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Noble metal free Fe and Cr dual-doped nanocrystalline titania $(Ti_{1-x-y}M_{x+y}O_2)$ for high selective photocatalytic conversion of benzene to phenol at ambient temperature

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Perumal Devaraji, Wan-Kuen Jo*

Department of Environmental Engineering, Kyungpook National University, Daegu 702-701, South Korea

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Keywords: Disordered mesoporous nanocrystalline Solution combustion synthesis Functional application Electron-trapping level	Metal (Fe and Cr)-incorporated mesoporous nanocrystalline titania $(Ti_{1-x-y}M_{x+y}O_2, \text{ or }TiMxO_2)$ was synthe- sized using a simple solution combustion method. Structural characterization, microscopy, and spectroscopy techniques confirmed the incorporation of Fe and Cr into the TiO ₂ lattice. Photocatalytic benzene oxidation to phenol was investigated under ambient conditions, and under solar stimulator (AM1.5 or one sun condition) and ultraviolet (UV) irradiation. Compared to pristine TiO ₂ , TiO ₂ doped with 2 at% of Fe (Ti _{0.98} Fe _{0.02} O ₂) exhibited a higher catalytic activity for benzene-to-phenol oxidation, highlighting the importance of the introduction of the Fe dopant. Introduction of Fe and Cr into the TiO ₂ (Ti _{0.98} Fe _{0.01} Cr _{0.01} O ₂) lattice further enhanced the oxidation of benzene to phenol under UV light and gave a phenol yield that was ~2 times higher than that given by Ti _{0.98} Fe _{0.02} O ₂ . The high photocatalytic activity of Ti _{1-x-y} M _{x+y} O ₂ and good photocurrent behaviour were mainly ascribed to the generation of an electron trapping level composed of Fe ³⁺ and Cr ³⁺ in the TiO ₂ con- duction band, disordered mesoporosity, high mobility, and a short diffusion length for charge carriers.

1. Introduction

Photocatalytic semiconductor materials have attracted attention as a solution for current energy and environmental problems [1,2]. Among the various wide-band-gap semiconductor photocatalysts, TiO₂ has been studied extensively because it demonstrates extraordinary chemical stability against photocorrosion and because holes with high oxidizing power are generated in the valence band upon light absorption [3,4]. TiO₂ is a semiconductor material with a wide band gap of 3.2 eV and is activated only under ultraviolet (UV) light. Phenol is one of the most important organic chemicals in industry. Currently, phenol is synthesized via the three-step cumene process at 250 °C and a pressure of 30 bar [5,6]. In this process, the explosive cumene hydroperoxide is formed as an intermediate and acetone is formed as a major side product. Therefore, an alternative green and one-step synthetic route for phenol would be ideal to replace the cumene process [7]. Although several heterogeneous photocatalysts for the hydroxylation of benzene to phenol have been reported to date, there have been no significant breakthroughs [7-26]. Park et al. demonstrated that the addition of polyoxometalates to the TiO2 suspension increases the phenol yield [7]. In 2005, Shiraishi et al. reported the photocatalytic conversion of benzene to phenol over mesoporous TiO₂ under UV light irradiation in aqueous media [8]. Tanarungsm et al. conducted liquidphase photocatalytic hydroxylation of benzene to phenol with FeVCu/ TiO₂ as the photocatalyst under UV light and demonstrated that the trimetallic photocatalyst could improve phenol yield (9.7%) and selectivity (52%) [11]. Recently, the one-step oxidation of benzene to phenol on layered double hydroxides was reviewed [12].

In early 1981, Fujihira et al. examined the photocatalytic oxidation of toluene on TiO₂ in the presence of hydrogen peroxide with UV light irradiation by a 500 W Xe lamp [13]. Palmisano et al. have demonstrated the photocatalytic selective conversion of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde over TiO2 in an aqueous medium under UV light [14]. Masami et al. demonstrated that doping TiO₂ with metal ions, such as Ir, Cr, Ru, or Rh, led to the generation of an electron acceptor level in the conduction band (CB), which trapped the excited electrons and increased the number of holes available in the valence band (VB). Addition of grafted Fe³⁺ ions enhanced the electron transfer process in TiO₂, which in turn improved the photocatalytic activity [15]. Han et al. have conducted the photocatalytic oxidation of benzene to phenol using $[Ru^{II}(Me_2phen)_3]^{2+}$ as a photocatalyst in the presence of O₂ and H₂O [16]. Min et al. reported that doped Fe³⁺ along with surface-grafted Fe³⁺ on TiO₂ increased the availability of holes in the VB, which enhanced the photocatalytic oxidation of organic compounds

E-mail address: wkjo@knu.ac.kr (W.-K. Jo).

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^{*} Corresponding author.

[4]. Fe-g-C₃N₄ (Fe-CN)/ titanium silicate zeolite (TS-1) hybrid materials have also been utilized for the photocatalytic oxidation of benzene to phenol under visible light irradiation. It was found that Fe doping in Fe-CN/TS-1 improved the photocatalytic activity of these materials and 10% phenol yield was achieved [17]. Wang et al. conducted the direct oxidation of benzene to phenol with ferrocene-modified carbon nitride under outdoor sunlight irradiation and demonstrated that the use of this photocatalyst improved the phenol yield to 14.4% as compared with unmodified mesoporous graphitic carbon nitride (mpg-C₃N₄) and ferrocene carboxyaldehyde [18]. Fe-doped g-C₃N₄ coated on SBA-15 catalyzed the oxidation of benzene to phenol at 60 °C under visible light [19]. An FeCl₃/mpg-C₃N₄ hybrid gave 38% benzene conversion and 97% phenol selectivity with light of $\lambda \ge 420$ nm at 60 °C and only 4% benzene conversion at 25 °C [20]. Dengke et al. reported that Fe-based metal-organic frameworks could catalyze the selective hydroxylation of benzene to phenol under visible light irradiation [21]. There are some reports on the hydroxylation of benzene to phenol over Au/TiO₂; the excited electrons are stored in the Au nanoparticles and facilitate the oxidation of benzene by TiO₂ [22-25]. Ide et al. have reported that benzene oxidation under visible light irradiation on immobilized gold nanoparticles supported with layered titanate results in 62% yield and 96% phenol selectivity [22]. However, the above result was possible only in the presence of a few hundred ppm (x) of benzene with the addition of a large excess of seed phenol ($\geq 10x$). No phenol production was observed in the absence of seed phenol [22]. The synthesis of phenol via benzene oxidation over Au/TiO2 has also been reported; a phenol yield of 13% with 89% selectivity was achieved after 24 h under a CO₂ atmosphere (230 kPa) and 1 sun irradiation conditions [23]. However, Au is an expensive noble metal and therefore, numerous efforts have been undertaken to replace Au with low-cost materials [10,26,27]. The above survey highlights the challenges involved in designing a low-cost, effective, and efficient new photocatalyst that gives high benzene conversions and phenol selectivities at ambient temperature and pressure.

