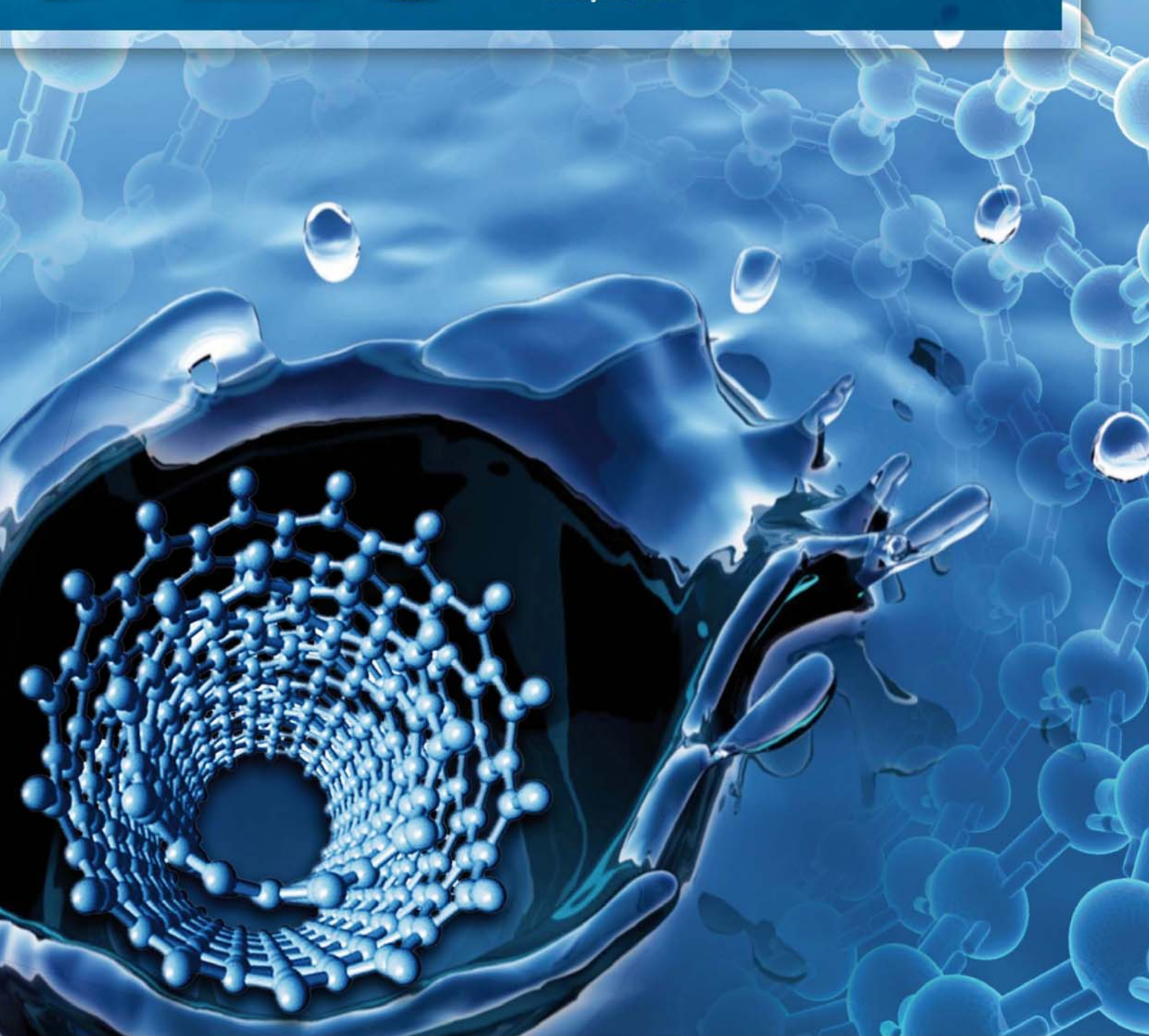


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Effect of transition metal doping under reducing calcination atmosphere on photocatalytic property of TiO₂ immobilized on SiO₂ beads

