) and photosensitization (II) in the Ce³⁺-TiO₂/MB system under visible illumination
21 could be ignored. Therefore, the MB degradation with Ce³⁺-TiO₂ hydrosol under visible
22 illumination might be dominated by the mechanisms (III) and (IV), and the interband Ce 4*f* levels
23 lead the enhanced visible-response photocatalytic activity for MB degradation.

24
25 Since 2,3-DCP had no significant absorption of either UVA or visible light. The 2,3-DCP
26 degradation with Ce³⁺-TiO₂ hydrosols should mainly result from the mechanism (IV). However, it
27 has been noted that 2,3-DCP was degraded by the pure TiO₂ hydrosol under visible illumination
28 with *k* value significantly higher than that of “Blank”. This result demonstrated that the pure
29 TiO₂/2,3-DCP system had certain visible-response. Agrios et al. [20, 21] observed that 2,4,5-
30 trichlorophenol formed a charge-transfer complex on TiO₂ and correlated the charge transfer
31 surface complex formation with visible light absorption among several chlorophenols. They pointed

1 out that surface complex formation on pure TiO₂ was responsible for the visible-light-induced
2 photocatalytic transformation of substrates that do not absorb visible photons by them alone. Choi
3 et al. [22] demonstrated that 4-chlorophenol, as one of the most common substrates used in many
4 studies of photocatalytic degradation, can be actually degraded and mineralized under visible
5 irradiation ($\lambda > 420$ nm). The visible light reactivity of 4-chlorophenol was correlated with the
6 surface complex formation that was supported by the diffuse reflectance UV-Vis spectra and
7 visible-light-induced photocurrent generation. Other phenolic compounds showed similar visible
8 light reactivity. Since 2,3-DCP is a member of phenolic compounds, the mechanisms of 2,3-DCP
9 degradation with Ce³⁺-TiO₂ hydrosol under visible illumination should include the Ce 4f level
10 function as the interband photocatalysis mechanism and plus the charge transfer surface complex
11 formation. It should be noted that the ·O₂⁻ can be generated through O₂ capturing the electrons in
12 two ways: (i) the electron of Ce-TiO₂ was directly irradiated to Ce 4f level under visible light
13 illumination; (ii) the electron of TiO₂-DCP complex was transferred to conduction band of TiO₂, so
14 the ·O₂⁻ can also contribute to the 2,3-DCP degradation. The possible reaction mechanisms of 2,3-
15 DCP degradation with Ce³⁺-TiO₂ hydrosol under visible illumination are summarized in Fig. 7.

16

17 **[Fig. 7]**

18

19 **3.4 Photocatalytic activity in gaseous phase**

20 To evaluate the effects of Ce³⁺ content on the photocatalytic activity of Ce³⁺-TiO₂ hydrosols in
21 gaseous phase, two sets of tests for degradations of gaseous benzene with different catalysts under
22 UVA and visible illumination were conducted. The experimental results in Fig. 8 showed that the
23 photocatalytic activity of Ce³⁺-TiO₂ hydrosols for benzene degradation in gaseous phase was also
24 significantly affected by the Ce³⁺ content. From the kinetic data shown in Fig. 8c, the results
25 indicated that the benzene degradation under UVA or visible illumination both increased with the
26 increase of Ce³⁺ content initially, but declined while the Ce³⁺ content reached 1.0%, and this was
27 well consistent with the results of MB and 2,3-DCP degradation in aqueous phase.

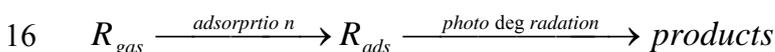
28

29 **[Fig. 8]**

30

1 It is found that the benzene degradation by pure TiO₂ hydrosol under visible illumination was so
 2 weak that can be ignored. Based on the above-mentioned mechanisms, the benzene
 3 photodegradation by Ce³⁺-TiO₂ hydrosols was attributed to neither the photolysis nor the
 4 photosensitization of TiO₂-benzene system. The enhancement of electron-hole pair separation
 5 owing to lanthanide ion doping was previously proved by the PL emission spectra [23], as a result
 6 of the enhanced activity for BTEX degradation. Hence, it can be concluded that the enhanced
 7 photocatalytic activity by Ce³⁺ doping under UVA or visible illumination should be dominated by
 8 the mechanism (IV): the interband Ce 4*f* levels lead higher electron-hole separating efficiency and
 9 enhanced visible light response.