Doping with transition metal ions like Cr, Ir, Ru, and Rh leads to the generation of a new acceptor level in the CB of TiO₂, which acts as an electron trapping center and facilitates the reduction of molecular oxygen to H₂O₂ during the photocatalytic reaction. High photocatalytic activity is observed for a grafted Fe³⁺ co-catalyst on Fe-doped TiO₂ because Fe doping significantly enhances the electron-hole separation and thus minimizes charge carrier recombination. This minimization of charge carrier recombination is essential for redox reactions [15,17]. Soria et al. have demonstrated that bulk Fe^{3+} doping into TiO₂ results in better photocatalytic activity for NH₃ reduction under UV light irradiation as compared to surface-dispersed Fe³⁺ [28]. TiO₂ doped with Fe and Cr is useful for the oxidation of benzene and many other oxidation reactions [29,30]. The oxidative degradation of phenol and methylene blue using TiO₂ doped with Fe, Cr, and other single metals under visible and UV light (> 320 nm) irradiation have been examined [30]. In our recently published study, we demonstrated that the incorporation of V in the TiO₂ lattice generates a V⁵⁺ energy level below the CB of TiO₂, which helps to trap the excited electrons, and that Au deposited over vanadium-doped TiO2 acts as an electron sink. The Schottky junction between Au and TiO₂, and V⁵⁺ synergistically increase the availability of holes in the VB of TiO₂, which can enhance the photocatalytic conversion of benzene to phenol under UV light irradiation; 18% benzene conversion was achieved, along with a phenol yield and selectivity of 15.9% and 88%, respectively [31]. For better catalytic activity, it is important to prepare Fe and Cr co-doped TiO₂ systems with mesoporosity. Ordered mesoporous materials have high surface areas and long diffusion lengths. Consequently, the reactant and product molecules have to diffuse a long distance to and from the active sites. In these materials, there are a higher number of surface active sites present on the porous channels. Hence, the short diffusion lengths associated with disordered mesoporous materials are likely to be helpful in minimizing the diffusion problem [32-35]. This is expected

to enhance the catalytic activity and selectivity for the target product.

In the present study, we synthesized anatase TiO₂ doped with 2 at% of Fe and Cr (TiMx = $Ti_{0.98}M_{0.02}O_2$) by following a solution combustion method (SCM), which exhibits advantages of lower costs, simple and shorter synthesis time (within 15 min) compared to other methods. The photocatalytic oxidation of benzene to phenol was carried out in a biphasic system under UV/visible light under ambient conditions. After 12 h of UV irradiation in the presence of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, 28% benzene conversion and 25.2% and 90% phenol yield and selectivity, respectively, were achieved. The present study is one of the major efforts to synthesize rationally designed photocatalytic materials for the application of organic conversion, water splitting and pollutant degradation in our laboratories [31].

2. Experimental

2.1. Preparation of the photocatalysts

All chemicals used in this study were of analytical grade and used as received. Ti[OCH(CH₃)₂]₄, CrCl₃·6H₂O, and Fe(NO₃)₃·9H₂O were used as Ti, Cr, and Fe precursors, respectively, and urea was used as a fuel. TiMx materials were synthesized using the solution combustion synthesis method (SCM) [32]. The synthesis of TiO_2 doped with 2 at% M was carried out with a 1:1 M ratio of the metal ions (Ti + M (Fe + Cr)) to urea, but with different Fe:Cr ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. In a typical synthesis procedure, the required amounts of the reactants were dissolved in water and introduced into a 250 mL beaker. The aqueous solution was stirred to get homogeneous solution and then kept in a muffle furnace that was pre-heated at 400 °C. After the solution was introduced into the muffle furnace, the water began to evaporate. This was followed by smoldering-type combustion, and the resulting materials were designated as Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂, Ti_{0.98}Fe_{0.02}O₂, Ti_{0.98}Fe_{0.015}Cr_{0.005}O₂, $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2\text{, and }Ti_{0.98}Cr_{0.02}O_2\text{, where the subscripts im$ mediately after Fe or Cr indicate the doping amount, in at%). Similarly, TiO₂ was synthesized without adding any Fe or Cr precursor.

2.2. Characterization

To examine the structural properties of the as-synthesized materials, various characterization methods were used. Powder X-ray diffraction (PXRD) data were recorded using a PANalytical X'Pert Pro dual goniometer X-ray diffractometer with Cu-Ka (1.5418 Å) radiation and a Ni filter, and the data were collected using a flat holder in the Bragg-Brentano geometry (0.2°). High-resolution transmission electron microscopy (HRTEM), field emission scanning electron microscopy (FE-SEM), N2 adsorption-desorption isotherm measurements, UV-vis absorption spectroscopy, photoluminescence (PL) spectroscopy, energydispersive X-ray (EDX) spectroscopy, and X-ray photoelectron spectroscopy (XPS) were also conducted. An FE-SEM system (Hitachi SU8220) equipped with an EDX attachment (Horiba X-MaxN with a silicon DRIFT X-ray detector) was used to examine the surface morphologies and chemical compositions. Prior to SEM analysis, samples were coated with indium by ion sputtering (Hitachi, E-1030) for 60 s. HRTEM was performed on all photocatalysts using an FEI Titan G2ChemiSTEM Cs Probe microscope. The surface areas (SBET) and porosities of the materials were measured using a BET-BELSORP Mini II surface area analyzer; these measurements were carried out after degassing the materials at 300 °C. Raman analysis was carried out using a Renishaw (inVia reflex) spectrometer combined with a microscope in reflectance mode with a 632 nm excitation laser source and a spectral resolution of 0.5 cm⁻¹. XPS was performed using an ULVAC-PHI Quantera SXMTM scanning XPS microscope with an Al Ka radiation source or a Kratos Axis HSi photoelectron spectrometer equipped with a charge neutralizer and a monochromated Al Ka (1486.6 eV) radiation source. Diffuse reflectance UV-vis studies were performed using a Shimadzu UV-2600 spectrophotometer with $BaSO_4$ as the standard reference material. PL measurements were performed using a Shimadzu RF-6000 with a tunable excitation wavelength. All PL measurements were carried out with 325 nm excitation pulses.

2.3. Electrochemical measurements

Electrochemical measurements were conducted within a conventional three-electrode cell system, using platinum foil as the counter electrode and Ag/AgCl as the reference electrode. The working electrode was prepared by dispersing 5 mg of the photocatalyst in 100 μ L of diluted Nafion (1 wt%) in ethanol. The above mixture was ground well and the obtained slurry was spread uniformly over the conductive side of a 0.25 cm² indium tin oxide (ITO) glass plate and dried in air. Photocurrent (PEC) measurements were carried out in a Na₂SO₄ (0.2 M) electrolyte using a 300 W xenon arc lamp with an AM 1.5 filter [33].

2.4. Photocatalytic activity

Photocatalytic benzene oxidation reactions were conducted in a quartz round bottom flask for different time intervals with a 450 W mercury lamp ($\lambda = 200-400$ nm) using a flow-type double-jacketed quartz reactor. Several experiments were conducted under 1 sun illumination conditions using an AM 1.5 light source. In a typical experiment, 30 mg of the photocatalyst was dispersed in a quartz round bottom flask, and CH₃CN (2 mL), benzene (1 mL), and 25% H₂O₂ (2 mL) were added to afford the starting reaction mixture. CH₃CN was used as a solvent to dissolve H₂O₂ and benzene in the aqueous solution. The temperature of the double-jacketed reactor and quartz round bottom flask was maintained at 25 °C by allowing water to circulate. The reaction mixture was first stirred for 30 min in the dark, and then irradiated for 3–18 h. After irradiation, the organic and aqueous lavers were separated using a separating funnel. The products of benzene oxidation were analyzed using a gas chromatography (GC) system (Agilent 4890) equipped with a flame ionization detector (FID) and an HP-5% phenyl methyl siloxane capillary column. Analysis of both the organic and aqueous layers confirmed the presence of phenol. It should be noted that any other liquid products in the chromatogram were also included in the quantitative estimation. Gas chromatography/mass spectrometry (GCMS) analysis was performed to detect the intermediates or products (GC model: Perkin Elmer Clarus 680 with DB-5 column; $60 \text{ m} \times 0.32 \text{ mm}$ and film 1.0 µm; MS model: Perkin Elmer Clarus -SQ 8 T). NIST library was referred to analyze phenol and its fragmentation patterns. Additionally, H2O2 conversion was determined by a calorimetric titration method based on the formation of a yellow colored complex Ti^{IV}-H₂O₂, using a UV/Vis spectrophotometer at 410 nm [18].