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Abstract

TiO₂ immobilized on SiO₂ (TiO₂/SiO₂) have been prepared by sol-gel method and various ions of transition metals (Cr³⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) were doped on the photocatalyst using wet impregnation method under reducing calcination atmosphere. The photocatalytic activity of metal doped TiO₂/SiO₂ towards phenol degradation under black light irradiation were investigated and compared with undoped TiO₂/SiO₂. The results showed that the photoresponse of Cu²⁺ and Zn²⁺ doped TiO₂/SiO₂ were larger than undoped TiO₂/SiO₂, indicating that the photogenerated carriers were separated more efficiently in Cu²⁺ and Zn²⁺ doped TiO₂/SiO₂. The reactivity was in the order of Cu²⁺ > Zn²⁺ > Ni²⁺ > Cr³⁺ > Co²⁺. The different photoreactivity was ascribed to combine effect of the different ionic radii and photocorrosion tendency of the dopants. The sample was also characterized by surface analytical methods such as X-ray diffraction, scanning electron micrograph/electron dispersive X-ray analyzer and UV-Vis absorption spectrum.

Key words: heterogeneous photocatalysis; TiO₂; SiO₂ beads; metal doping; photodecomposition

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Introduction

TiO₂ is regarded as the most efficient and environmentally benign photocatalyst, and it has been most widely used for photodegradation of various pollutants. The TiO₂ photocatalyst has attracted much interest of many researchers in recent years for its ability to simultaneously address all the three classes of water contaminants: organic, inorganic and microbiological with minimal risk of the production of harmful byproducts (Bhatkhande et al., 2001; Reddy et al., 2007; Wang et al., 2004).

The titania acts photocatalytically by absorbing UV light ($\lambda < 380$ nm) to generate electron-hole pairs. These separated electrons and holes are then available to drive reduction and oxidation reactions, respectively. However, the fast electron-hole pair recombination decreases its catalytic efficiency (Tang et al., 2008). Besides this, the need of UV light for its excitation restricts the use of easily available sunlight and cheaper visible light. Further it is also necessary to deposit the photocatalyst on suitable support to avoid the need for postphotocatalytic filtration to remove the photocatalyst (Zhao et al., 1998).

It is well known that the absorption of photons with energy equal or higher than the potential difference between conduction and valence band energies results in the formation of conduction band electrons (e) and accompanying valence band holes (h⁺) and the photocatalytic reaction mostly takes place on the surface of the semiconductor. So the key issue to improve the efficiency of the photocatalytic process is to ensure that more photo-generated e and h⁺ can move to the surface of the semiconductor particles before they recombine in bulk.

Many attempts have been made to improve the photocatalytic activity by doping metal ions such as Pt, Pd, Au, and Ag. The doped metal ion enhances the photocatalytic activity by reducing electron-hole pair recombination and/or reducing the band gap. Au and Pt metal ions doping has successfully improved the activity of TiO₂ powder but these are very expensive and rare elements (Sakthivel et al., 2004; Xin et al., 2005; Zang et al., 1998; Subramanian et al., 2001).

Yang et al. (2007) reported that oxygen vacancies will be created when calcination was done under reducing atmosphere. The oxygen vacancies belong to positive centers and are easily excited to the conduction band and act as donor. The donor band level is at the bottom of conduction band. Because of the formation of donor band level in

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between valance band and conduction band, the photo-generated electrons can jump step by step and reduce the energy gap. A new and cheaper reducing calcination atmosphere has been used in this research work together with metal doping to enhance the light absorption intensity.

Matsuo and Nakano (1988) successfully prepared TiO_2 immobilized on SiO_2 beads ($\text{TiO}_2/\text{SiO}_2$) with enhanced photocatalytic activity. In our research work, the $\text{TiO}_2/\text{SiO}_2$ photocatalyst is modified by doping metal ions under reducing calcination atmosphere and their photocatalytic behavior was investigated. Phenol and its derivatives are widely distributed contaminants of natural waters and wastewater. Of these compounds, phenol is hard to be degraded (Zhang et al., 2000), therefore we employed the photodegradation of phenol as model reaction to investigate the photocatalytic activity of metal doped $\text{TiO}_2/\text{SiO}_2$.