10
 11 Besides, it is well known that the large surface area is favorable to the photocatalytic reaction, but
 12 in this study, the benzene degradation did not depend on the BET surface areas very much. To
 13 illustrate the reasons, we briefly reviewed the Langmuir-Hinshelwood approach [24] that assumes
 14 one reaction achieving adsorption equilibrium ($R_{gas} \rightarrow R_{ads}$) is followed by a single surface reaction
 15 step ($R_{ads} \rightarrow products$) illustrated by the following equation:



17 wherein the R_{gas} and R_{ads} represent the gaseous reactant and the adsorbed reactant, respectively.
 18 The adsorption rate of $R_{gas} \rightarrow R_{ads}$ is defined as r_{ads} , and the photodegradation rate of $R_{ads} \rightarrow$
 19 $products$ is defined as r_{pd} . Hence, when the $r_{ads} < r_{pd}$, the adsorption step ($R_{gas} \rightarrow R_{ads}$) should be
 20 the rate-determining step (RDS); in contrast, when the $r_{ads} > r_{pd}$, the photodegradation ($R_{ads} \rightarrow$
 21 $products$) should be the RDS. The values of adsorption rate constants for benzene on pure TiO₂
 22 were calculated (data not shown in figure) to be 0.1887 h⁻¹ (R²=0.8693), which was significantly
 23 higher than the k values in Fig. 8c, indicating that the slow photodegradation step should be the
 24 RDS under. Hence, this might be the reason why the rate of benzene degradation by Ce³⁺-TiO₂
 25 hydrosols under our experimental conditions was not affected by the BET surface areas
 26 significantly.

27
 28 **Conclusions**

29 The Ce³⁺-TiO₂ hydrosols with Ce³⁺ content from 0% to 1.5% as stable colloid solutions were
 30 successfully prepared by a coprecipitation-peptization method. The characteristics of these

1 hydrosols demonstrated that as the Ce^{3+} content increased, the crystalline size, the BET surface area
2 and transmittance decreased significantly, but the particle size increased. The results showed that
3 the overall photocatalytic activity of Ce^{3+} - TiO_2 hydrosols for MB and 2,3-DCP degradations in
4 aqueous phase under UVA and visible illumination was significantly higher than pure TiO_2
5 hydrosol due to the Ce 4f level-induced better separation of electron-hole pairs and visible light
6 response. Additionally, the formation surface-complex of TiO_2 and 2,3-DCP with visible-light-
7 response also contributed to the 2,3-DCP degradation. The experiments also confirmed that the
8 Ce^{3+} - TiO_2 hydrosols had the higher activity for benzene degradation in gaseous phase under UVA
9 and visible illumination. The 0.5-1% Ce^{3+} - TiO_2 hydrosols achieved the best performance in both of
10 aqueous and gaseous phases.

11

12 **Acknowledgements**

13 The authors would thank the Hong Kong Government Research Grant Committee for a financial
14 support to this work (RGC No: PolyU 5226/06E).

15

16 **References**

- 17 [1] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants
18 over titanium dioxide: A review of fundamentals, progress and problems, *J. Photochem.*
19 *Photobiol. C* 9 (2008) 1-12.
- 20 [2] K. Demeestere, J. Dewulf, H. Van Langenhove, Heterogeneous photocatalysis as an advanced
21 oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile
22 organic compounds in air: State of the art, *Crit. Rev. Environ. Sci. Technol.* 37 (2007) 489-538.
- 23 [3] N.I. Al-Salim, S.A. Bagshaw, A. Bittar, T. Kemmitt, A.J. McQuillan, A.M. Mills, M.J. Ryan,
24 Characterisation and activity of sol-gel-prepared TiO_2 photocatalysts modified with Ca, Sr or
25 Ba ion additives, *J. Mater. Chem.* 10 (2000) 2358-2363.
- 26 [4] T. Kawahara, T. Ozawa, M. Iwasaki, H. Tada, S. Ito, Photocatalytic activity of rutile-anatase
27 coupled TiO_2 particles prepared by a dissolution-reprecipitation method, *J. Colloid Interf. Sci.*
28 267 (2003) 377-381.
- 29 [5] D.H. Kuo, C.N. Shueh, Growth and properties of TiCl_4 -derived CVD titanium oxide films at