2.5. Control tests

Three different control experiments were performed for studying the photocatalytic oxidation of benzene under conditions of 1) $H_2^{16}O + H_2^{16}O_2 + air + benzene + CH_3CN$, 2) $H_2^{18}O + H_2^{16}O_2 + Ar + benzene + CH_3CN$, and 3) $H_2^{16}O + H_2^{16}O_2 + Ar + benzene + CH_3CN$. The final products were analyzed by GCMS.

3. Results and discussion

3.1. PXRD studies

The structural aspects of the prepared photocatalysts were investigated using PXRD. Fig. 1 shows that the PXRD patterns of all of the prepared $Ti_{1-x-y}M_{x+y}O_2$ catalysts matched with that of anatase phase TiO_2 (JCPDS 21-1272). No additional peaks that corresponded to Fe or Cr oxides were observed, clearly indicating that all of the $Ti_{1-x-y}M_{x+y}O_2$ materials retained the anatase phase of TiO_2 and that



Fig. 1. PXRD patterns of different materials, namely, (a) TiO_2 , (b) $Ti_{0.98}Fe_{0.02}O_2$, (c) $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$, (d) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and (e) $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$.

the doping level did not change the crystal structure of TiO₂ [34]. The absence of any oxides of Fe or Cr in Ti_{1-x-y}M_{x+y}O₂ illustrates the advantage of the SCM approach for incorporating Fe and Cr into the TiO₂ lattice [35]. The observed peak broadening confirmed the presence of nanosize crystalline particles. The XRD pattern did not show any peak shift after metal doping, most likely due to the low content of the dopant introduced into the TiO₂ lattice. The average crystallite size was estimated using the Scherrer equation to be approximately 19 nm, which was also confirmed by SEM and HRTEM analysis.

3.2. Surface area analysis

N2 adsorption-desorption isotherms were obtained in order to investigate the textural properties and mesoporous nature of TiO₂, Ti_{0.98}Fe_{0.02}O₂, Ti_{0.98}Fe_{0.015}Cr_{0.005}O₂, Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂, and Ti_{0.98}Fe_{0.005}Cr_{0.015}O₂. Fig. 2a shows the N₂ adsorption-desorption isotherms measured at 77 K; the Brunauer-Emmett-Teller (BET) method was used for surface area analysis, and the Barrett-Joyner-Halenda (BJH) method was used to determine the pore size distribution, which is shown in Fig. 2b. A type IV adsorption-desorption isotherm with an H2 hysteresis loop was observed for TiO₂ and all TiMx substrates, which confirmed the presence of mesopores [36,37]. The measured BET surface areas (S $_{\rm BET}$), pore sizes, and pore volumes of all materials are shown in Table 1. Ti_{0.98}Fe_{0.02}O₂ has mesopores with a higher surface area $(132 \text{ m}^2/\text{g})$ than those of TiO₂ (97 m²/g). Increasing the amount of Cr increased the surface area from $154 \text{ m}^2/\text{g}$ in the case of $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$ to 161 m²/g for $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$; however, the surface area decreased to 154 m²/g for Ti_{0.98}Fe_{0.005}Cr_{0.015}O₂. Significant changes in the pore size and pore volume were observed for $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$. The high surface area of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ of $161 \text{ m}^2/\text{g}$ confirmed the presence of mesopores with more active sites on the surface; this is a very critical factor for enhancing photocatalytic activity. Introduction of higher amounts of Cr further decreased the surface area and the pore volume, which indicated that the Cr ions had diffused into the bulk and blocked the pores of the material. These observations were fully supported by microscopy results. The observed average pore size distribution was approximately 5.3 \pm 0.1 nm and the average pore volume was 0.16 \pm 0.02 cm³/g. Fig. 2b shows the pore size distribution profiles, which indicate the presence of mesopores in all of the materials. In the case of $\rm Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$ (Fig. 2b), a significant decrease in the pore size indicates the introduction of more Cr ions into the pores.



Fig. 2. (a–e) N_2 adsorption-desorption isotherm and (f) pore size distribution profile of TiO_{2} , $Ti_{0.98}Fe_{0.02}O_2$, $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$, $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$ materials respectively.

Table	1

Catalyst	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)
TiO ₂	97	6.0	0.14
Ti _{0.98} Fe _{0.02} O ₂	132	5.5	0.17
Ti _{0.98} Fe _{0.015} Cr _{0.005} O ₂	154	5.5	0.18
Ti _{0.098} Fe _{0.01} Cr _{0.01} O ₂	161	5.5	0.19
${\rm Ti}_{0.98}{\rm Fe}_{0.005}{\rm Cr}_{0.015}{\rm O}_2$	154	4.3	0.16

3.3. HRTEM and SEM

The textural properties and morphologies of the materials were investigated by HRTEM and SEM. The HRTEM images of $Ti_{0.98}Fe_{0.02}O_2$ and $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ are shown in Fig. 3. It is evident that $Ti_{0.98}Fe_{0.02}O_2$ and $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ (and TiO_2 , Fig. S1 in the Supporting information (SI)) are well-interconnected spherical particles with disordered mesoporous structures (Fig. 3a and b). $Ti_{0.98}Fe_{0.02}O_2$ and $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ show similar textural characteristics as those of TiO_2 [34]. Both $Ti_{0.98}Fe_{0.02}O_2$ and $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ have particle sizes of 8–19 nm; larger nanoparticles were also observed by SEM (Fig. S1 in the SI). The d-spacing of 0.35 nm corresponds to the (101) plane of TiO_2 [38]. These results are consistent with the PXRD and N_2 adsorption-desorption isotherm results. Disordered mesoporosity is usually associated with short diffusion lengths and arises from the inter



Fig. 3. HRTEM images of a) $Ti_{0.98}Fe_{0.02}O_2$, b) and c) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and d–h) represent the respective elemental mapping images of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ sample. Color coding for different elements is shown on the images (Ti, red; Fe, blue; Cr, green; and O, cyan) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



Fig. 4. UV–vis spectra of (a) TiO_2 , (b) $Ti_{0.98}Fe_{0.02}O_2$, (c) $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$, (d) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and (e) $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$.

growth of nanoparticles, which can also result in the formation of aggregates with additional framework void space. These mesopores are only a few nanometers in depth, unlike conventional ordered mesoporous materials [31-39]. The HRTEM image (Fig. 3b) shows that the particles are well connected with each other, ensuring that they are electrically interconnected, which leads to increased mobility of the excited charge carriers to the surface of the photocatalyst where the reaction takes place. XPS results confirmed the presence of Fe³⁺ and ${\rm Cr}^{3\, +}.$ To verify the homogeneous distribution of Cr and Fe in the ${\rm TiO}_2$ matrix, HRTEM-EDX was conducted on Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ (Fig. 3c). All of the elements can be seen clearly (Fig. 3d-h), and it was found that Fe³⁺ and Cr³⁺ were highly dispersed (Fig. 3e and f, respectively). SEM-EDX also well supported with the above results (Fig. S2 in the SI). These observations confirmed the doping and uniform distribution of the metal ions on the surface and in the pores of the parent TiO₂ matrix. This feature of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ is essential for separating the charge carriers by trapping and, hence, enhancing their mobility towards the photocatalyst surface from the bulk. It is important to note that both Fe³⁺ and Cr³⁺ can act as electron trapping centers and synergistically enhance the hole utilization, and hence reduce charge recombination. This aspect is very important in the context of oxidation reactions. The porosity of the material was confirmed by the results of the adsorption isotherm studies and was in good agreement with the HRTEM images.