1 Experimental

1.1 Preparation of catalyst

The photocatalyst was prepared using titanium tetraisopropoxide (TIP), isopropanol (IPA) and CARICTQ-30 SiO_2 beads. Analytical grade chemicals of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as precursor for metal ion doping. The porous SiO_2 beads (2.8–3.2 mm diameter; BET surface area = $107 \text{ m}^2/\text{g}$) were impregnated with a 1:1 molar mixture of TIP and IPA for 1 day. Then it was hydrolyzed under flowing humid air for 1 night and finally calcined at 500°C for 2 hr under reducing atmosphere in an alumina crucible (Chand et al., 2009) to obtain TiO_2 photocatalyst supported on SiO_2 beads ($\text{TiO}_2/\text{SiO}_2$ photocatalyst). For further preparation of metal-doped $\text{TiO}_2/\text{SiO}_2$ catalyst, $\text{TiO}_2/\text{SiO}_2$ photocatalyst was impregnated with an aqueous solution (0.1 mol%, 0.5 mol%, 1.0 mol%, and 2.0 mol% with respect to Ti) of the metal ions for one night followed by drying under reducing atmosphere in an alumina crucible at 500°C . The catalysts prepared by this procedure with various M/Ti molar ratios were assigned as $\text{M}_x\text{TiO}_2/\text{SiO}_2$. Where, M stands for the doped metal ion and x stands for the M/Ti molar ratio which was of 0.1 mol%, 0.5 mol%, 1.0 mol% and 2.0 mol%.

1.2 Photocatalytic activity

Phenol was chosen as model organic pollutant and the photocatalytic activity of the catalyst was evaluated by its decomposition. The photocatalytic degradation of phenol solution (initial phenol concentration, $C_0 = 5 \text{ mg/L}$) was carried out in a laboratory scale photoreactor as shown in Fig. 1. The photocatalyst (ca. 7 g) was packed into a tube reactor (10 mm \times 270 mm) which was connected to a peristaltic pump. Prior to photoreactions, washing was done by circulating Milli Q water for 30 min. Then after phenol solution was circulated continuously with the

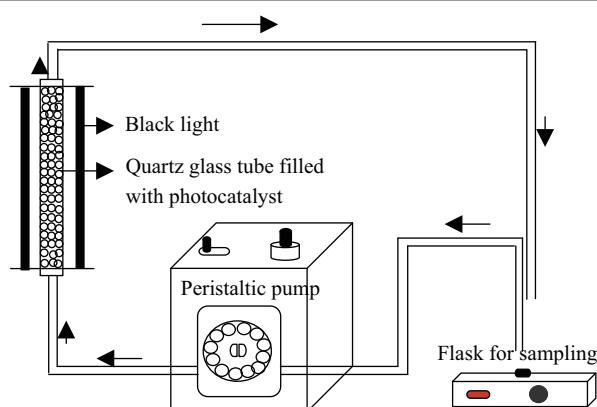


Fig. 1 Schematic reactor system for photocatalytic decomposition. Experimental conditions: dimension of glass tube reactor, 10 mm \times 270 mm; 4 black light, 6 W each; volume of phenol, 200 mL; initial phenol concentration, 5 mg/L; and flow rate, 100 mL/min.

flow rate of 100 mL/min. After adsorption equilibrium was achieved, the light source (Black light, 6 W \times 4) was switched on. The time when the light irradiation starts, was considered as zero time. Small aliquots were carefully withdrawn from the mixture at time intervals to follow the kinetics of the reaction. Samples were collected at regular intervals and analyzed by Hewlett Packard 1100 Liquid chromatography (1100 HPLC, Agilent, Germany) to measure the disappearance of phenol.

1.3 Characterization

Phase purity was checked with X-ray diffractometer (6100, Shimadzu, Japan). The surface elemental composition was determined by an energy dispersive X-ray detector (EDX), which was mounted in a scanning electron microscope (S-3000N, Hitachi, Japan). The UV-Vis absorption spectra were measured at 25°C by a USB 4000 UV-Vis miniature fiber optic spectrometer (USB 4000 UV-Vis, Ocean Optics, USA).