- 1 various C-2/H-2 inputs, Chem. Vap. Deposit. 9 (2003) 265-271.
- 2 [6] Y.B. Xie, C.W. Yuan, Photocatalytic activity and recycle application of titanium dioxide sol for
3 X-3B photodegradation, J. Mol. Catal. A. 206 (2003) 419-428.
- 4 [7] T.X. Liu, F.B. Li, X.Z. Li, TiO₂ Hydrosols with high activity for photocatalytic degradation of
5 formaldehyde in a gaseous phase, J. Hazard. Mater. 152 (2007) 347-355.
- 6 [8] T.X. Liu, F.B. Li, X.Z. Li, Effects of peptizing conditions on nanometer properties and
7 photocatalytic activity of TiO₂ hydrosols prepared by H₂TiO₃, J. Hazard. Mater. 155 (2008)
8 90-99.
- 9 [9] Y.Q. Wang, H.M. Cheng, Y.Z. Hao, J.M. Ma, W.H. Li, S.M. Cai, Photoelectrochemical
10 properties of metalion-doped TiO₂ nanocrystalline electrodes, Thin Solid Films 349 (1999)
11 120-125.
- 12 [10] W. Xu, Y. Gao, H.Q. Liu, The preparation, characterization, and their photocatalytic activities
13 of rare-earthdoped TiO₂ nanoparticles, J. Catal. 207 (2002) 151-157.
- 14 [11] W.Y. Su, E.X. Chen, L. Wu, X.C. Wang, X.X. Wang, X.Z. Fu, Visible light photocatalysis on
15 praseodymium(III)-nitrate-modified TiO₂ prepared by an ultrasound method, Appl. Catal. B 77
16 (2008) 264-271.
- 17 [12] Z.M. Shi, L.N. Jin, Influence of La³⁺/Ce³⁺-doping on phase transformation and crystal growth
18 in TiO₂-15wt% ZnO gels, J. Non-Crystal. Solids 355 (2009) 213-220.
- 19 [13] C.H. Liang, C.S. Liu, F.B. Li, F. Wu, The effect of Praseodymium on the adsorption and
20 photocatalytic degradation of azo dye in aqueous Pr³⁺-TiO₂ suspension, Chem. Eng. J. 147
21 (2009) 219-225.
- 22 [14] F.B. Li, X.Z. Li, M.F. Hou, K.W. Cheah, W.C.H. Choy, Enhanced photocatalytic activity of
23 Ce³⁺-TiO₂ for 2-mercaptobenzothiazole degradation in aqueous suspension for odour control,
24 Appl. Catal. A 285 (2005) 181-189.
- 25 [15] Y.B. Xie, C.W. Yuan, Visible-light responsive cerium ion modified titania sol and
26 nanocrystallites for X-3B dye photodegradation, Appl. Catal. B 46 (2003) 251-259.

- 1 [16] J.H. Huang, X.C. Wang, Y.D. Hou, X.F. Chen, L. Wu and X.Z. Fu, Degradation of benzene
2 over a zinc germanate photocatalyst under ambient conditions, *Environ. Sci. Technol.* 42 (2008)
3 7387-7391.
- 4 [17] J.G. Yu, G.H. Wang, B. Cheng and M.H. Zhou, Effects of hydrothermal temperature and time
5 on the photocatalytic activity and microstructures of bimodal mesoporous TiO₂ powders, *Appl.*
6 *Catal. B* 69 (2007) 171-180.
- 7 [18] S.L. Gregg, K.S.W. Sing, Adsorption, surface area and porosity, Academic Press, London,
8 1982.
- 9 [19] K.T. Ranjit, I. Willner, S.H. Bossmann, A.M. Braun, Lanthanide oxide-doped titanium dioxide
10 photocatalysts: Novel photocatalysts for the enhanced degradation of p-chlorophenoxyacetic
11 acid, *Environ. Sci. Technol.* 35 (2001) 1544-1549.
- 12 [20] A.G. Agrios, K.A. Gray, E. Weitz, Photocatalytic transformation of 2,4,5-trichlorophenol on
13 TiO₂ under sub-band-gap illumination, *Langmuir* 19 (2003) 1402-1409.
- 14 [21] A.G. Agrios, K.A. Gray, E. Weitz, Narrow-band irradiation of a homologous series of
15 chlorophenols on TiO₂: Charge-transfer complex formation and reactivity, *Langmuir* 20 (2004)
16 5911-5917.
- 17 [22] S.H. Kim, W.Y. Choi, Visible-light-induced photocatalytic degradation of 4-Chlorophenol and
18 phenolic compounds in aqueous suspension of pure titania: demonstrating the existence of a
19 surface-complex-mediated path, *J. Phys. Chem. B* 109 (2005) 5143-5149.
- 20 [23] F.B. Li, X.Z. Li, C.H. Ao, S.C. Lee, M.F. Hou, Enhanced photocatalytic degradation of VOCs
21 using Ln³⁺-TiO₂ catalysts for indoor air purification, *Chemosphere* 59 (2005) 787-800.
- 22 [24] D.F. Ollis, Kinetics of liquid phase photocatalyzed reactions: an illuminating approach, *J. Phys.*
23 *Chem. B* 109 (2005) 2439-2444.