3.4. UV-vis absorption studies

UV-Vis absorption spectra were recorded to investigate the optical properties, extent of the effect of doping, and nature of the doped Fe and Cr species within the materials. Fig. 4 shows these UV-vis absorption spectra; the insets show the colors associated with TiO₂ and all of the TiMx materials. TiO2 shows absorption up to 380 nm in the UV region with a band gap of 3.2 eV, which is typical for titania. A red shift in the absorption edge was observed for Ti_{0.98}Fe_{0.02}O₂, which showed absorption at 400-600 nm in the visible light region, indicating the presence of Fe^{3+} in the TiO_2 lattice and the generation of a new Fe^{3+} 3d energy level in the TiO₂ CB, narrowing the band gap [40–43]. A pronounced narrow peak was observed at 480 nm for Ti_{0.98}Fe_{0.02}O₂, which corresponded to the d-d electronic transitions of iron atoms [44]. With increasing Cr content, the visible light absorption by the materials increased and the band gap decreased; the band gap of $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$ was $2.7\,eV,$ which was lower than that of $Ti_{0.98}Fe_{0.02}O_2$ (2.9 eV). The highest visible light absorption was observed for $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, which has a band gap of 2.6 eV, and no significant changes were observed in the absorption for Ti_{0.98}Fe_{0.005}Cr_{0.015}O₂. Two broad absorption peaks were observed for Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂, namely, an absorption peak with an onset at \sim 600 nm and a broad absorption ranging from 630 to 800 nm, which were attributed to the charge transfer from Cr^{3+} to Ti^{4+} and the d-d transitions of ${}^{4}A_{2g}$ to ${}^{4}T_{1g}$ in Cr³⁺ ions, respectively [15,16,45]. This suggested that the oxidation state of both Fe and Cr in the TiMx materials was +3. This conclusion was consistent with the XPS results. The inset in Fig. 4 shows the color changes in the samples from white (a) to pale yellow (b), then light brown (c) to brown (d), and finally dark brown (e). These color changes in the sample reflect the changes in the optical properties of the materials resulting from doping with Fe and Cr, which reduce the optical band gap of TiO2 and enhance the visible light absorption. These experimental observations suggest that there is a strong interaction between Fe, Cr, and TiO₂, and that the new energy level formed below the CB because of metal doping assists the separation of charge carriers [46-49].

3.5. Photoluminescence studies

The PL emission spectra of TiO₂ and all of the TiMx materials



 $\begin{array}{l} \mbox{Fig. 5. Photoluminescence studies (PL) of (a) TiO_2, (b) $Ti_{0.98}Fe_{0.02}O_2$, (c) $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$ (d) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and (e) $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$. \end{tabular}$

(Fig. 5) were measured using an excitation wavelength of 325 nm. The PL experiments revealed a decrease in the TiO₂ and emission intensity of the metal-doped TiO₂ as compared to that of undoped TiO₂ and, hence, a reduction in charge recombination. TiMx showed characteristic emission features at around 395, 405, 434, 446, and 464 nm. TiO₂ showed high-intensity emission peaks at 395 and 464 nm, which were attributed to the band gap transition and to the band edge free exciton emission, respectively [46]. The broad emission feature that starts at 441 nm may have resulted from the charge-transfer transition from Ti^{3+} to oxygen anions in a $[TiO_6]^{8-}$ complex that was present in the material along the (101) planes. All of the emission features were significantly smaller when Fe was introduced into the TiO₂ lattice and even smaller after co-doping with Fe and Cr. While Tio 98Fe0 02O2 showed emission features with the lowest intensity, undoped TiO₂ showed emission features with the highest intensity, indicating that the excited electrons are trapped by Fe³⁺ in TiO₂ under light illumination, which enhances the charge carrier separation and minimizes the electron-hole recombination [47]. The intensities of all emission features decreased exponentially with increasing Cr doping. However, the emission spectra of Ti_{0.98}Fe_{0.005}Cr_{0.015}O₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ were similar, likely due to a small difference in the amounts of Fe and Cr between the two photocatalysts. This observation is consistent with the results of the UV-vis absorption studies. The above discussion shows that excited electrons are synergistically trapped by both Fe and Cr [46-49], which increases the availability of holes for oxidation on the titania surface and leads to an effective charge separation. This also suggests that there are electronic interactions between Fe³⁺, Cr³⁺, and TiO₂. On the basis of PL studies, it can be inferred that the materials prepared using the SCM show substantially lower charge recombination owing to selective electron trapping by Fe^{3+} and Cr^{3+} in TiO₂, which enhances the availability of holes for oxidation.

3.6. Raman analysis

Fig. 6 shows the Raman spectra of TiO_2 and the TiMx photocatalysts. All photocatalysts showed the Raman-active fundamental modes [50,51] of anatase-phase titania. After Fe and Cr doping, the



Fig. 6. Raman spectra of (a) TiO_2 , (b) $Ti_{0.98}Fe_{0.02}O_2$, (c) $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$, (d) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and (e) $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$.



Fig. 7. XPS spectra (a) Ti 2p (along with XPS of TiO₂), (b) Fe 2p, and (c) Cr 2p for of fresh Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂.

intensities of all Raman-active modes decreased and a small peak shift from 145 to 147 cm⁻¹ was observed (Fig. 6 inset). The decrease in the peak intensity for all TiMx materials indicated that the incorporation of Fe and/or Cr into the TiO₂ lattice led to symmetry breaking in TiO₂ [32,50,51]. The shift in the peak at 145 cm⁻¹ confirmed the doping of Fe and Cr into the TiO₂ lattice. In addition, peak broadening confirmed the presence of nanosize particles, and these results were well supported by XRD. There were no characteristic peaks corresponding to Fe and Cr oxides in the Raman spectra, which implied the absence of Fe and Cr oxides in the TiMx materials [52].

3.7. X-ray photoelectron spectroscopy

XPS analysis was conducted in order to investigate the chemical compositions and electronic states of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂. Fig. 7 shows the XPS spectra for the Ti 2p, Fe 2p, and Cr 2p core levels of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂. The peaks at the binding energy of 458.6 \pm 0.1 eV (2p_{3/2}) for TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ (Fig. 7a) confirmed the presence of Ti⁴⁺ in all of the materials. Fe and Cr codoping in the titania lattice resulted in the appearance of a core-level Fe 2p_{3/2} and Fe 2p_{1/2} peaks at 711.3 and 724.1 eV, respectively (Fig. 7b), and a Cr 2p_{3/2} peak at 577 eV and low intensity peak at ~589 eV (Fig. 7c). These results indicate that the oxidation states of both Fe [53,54] and Cr [55] are predominantly +3 in Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂. The surface atom concentrations of Fe and Cr were 0.48% and 0.6%, respectively. The O 1 s core-level peaks for TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ appeared at 529.9 \pm 0.1 eV (Fig. S3 in the SI).

It was found that doping TiO₂ with Fe and Cr did not affect the binding energy. For more details on the band gap reduction and for a deeper understanding of benzene oxidation, the valence band XPS spectra of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ were recorded (Fig. 8a). The density of state (DOS) was determined with the help of UV-vis absorption spectroscopy (Fig. 8b) and the valence band XPS results. TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ showed valence band maximum (VBM) energies of ~ 2.62 and ~ 2.55 eV, and optical band gap energies of 3.2 and 2.6 eV, respectively. Therefore, the conduction band minima (CBM) of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ were calculated to be approximately -0.58 and $-0.05 \,\text{eV}$, respectively. Based on the above results, the absorption onset of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ was located at $\,\sim\!2.55\,eV$ and the maximum energy associated with the band tail was $\sim 1.90 \text{ eV}$. Therefore, the substantial narrowing of the band gap of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ was attributed to slight VB tailing [56]. Combining the experimental results with optical band gap calculations from the absorption measurements, it was suggested that doping with Fe and Cr reduces the band gap of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂. Furthermore, it can be concluded that the VBM and CBM also decrease the band gap of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂.