1 **Tables**

2 Table 1 The ratios of sol to precipitate and UV-Visible transmittance

Ce ³⁺ content (%)	0	0.5%	1.0%	1.5%	2.0%	2.5%
Sol/ Precipitate* wt%	100 / 0	100 / 0	100 / 0	82.7 / 17.3	2.9 / 97.1	0 / 100
Transmittance [#] T%	77.41	76.91	67.15	48.91	>90	>98

3 “Sol/ Precipitate*” means the dry weight ratio of the solid titania in the obtained sol to the titania
4 precipitate which wasn’t transformed into sol by weighing the solid titania in the liquid before and
5 after filtration, respectively, and then calculating.

6 “Transmittance[#]” represents the transmittance of the hydrosol (the ratio of solid 0.05 wt%) at the
7 wavelength of 600 nm.

1 Table 2 The crystal size, particle size, surface area, pore volume, pore size of catalysts

Catalysts	Crystallite Size nm	Surface Area $\text{m}^2 \text{g}^{-1}$	Particle Size nm	Pore Size nm	Pore Volume $\text{cm}^3 \text{g}^{-1}$
Pure TiO_2	12.95	379.02	26.3	5.27	0.499
0.5% Ce^{3+} - TiO_2	12.14	330.72	27.9	5.18	0.429
1.0% Ce^{3+} - TiO_2	11.60	245.45	30.2	5.39	0.331
1.5% Ce^{3+} - TiO_2	10.38	158.68	32.8	5.29	0.210

2

1 **Figure captions:**

2 **Fig. 1.** The transmittance of pure TiO₂ hydrosol and Ce³⁺-TiO₂ hydrosols

3 **Fig. 2.** The particle size distributions of different pure TiO₂ hydrosol and Ce³⁺-TiO₂ hydrosols

4 **Fig. 3.** The XRD patterns of pure TiO₂ hydrosol and Ce³⁺-doped TiO₂ hydrosols

5 **Fig. 4.** (a) The N₂ adsorption-desorption isotherms of pure TiO₂ hydrosol and Ce³⁺-doped TiO₂
6 hydrosols; (b) The pore size distributions of pure TiO₂ hydrosol and Ce³⁺-doped TiO₂ hydrosols

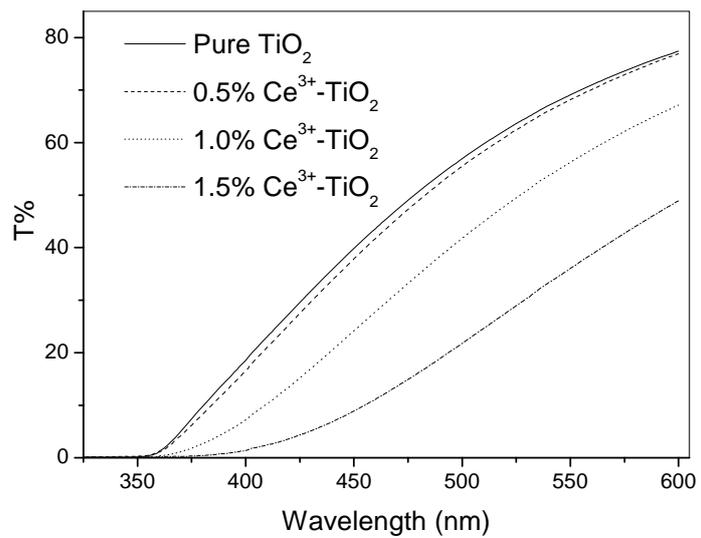
7 **Fig. 5.** The MB degradation by pure TiO₂ and Ce³⁺-TiO₂ hydrosols (a) under UVA illumination; (b)
8 under visible illumination; (c) the apparent kinetic constant, k vs. cerium ion content

9 **Fig. 6.** The 2,3-DCP degradation by pure TiO₂ and Ce³⁺-TiO₂ hydrosols (a) under UVA
10 illumination; (b) under visible illumination; (c) the apparent kinetic constant, k vs. cerium ion
11 content

12 **Fig. 7.** The proposed valence band structure of Ce³⁺-TiO₂ and the mechanisms of photoresponse
13 under visible light and photogenerated electron transfer in Ce³⁺-TiO₂/2,3-DCP system

14 **Fig. 8.** The benzene degradation by pure TiO₂ and Ce³⁺-TiO₂ hydrosols (a) under UVA illumination;
15 (b) under visible illumination; (c) the apparent kinetic constant, k vs. cerium ion content

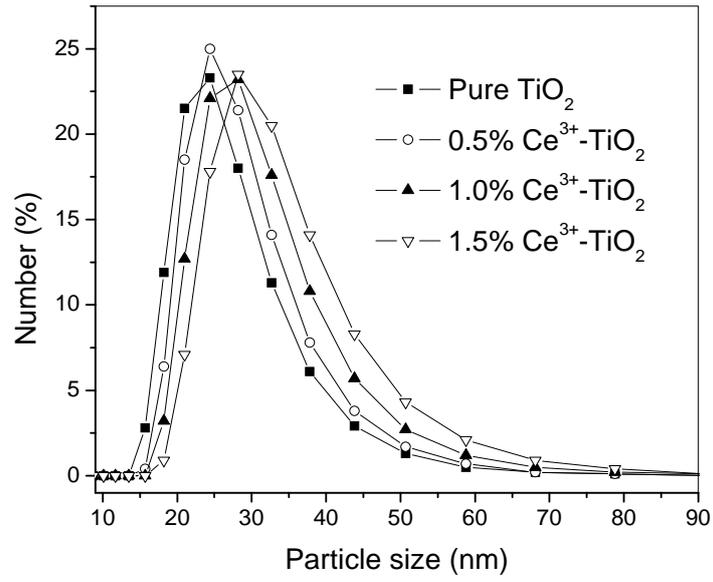
1 **Fig. 1.**



2

1

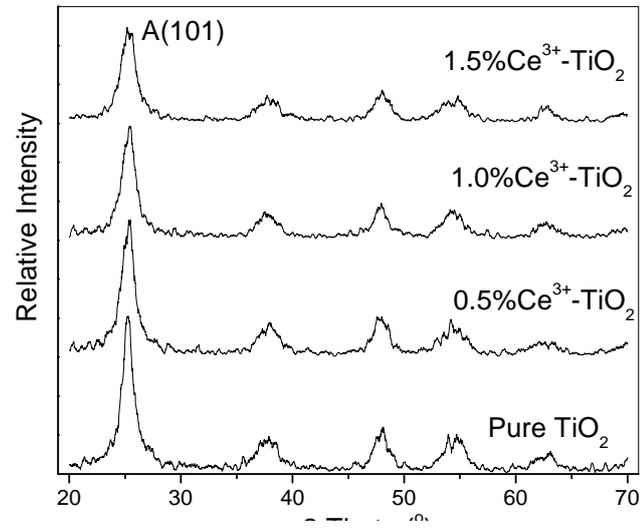
Fig. 2.



2

1

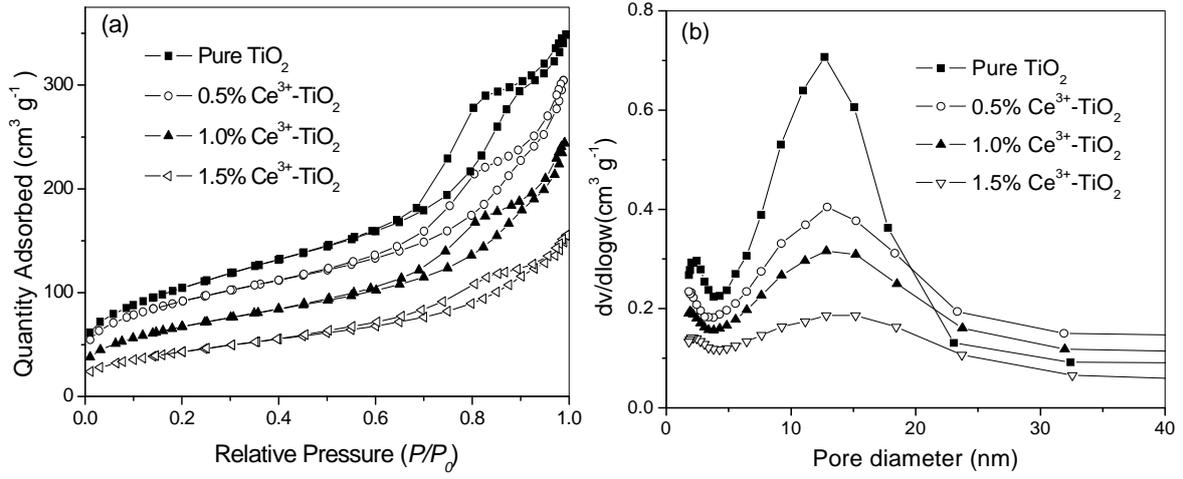
Fig. 3.