3.8. Photocatalytic benzene oxidation

The photocatalytic performances of all TiMx photocatalysts under UV and visible light irradiation for the oxidation of benzene to phenol for different time durations were evaluated and the results are shown in Table 2. In the absence of light illumination, $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$



Fig. 8. a) Valence band XPS spectra of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ and b) schematic diagram of density of state of TiO₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂.

Table 2

Photocatalytic benzene oxidation to phenol using M (= Fe and/or Cr) doped TiO_2 photocatalysts.

Photocatalyst	t (h)	Benzene	Phenol		
		conv. (%)	Yield (%)	Selectivity (%)	
Ti _{0.98} Fe _{0.02} O ₂	6	13 ± 0.5	$12.0~\pm~0.5$	92 ± 0.5	
Ti _{0.98} Fe _{0.02} O ₂	12	18 ± 0.3	$14.0~\pm~0.3$	77 ± 0.3	
Ti _{0.98} Fe _{0.015} Cr _{0.005} O ₂	6	$13.3~\pm~0.4$	12.2 ± 0.4	92 ± 0.4	
Ti _{0.98} Fe _{0.015} Cr _{0.005} O ₂	12	20 ± 0.6	18.2 ± 0.6	91 ± 0.6	
Ti _{0.98} Fe _{0.01} Cr _{0.01} O ₂	6	15 ± 0.4	14.1 ± 0.4	94 ± 0.4	
Ti _{0.98} Fe _{0.01} Cr _{0.01} O ₂	12	28 ± 0.5	25.2 ± 0.5	90 ± 0.5	
Ti _{0.98} Fe _{0.01} Cr _{0.01} O ₂ ^a	12	$26.8~\pm~0.6$	24.0 ± 0.6	89 ± 0.6	
Ti _{0.98} Fe _{0.005} Cr _{0.015} O ₂	12	26 ± 0.6	22.9 ± 0.6	88 ± 0.6	
Ti _{0.98} Cr _{0.02} O ₂	12	16 ± 0.4	$10.7~\pm~0.4$	67 ± 0.4	

 * Reaction conditions: catalyst 30 mg; benzene 1 ml, CH₃CN 2 ml; H₂O₂ (25%) 2 ml; light source used 450 W mercury lamp ($\lambda=$ 200–400 nm).

^a Dissolved oxygen was removed by argon bubbling for 30 min.

showed very low benzene conversion (~0.5%) with trace amounts of phenol after 24 h (Table S1 in the SI). The negligible conversion can be rationalized by considering that the conventional Fenton oxidation reaction is homogeneous, whereas the reaction in the current study is heterogeneous. Moreover, strong acids, such as HClO₄, CF₃COOH, and H₂SO₄, are necessary for the Fenton oxidation reaction [17–19] while the photocatalytic benzene oxidation reaction was performed in the absence of any acid. Therefore, the benzene oxidation reaction would occur primarily via a photocatalytic process with assistance of H₂O₂, without a significant contribution of Fenton reaction to the conversion of benzene.

Using Ti_{0.98}Fe_{0.02}O₂, 13% benzene conversion with 92% selectivity was attained after 6 h of irradiation (Table 2). The conversion of benzene increased to 18% when the irradiation time was increased to 12 h. However, the reaction selectivity toward the phenol product decreased to 77% with prolonged reaction time, primarily due to further oxidation of the generated phenol to side products such as hydroquinone. In addition, a qualitative analysis of the gaseous products was carried out using a GC system equipped with a thermal conductivity detector. It was found that small amounts of hydrogen and CO2 were produced in the reaction, likely due to the reformation of organic compounds via secondary reactions [31,57–61]. Some of the generated charge carriers were consumed in these secondaryreactions, affecting the yield and selectivity for the primary product (phenol). However, we believe that this occurs mainly to maintain the charge neutrality of the system, which prevents the electron-hole recombination in the photocatalyst. In addition, the conversion of benzene (16%) achieved using Ti_{0.98}Cr_{0.02}O₂ after 12 h irradiation was close to that attained using Ti_{0.98}Fe_{0.02}O₂ (18%) after 12 h irradiation.

The introduction of different amounts of Cr and Fe into the TiO₂ lattice led to higher benzene conversions, yields, and selectivities than those obtained with Fe-doped $\rm TiO_2$ (Ti_{0.98}Fe_{0.02}O_2) after 12 h of UV irradiation. The results are shown in Table 2. Co-doping with Fe and Cr resulted further increasing of benzene conversions and phenol yields for $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2.$ The results obtained from different irradiation time are shown in Fig. 9a, while the phenol yields obtained are shown in Fig. 9b. The benzene conversion and phenol yield were significantly increased from 3 to 12 h under light irradiation, which highlighted the importance of Fe³⁺ and Cr³⁺ dopants in the trapping of excited electrons. Ti_{0.98}Fe_{0.005}Cr_{0.015}O₂ displayed low benzene conversion (26%) and phenol yield (22.9%) compared with those obtained using Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ photocatalyst (Table 2). The selectivity of phenol was decreased to 88%. The Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ sample exhibited a benzene conversion of 28% (turnover frequency (TOF) = 38.7 h^{-1} ; Table S2 in the SI) with the phenol yield and selectivity of 25.2% and 90%, respectively.

Fig. 10 shows the phenol yields obtained using different

photocatalysts under 12 h UV irradiation. Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ photocatalyst showed the highest photocatalytic activity, indicating that an optimal level of Fe³⁺ and Cr³⁺ doping (1 at% each) is necessary. The starting reaction solution (colorless) underwent a color change to brown toward the end of the reaction (Fig. S4 in the SI), indicating that this reaction took place photocatalytically. However, the phenol selectivity decreased from 90% to 80% after 18 h of irradiation because of the secondary reactions.

Control experiments for benzene oxidation either without a photocatalyst or under dark conditions were also carried out (Table S1 in the SI). No changes in the starting reactant molecules were observed in the reactions carried out without any catalyst in the dark. UV irradiation for 18 h in the absence of any photocatalyst led to some photochemical oxidation of benzene. The formation of side products indicated the possibility of a free radical mechanism, which operated exclusively under these conditions because of photochemical conversion and homogeneous cleavage of hydrogen peroxide.

Other control experiments were performed for the photocatalytic benzene oxidation under conditions of $H_2^{16}O + H_2^{16}O_2 + Argon (Ar)$ + benzene + CH_3CN , $H_2^{16}O$ + $H_2^{16}O_2$ + Air + benzene + CH_3CN , and $H_2^{18}O + H_2^{16}O_2 + Ar + benzene + CH_3CN$) to examine the origin of oxygen in the final product phenol. The yields obtained under later two experimental conditions were similar each other ($\sim 25\%$) (Table 2), indicating that the contribution of oxygen to the formation of reactive hydroxyl radicals was not significant in our photocatalytic system. A possible explanation is that trapping of photo-excited electron by Cr^{3+} and Fe^{3+} dopant levels is more predominant than that by oxygen molecule. Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ showed the highest activity under UV light, which underscores the importance of energetic holes on the titania surface for benzene oxidation. The low activity of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ under 1 sun illumination conditions (AM 1.5) suggested that the photocatalytic activity for benzene oxidation depended on the VB position (discussed in the proposed mechanism section) of TiO_2 [43]. The pristine TiO_2 sample showed a lower activity than that of the TiMx materials, underscoring the important role of metal doping (Fe and Cr) in effective charge separation. Photocurrent measurements for Ti_{0.98}Fe_{0.02}O₂ and Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ under simulated solar light with a cut-off filter indicated that light only having $\lambda \ge 400$ nm passed through (Fig. 11). The photocurrent generated by Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ was about four times higher than that of Ti_{0.98}Fe_{0.02}O₂ under visible light irradiation ($\lambda \ge 400$ nm), indicating a greater visible light absorption by the former. The higher photocurrent of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ was ascribed to more holes and electrons generated by this sample. The effective utilization of holes would lead to higher photooxidation of benzene to phenol by $\text{Ti}_{0.98}\text{Fe}_{0.01}\text{Cr}_{0.01}\text{O}_2.$ There were no significant changes in the photocatalytic activities of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ after three repeated reactions, which illustrated the stability of the catalyst in continuous operating mode (Fig. S5 in the SI). In addition, there was no significant variation in the photocurrent measurements of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ (Fig. 11). The XRD and XPS analyses showed no changes in the corresponding patterns between the fresh and used samples, confirming the high stability of the photocatalyst after three consecutive reactions (Figs. S6 and S7 in the SI, respectively).

As shown in Table 3, the benzene conversion (25%), phenol yield (22.5%), and selectivity (90%) obtained using the $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ photocatalyst were higher than or comparable with those obtained using other photocatalysts with or without containing a noble metal reported in earlier studies [8,17–19,21,23,31,58,62–65,57]. For example, MOFs based MIL-100(Fe) nanosphere photocatalyst displayed a benzene conversion of 34.4% with a phenol selectivity of 98% under visible light irradiation [62]. A mesoporous titania (mTiO₂) showed a phenol yield of 19% with a selectivity of 83% under UV-light irradiation [8]. Fe-g-C₃N₄/SBA-15 photocatalyst exhibited a benzene conversion of 11.9% with a phenol selectivity of 83% [19]. An Au/Ti_{0.98}V_{0.02}O₂ photocatalyst provided a benzene conversion of 18% with a phenol yield of 15.9% was achieved under UV-light irradiation [31].



Fig. 9. Time-dependent photocatalytic benzene oxidation results for (a) benzene conversion and phenol selectivity and (b) phenol yield with Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ after UV irradiation.



Fig. 10. Phenol yields observed with (a) $Ti_{0.98}Cr_{0.02}O_2$, (b) $Ti_{0.98}Fe_{0.02}O_2$, (c) $Ti_{0.98}Fe_{0.015}Cr_{0.005}O_2$, (d) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$, and (e) $Ti_{0.98}Fe_{0.005}Cr_{0.015}O_2$ for 12 h UV irradiation.



Fig. 11. Photocurrent measurements of (a) $Ti_{0.98}Fe_{0.02}O_2$ and (b) $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ with a solar simulated light source, $\lambda\geq 400$ nm.

Leaf structured ZnO nano photocatalyst showed a benzene conversion of 5.2% with a phenol selectivity of 92% under UV-light irradiation [57]. And also, current photocatalyst showed a higher photocatalytic activity than those obtained using Fe₅V_{2.5}Cu_{2.5}/TiO₂ [63], Fe/activated carbon [64], Fe/SBA-16 catalyst [65], Fe-CN/TS-1 [17], Fc-MCN_{1.0}-5 [18], and Au/TiO₂ [23]. The superior or comparable photocatalytic efficiency of Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂ was primarily attributed to the synergistic effect of Fe and Cr co-doping for trapping charge carriers. The superior photocatalytic efficiency of $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ to the other photocatalysts was primarily attributed to the synergistic effect of Fe and Cr co-doping for trapping charge carriers. Consequently, the photocatalyst developed in the current study can be used to achieve costeffective and highly efficient phenol production. Although TiO₂ doped with Fe and Cr showed visible light absorption, low benzene conversion was observed even after irradiation for 24 h with visible light (AM1.5). This indicated that a small number of holes were generated as compared to those generated upon UV light irradiation. Further fundamental studies are required to improve the performance of the photocatalyst under 1 sun illumination condition. Longer irradiation times with visible light increase the photocatalytic activity linearly.

However, the phenol selectivity decreased from 90% to 80% after 18 h of irradiation; this is mainly due to the over-oxidation of generated phenol to other side products such as p-benzoquinone (p-BQ), hydroquinone (HyQ), H₂, and/or CO₂ [58–61]. For example, Likozar et al. observed p-BQ as a side product during the photocatalytic oxidation of benzene to phenol over carbon nanotube (CNT)-supported Cu and TiO₂ photocatalytic system under UV-light irradiation [58]. They also carried out the UV light-assisted photocatalytic degradation of phenol on TiO₂ photocatalyst and observed that BQ and HyQ were as main intermediates, which were mineralized to CO₂ after prolonged reaction time [59]. Bui et al. examined the photocatalytic degradation of benzene over TiO2 under UV-light irradiation and reported a small amount of BQ, HyQ, and CO₂ generated during the reaction [60]. Also, a phenol degradation over TiO2-nanotube under UV-light irradiation led to the generation of benzoquinone as a side product [61]. The GCMS results obtained in our study show that p-benzoquinone was generated as a major organic side product during the conversion reaction of benzene to phenol (Fig. S8 in the SI).

3.9. Proposed mechanism

A possible mechanism for the oxidation of benzene to phenol was proposed (Fig. 12) on the basis of the photocatalytic experiments carried out under different conditions, characterization studies, GCMS

Table 3

Comparison (of photocatalytic	activity of	f Ti _{0.98} Fe _{0.01} Cr ₀	$_{01}O_2$ with o	ther reported	photocatalysts	(or catalyst) f	for benzene	oxidation to	phenol	reaction
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S.No.	Photocatalyst (or catalyst)	Condition	Benzene conversion (%)	Phenol Yield (%)	Phenol Selectivity (%)	Reference
1.	mTiO ₂	UV-light	23	19	83	[8]
2.	Fe-CN/TS-1	Visible light	-	10	18.4	[17]
3.	Fc-MCN _{1.0} -5	Visible light	-	14.4	26.4	[18]
4.	Fe-g-C ₃ N ₄ /SBA-15	Visible light	11.9	-	20.7	[19]
5.	MIL-100 (Fe) bulk	Visible light	30.6	29.4	96	[21]
6.	Au/TiO ₂	Visible light	-	13	89	[23]
7.	Au/Ti _{0.98} V _{0.02} O ₂	UV-light	18	15.9	88	[31]
8.	ZnO	UV-light	5.2	4.8	92	[58]
9.	MIL-100 (Fe) nanosphere	Visible light	34.4	-	98	[62]
10.	Fe ₅ V _{2.5} Cu _{2.5} /TiO ₂	303 K	9.8	7.2	73	[63]
11.	Fe/activated carbon	303 K	19.6	17.5	89.3	[64]
12.	Fe/SBA-16	65 °C	12.1	11.7	96.4	[65]
13.	${\rm Ti}_{0.98}{\rm Fe}_{0.01}{\rm Cr}_{0.01}{\rm O}_2$	UV-light	28	25.2	90	This work

analysis, isotopic measurements, valence band XPS results, and previous literature. In the proposed mechanism, phenol was thought to be generated via two reaction paths, namely path-A and path-B. TiO₂ generates electron and hole charge carriers upon UV light absorption. The photogenerated electrons are excited from the VB to the CB via the electron trapping level resulting from doping with Fe³⁺ and Cr³⁺ [15–18]. In path-A, the trapped electrons in the dopant level reduce Fe^{3+} to Fe^{2+} , which then reacts with H_2O_2 and a proton (from H_2O) to produce a hydroxyl radical and Fe³⁺. The formed hydroxyl radicals attack the aromatic benzene ring to form hydroxycyclohexadienyl radicals [15-18,66-68]. The photogenerated positive holes in the VB or Fe³⁺ oxidize the hydroxycyclohexadienyl radicals to phenol via a deprotonation process to restart the photocatalytic cyclic reaction [60,66–69]. The control tests suggested that trapping of photo-excited electron by Cr³⁺ and Fe³⁺ dopant levels is more predominant than that by oxygen molecule. In path-B, the generated holes in the VB of TiO₂ react with benzene to produce benzene radical ions. These radical ions react with hydroxyl radicals to form phenol, likely via the deprotonation of an unstable intermediate [31,49]. In the absence of peroxide and under dark condition, no benzene oxidation occurred, confirming that both of these conditions are crucial for benzene oxidation reactions. Phenol incorporated with ¹⁶O (m/z 94) was observed in the GCMS spectra, when ¹⁶O water was used for photocatalytic benzene oxidation (Fig. S9 in the SI), indicating that the hydroxyl radical was originated from water only. However, both 16 O (m/z 94) and 18 O (m/z 96)-incorporated phenols were observed, when ¹⁸O- water was used for the photocatalytic benzene oxidation (Fig. S10 in the SI), indicating that

the hydroxyl radical was originated from both water and H_2O_2 .