2

1

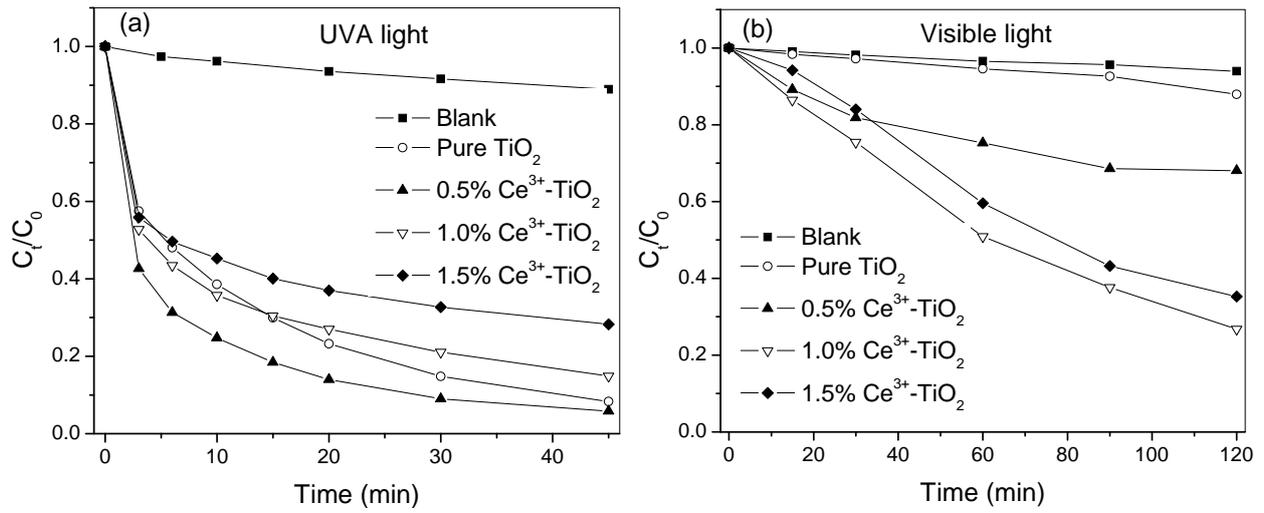
Fig. 4.



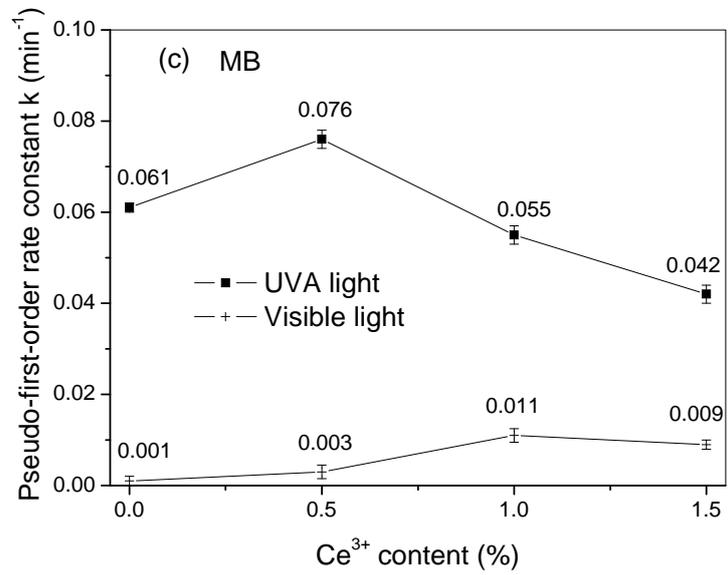
2

1

Fig. 5.