Upon irradiation, the formation of gaseous products such as CO₂ and H₂ was observed, likely due to the photocatalytic reforming of benzene, acetonitrile, and/or phenol in possible secondary reactions through the consumption of holes in the VB of titania. Based on the carbon balance concept, the phenol selectivity was 90%, while the rest 10% was assigned to unknown byproducts. PL and optical studies revealed the formation of an electron trapping level in the CB of TiO₂ due to Fe³⁺ and Cr³⁺ doping. The PL emission features were observed to be weaker after the incorporation of Fe, indicateing the entrapment of excited electrons. This phenomenon enhances the charge carrier separation and lowers the incidence of their recombination. Thus, more holes are available in the VB of TiO₂ for benzene oxidation. Co-doping with Fe and Cr led to further reduction of emission intensity, indicating that Fe and Cr synergistically capture the excited electrons in the trapping level. The photogenerated holes are then effectively utilized for benzene oxidation, highlighting the importance and role of Fe and Cr as trapping centers. Meanwhile, surface defects or non-radiative decay may reduce PL intensity, but they are not likely to be a major contributor for the reduced PL intensity in our photocatalytic system.

Since the VBM of the $Ti_{0.98}Fe_{0.01}Cr_{0.01}O_2$ catalyst is located at 2.55 eV, the DOS from the valence band XPS spectra (Fig. 8b) and the photocatalytic benzene oxidation reaction appear to demonstrate that benzene oxidation occurs on the surfaces of TiO_2 and that Fe and Cr assist in the trapping of excited electrons and generation of hydroxyl radicals. This underscores the necessity of wide-band-gap semiconductor materials such as TiO_2 and ZnO [57] with valence band



Fig. 12. Possible mechanism of photocatalytic benzene oxidation to phenol.

maxima of $\sim 2.5 \text{ eV}$ for benzene oxidation. The electrons in the CB of TiO₂ can undergo three different processes under the reaction conditions: (a) recombination, (b) consumption by H_2O_2 or (c) trapping by Fe^{3+} and Cr^{3+} . The increase in phenol yield from 14% ($Ti_{0.98}Fe_{0.02}O_2$) to 25.2% ($Ti_{0.98}Fe_{0.01}C_{0.01}O_2$) underscores the prevalence of processes b and c, which help the reaction. A colorimetric titration test showed that 97% of the initially added H₂O₂ was used for the benzene oxidation reaction (Eq. S1 in the SI).

The phenol production selectivity was obtained in the range of 67–92% for our catalysts, indicating the formation of side products. As mentioned earlier, the GCMS results obtained in our study showed that p-benzoquinone was a major organic side product during the conversion reaction of benzene to phenol (Fig. S8 in the SI). In addition, hydroquinone, CO2, and H2 can be produced during the benzene-tophenol conversion reactions [31].

4. Conclusion

The SCM approach was employed for the synthesis of disordered mesoporous Ti_{0.98}Fe_{0.02}O₂ and Ti_{0.98}(Fe + Cr)_{0.02}O₂ nanocrystalline photocatalysts. XPS, Raman analysis, EDX spectroscopy, and other characterization studies confirmed the doping of Fe and Cr into the TiO₂ matrix. PL studies revealed an electron transfer mechanism between the metal dopants and titania. The mobility of the photoexcited charge carriers was enhanced by a disordered mesoporous structure, and the electrically interconnected and integrated $Ti_{0.98}(Fe + Cr)_{0.02}O_2$ nanocrystallites. Moreover, doping with metal ions reduced the recombination of excited charge carriers and thus expedited their separation and migration to the surface of the catalyst for enhanced reactivity. Introduction of Fe³⁺ and Cr³⁺ increased the conversion of benzene and the selectivity of phenol. Co-doping with Fe and Cr resulted in visible light absorption because of the formation of a trapping level in the band gap of TiO₂, and co-doped TiO₂ (Ti_{0.98}Fe_{0.01}Cr_{0.01}O₂) generated four times as much current as Fe-doped TiO_2 ($Ti_{0.98}Fe_{0.02}O_2$). Fe and Cr would act as electron trapping centers and assist in charge separation. This would increase the diffusion and availability of holes on the titania surface and enhance their utilization for oxidation, which led to high phenol yields. Visible light absorption and efficiency of light energy into current or chemical energy conversion highlight the potential of $Ti_{0.98}$ (Fe + Cr)_{0.02}O₂ photocatalyst for the application of C-H activation, optoelectronics and variety organic transformation reactions.

Disclosure statement

The author declares that no conflicting actual or potential interests exist.

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Appendix A. Supplementary data

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References

- [1] K. Maeda, K. Domen, J. Phys. Chem. Lett. 18 (2010) 2655-2661.
- [2] A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C 1 (2000) 1–21. [3] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253-278.
- [4] L. Min, Q. Xiaoqing, M. Mashiro, H. Kazuhito, J. Am. Chem. Soc. 135 (2013) 10064-10072.
- [5] N. Herron, C.A. Tolman, J. Am. Chem. Soc. 109 (1987) 2837-2839.