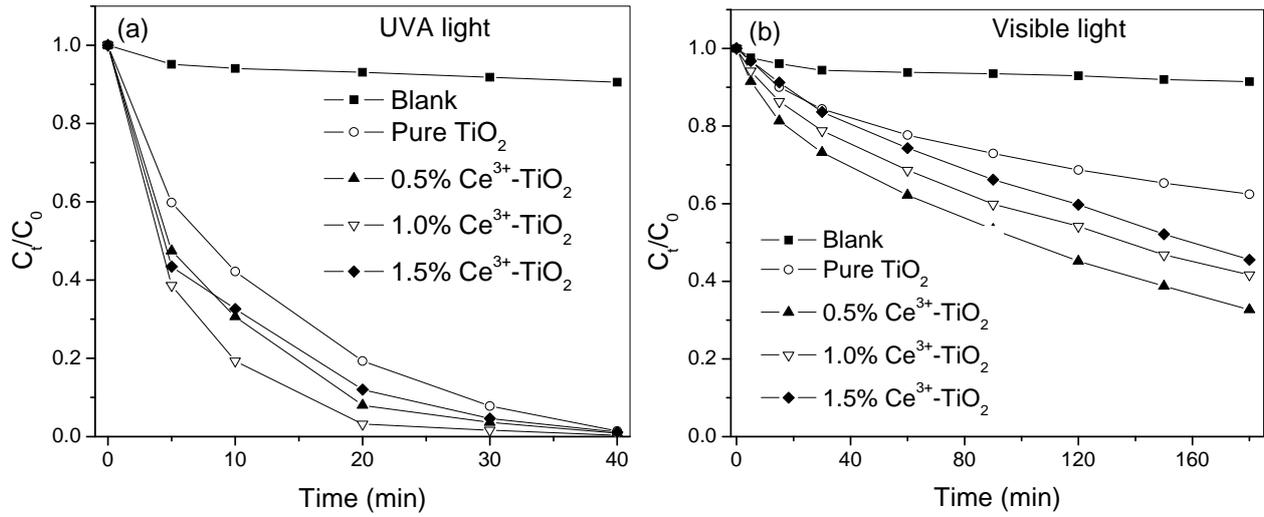
2



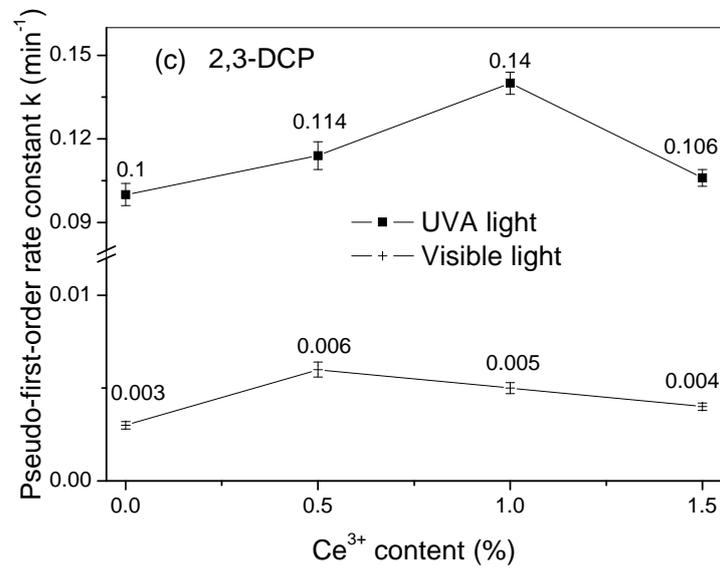
3

1

Fig. 6.