- [6] H. Mimoun, L. Saussine, E. Daire, M. Postel, J. Fischer, R. Weiss, J. Am. Chem. Soc. 105 (1983) 3101-3110.
- [7] H. Park, W. Choi, Catal. Today 101 (2005) 291-297.
- [8] Y. Shiraishi, N. Saito, T. Hirai, J. Am. Chem. Soc. 127 (2005) 12820-12822.
- [9] O. Tomita, B. Ohtani, R. Abe, Catal. Sci. Technol. 4 (2014) 3850-3860.
- [10] O. Tomita, R. Abe, B. Ohtani, Chem. Lett. 40 (2011) 1405-1407.
- [11] G. Tanarungsun, W. Kiatkittipong, S. Assabumrungrat, H. Yamada, T. Tagawa, P. Praserthdam, J. Ind. Eng. Chem. 13 (2007) 870-877.
- A. Antonyraj, K. Churchil, Srinivasan, Catal. Surv. Asia 17 (2013) 47-70. [12]
- [13] M. Fujihira, Y. Satoh, T. Osa, Nature 293 (1981) 206-208.
- [14] G. Palmisano, S. Yurdakal, V. Augugliaro, V. Loddo, L. Palmisano, J. Adv. Synth. Catal. 349 (2007) 964-970.
- [15] M. Nishikawa, W. Shiroishi, H. Honghao, H. Suizu, H. Nagai, N. Saito, J. Phys. Chem. A 121 (2017) 5991-5997.
- [16] J.W. Han, Y.M. Lee, W. Nam, S. Fukuzumi, Chem. Sci. 8 (2017) 7119–7125.
- [17] X. Ye, Y. Cui, X. Qiu, X. Wang, Appl. Catal. B 152-153 (2014) 383-389.
- [18] X. Ye, Y. Cui, X. Wang, ChemSusChem 7 (2014) 738-742.
- [19] X. Chen, J. Zhang, X. Fu, M. Antonietti, X. Wang, J. Am. Chem. Soc. 131 (2009) 11658-11659.
- [20] P. Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, RSC Adv. 3 (2013) 5121-5126.
- [21] D. Wang, M. Wang, Z. Li, ACS Catal. 5 (2015) 6852-6857.
- [22] Y. Ide, M. Matsuoka, M. Ogawa, J. Am. Chem. Soc. 132 (2010) 16762-16764. [23] Y. Ide, N. Nakamura, H. Hattori, R. Ogino, M. Ogawa, M. Sadakane, T. Sano, Chem.
- Commun. 47 (2011) 11531-11533. [24] Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Dai, M.-H. Whangbo, J. Mater. Chem. 21
- (2011) 9079-9087. [25] Z. Zheng, B. Huang, X. Meng, J. Wang, S. Wang, Z. Lou, Z. Wang, X. Qin, X. Zhang,
- Y. Dai, Chem. Commun. 49 (2013) 868-870.
- [26] R. Su, L. Kesavan, M.M. Jensen, R. Tiruvalam, Q. He, N. Dimitratos, S. Wendt, M. Glasius, C.J. Kiely, G.J. Hutchings, F. Besenbacher, Chem. Commun. 50 (2014) 12612
- [27] J. Yu, Y. Hai, B. Cheng, J. Phys. Chem. C 115 (2011) 4953-4958.
- [28] J. Soria, J.C. Conesa, V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, J. Phys. Chem. 95 (1991) 274–282.
- [29] J. Kou, C. Lu, J. Wang, Y. Chen, Z. Xu, R.S. Varma, Chem. Rev. 117 (2017) 1445–1514.
- [30] J. Choi, H. Park, M.R. Hoffmann, J. Phys. Chem. C 114 (2010) 783-792.
- [31] P. Devaraji, N.K. Sathu, C.S. Gopinath, ACS Catal. 4 (2014) 2844–2853.
- [32] K. Sivaranjani, A. Verma, C.S. Gopinath, Green Chem. 14 (2012) 461-471.
- [33] W.K. Jo, S. Kumar, M.A. Isaacs, A.F. Lee, S. Karthikeyan, Appl. Catal. B 201 (2017) 159-168.
- [34] K. Sivaranjani, C.S. Gopinath, J. Mater, Chem. 21 (2011) 2639-2647.
- [35] A. Varma, A.S. Mukasyan, A.S. Rogachev, K.V. Manukyan, Chem. Rev. 116 (2016) 14493-14586.
- [36] P.C.S. Bezerra, R.P. Cavalcante, A. Garcia, H. Wender, M.A.U. Martines, G.A. Casagrande, J. Giménez, P. Marco, S.C. Oliveiraa, A.M. Jr, J. Braz. Chem. Soc. 28 (2017) 1788-1802.
- [37] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603-619.
- [38] X. Chen, L. Liu, P.Y. Yu, S.S. Mao, Science 331 (2011) 746-750.
- [39] K. Sivaranjani, S.R. Ambal, T. Das, K. Roy, S. Bhattacharyya, C.S. Gopinath, ChemCatChem 6 (2014) 522-530.
- [40] K.K. Patra, B.D. Bhuskute, C.S. Gopinath, Sci. Rep. 7 (2017) 6515. [41] Z. Luo, J.C. Smith, W.H. Woodward, A.W. Jr, J. Phys. Chem. C 116 (2012)
- 7219-7226
- [42] M. Asilturk, J. Photochem. Photobiol. A 203 (2009) 64-71.
- [43] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669-13679.
- [44] M.A.A. Mamun, Y. Kusumoto, M.S. Islam, J. Mater. Chem. 22 (2012) 5460-5469. [45] X. Fan, X. Chen, S. Zhu, Z. Li, T. Yu, J. Ye, Z. Zou, J. Mol. Catal. A 284 (2008)
- 155-160.
- [46] H. Dang, X. Dong, Y. Dong, Y. Zhang, S. Hampshire, Int. J. Hydrogen Energy 38 (2013) 2126-2135.
- [47] X.Y. Li, P.L. Yue, C. Kutal, New J. Chem. 27 (2003) 1264-1269.
- [48] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, J. Phys. Chem. Solid. 63 (2002) 1909-1920.
- [49] A. Litke, E.J.M. Hensen, J.P. Hofmann, J. Phys. Chem. C 121 (2017) 10153-10162. [50] K. Bhattacharya, S. Varma, A.K. Tripathi, S.R. Bharadwaj, A.K. Tyagi, J. Phys.
- Chem. C 112 (2008) 19102-19112. [51] R.S. Zeferino, M.B. Flores, U. Pal, J. Appl. Phys. 109 (2011) 014308.
- [52] H. Ren, P. Koshy, F. Cao, C.C. Sorrell, Inorg. Chem. 16 (2016) 8071-8081.
- [53] S. Mansingh, D.K. Padhi, K.M. Parida, Int. J. Hydrogen Energy 41 (2016)
- 14133-14146.
- [54] D. Channei, B. Inceesungvorn, N. Wetchakun, S. Ukitnukun, A. Nattestad, J. Chen, S. Phanichphan, Sci. Rep. 4 (2014) 5757.
- [55] Y.H. Peng, G.F. Huang, W.Q. Huang, Adv. Power Technol. 23 (2012) 8-12.
- [56] S.A. Ansari, M.H. Cho, Sci. Rep. 6 (2016) 25405.
- [57] N.K. Sathu, P. Devaraji, C.S. Gopinath, J. Nanosci. Nanotechnol. 16 (2016) 9203-9208.
- [58] V.D.B.C. Dasireddy, B. Likozar, J. Taiwan Inst. Chem. Eng. 82 (2018) 331-341.
- M. Krivec, A. Pohar, B. Likozar, G. Drazic, AIChE J. 61 (2015) 572-581. [59] [60] T.D. Bui, A. Kimura, S. Ikeda, M. Matsumura, J. Am. Chem. Soc. 132 (2010)
- 8453-8458.
- L. Suhadolnik, A. Pohar, B. Likozar, M. Ceh, Chem. Eng. J. 303 (2016) 292-301. [61]
- B. Xu, Z. Chen, B. Han, C. Li, Catal. Commun. 98 (2017) 112-115. [62] [63] G. Tanarungsun, W. Kiatkittipong, P. Praserthdam, H. Yamada, T. Tagawa, S. Assabumrungrat, J. Ind. Eng. Chem. 14 (2008) 596-601.

- [64] Y. Zhong, G. Li, L. Zhu, Y. Yan, G. Wu, C. Hu, J. Mol. Catal. A Chem. 272 (2007) 169–173.
- [65] M. Jourshabani, A. Badiei, Z. Shariatinia, N. Lashgari, G.M. Ziarani, Ind. Eng. Chem. Res. 55 (2016) 3900-3908.
- [66] A. Kunai, S. Hata, S. Ito, K. Sasaki, J. Am. Chem. Soc. 108 (1986) 6012-6016.

- [67] C. Walling, Acc. Chem. Res. 8 (1975) 125–131.
 [68] J.R.L. Smith, R.O.C. Norman, J. Chem. Soc. 113 (1963) 2897–2905.
 [69] S. George, S. Pokhrel, Z. Ji, B.L. Henderson, T. Xia, L. Li, J.I. Zink, A.E. Nel, L. Madler, J. Am. Chem. Soc. 133 (2011) 11270–11278.