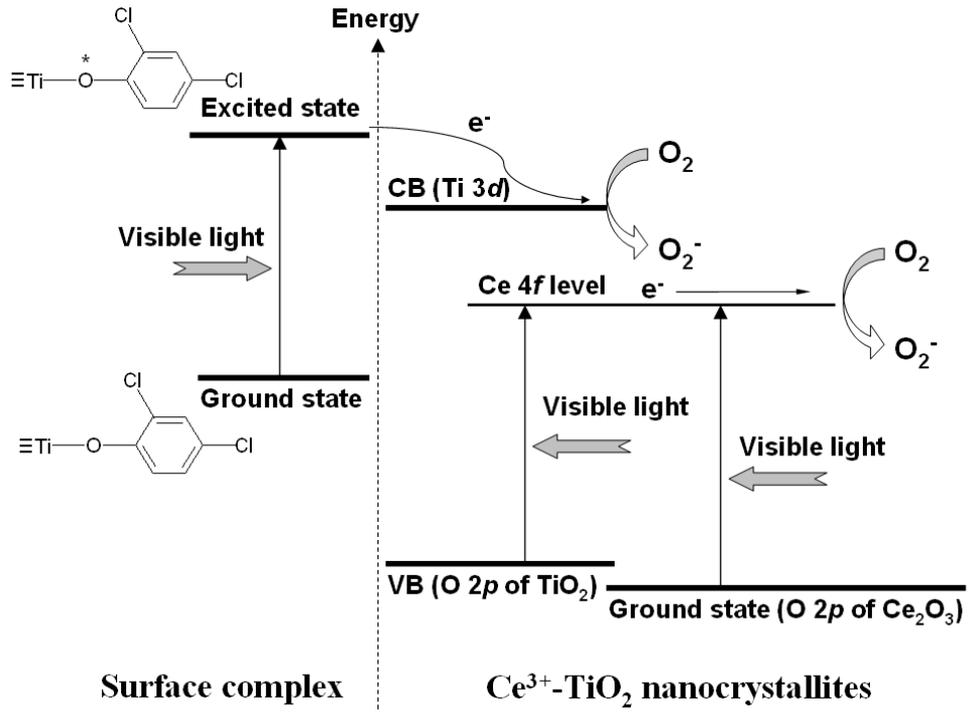
2



3

1

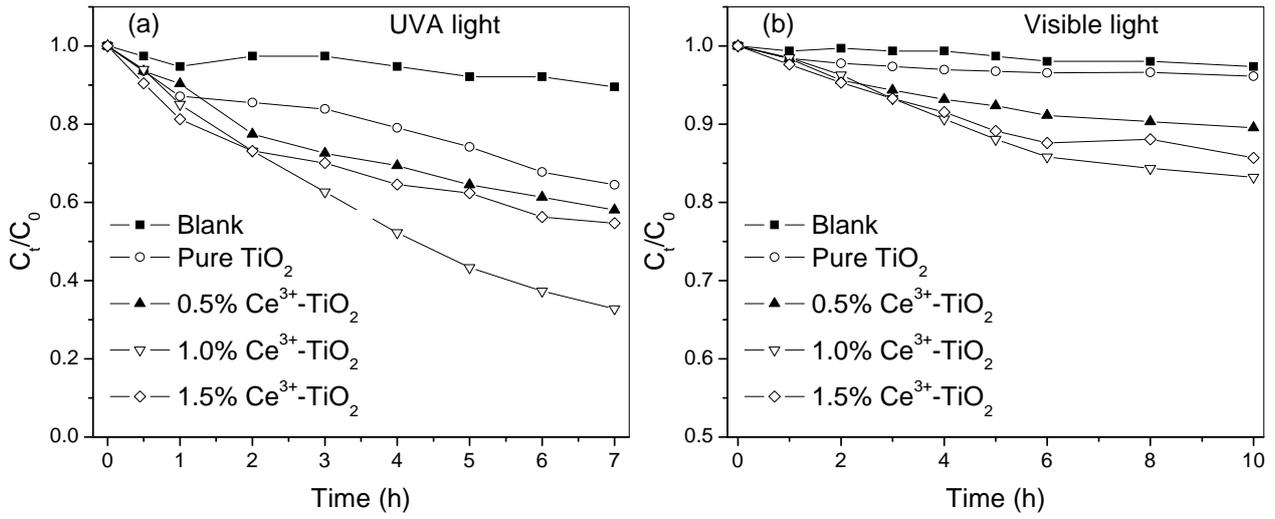
Fig. 7.



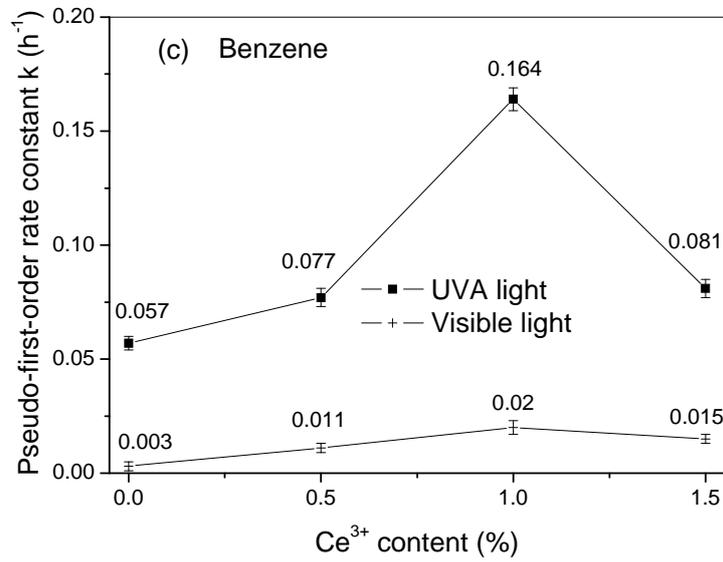
2

1

Fig. 8.



2



3

4