2 Results and discussion

2.1 Characteristics

Figure 2 shows the XRD patterns of the SiO_2 , $\text{TiO}_2/\text{SiO}_2$, and $\text{Cu}_{0.1}\text{TiO}_2/\text{SiO}_2$ samples. The XRD patterns of other 0.1 mol $\text{TiO}_2/\text{SiO}_2$ samples were also exactly similar to that of $\text{Cu}_{0.1}\text{TiO}_2/\text{SiO}_2$ (figure omitted). XRD patterns of all the samples studied gave a broad peak corresponding to SiO_2 centered at 23° . Peaks at 25° , 38° , 48° , and 54° corresponding to TiO_2 anatase phase, which is the most reactive form of TiO_2 (Barakat et al., 2005) were obtained in all the samples. This indicates that doping with transition metal ions such as Cr^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} did not influence the crystal patterns of the TiO_2 photocatalyst. Moreover, the intensities of the peaks were almost the same indicating that their crystallites after

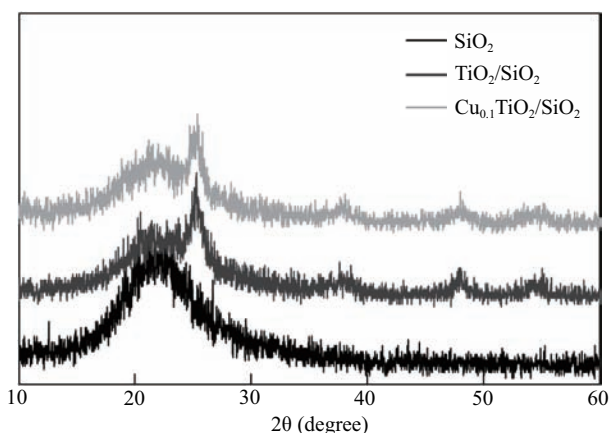


Fig. 2 X-ray diffractogram of SiO_2 , $\text{TiO}_2/\text{SiO}_2$, and 0.1 mol% Cu doped $\text{TiO}_2/\text{SiO}_2$.

doping did not change. The characteristic peaks indicating the doped metal ions were not detected implying either doped metal was incorporated in the crystalline of TiO_2 or the metal oxide was highly dispersed and its size was very small due to a relatively low metal loading (Srinivasan et al., 2006).

Table 1 presents the quantitative analysis calculated from the SEM/EDX. The quantitative analysis revealed much higher M/Ti ratios for all 0.1 mol $\text{TiO}_2/\text{SiO}_2$. SEM/EDX can only detect elements in the outer most surface (ca. 1 μm in depth from a sample surface) of a sample. The results indicate that metal was dispersed mostly on the surface of the prepared catalysts.

The UV-Vis absorption spectra of the $\text{TiO}_2/\text{SiO}_2$ and $\text{M}_{0.1}\text{TiO}_2/\text{SiO}_2$ are depicted in **Fig. 3**. $\text{TiO}_2/\text{SiO}_2$ shows absorption in near UV region (300–400 nm). The introduction of copper ions into TiO_2 led to significant red shift and slightly improved absorption at the visible light region (>400 nm). The red shift indicates the lowering of band gap energy of TiO_2 sub band gap formation as described earlier. Introduction of zinc ion also led to significant shift of absorption band towards visible region but with slight decrease in absorption intensity. The introduction of other metal ions studied decreases the absorption intensity significantly although there is slight increase of absorption in visible region.

Table 1 Elements and their atomic percentage on the surface as detected by SEM/EDAX

Sample	Element (atom%)			
	O	Si	Ti	M
SiO_2	67.67	32.33	–	–
$\text{TiO}_2/\text{SiO}_2$	66.65	21.57	11.79	–
$\text{Cr}_{0.1}\text{TiO}_2/\text{SiO}_2$	58.43	30.99	9.99	0.60
$\text{Co}_{0.1}\text{TiO}_2/\text{SiO}_2$	59.69	27.49	10.98	0.84
$\text{Ni}_{0.1}\text{TiO}_2/\text{SiO}_2$	60.78	29.29	8.98	0.95
$\text{Cu}_{0.1}\text{TiO}_2/\text{SiO}_2$	67.70	21.41	9.98	0.91
$\text{Zn}_{0.1}\text{TiO}_2/\text{SiO}_2$	60.14	29.55	9.35	0.95

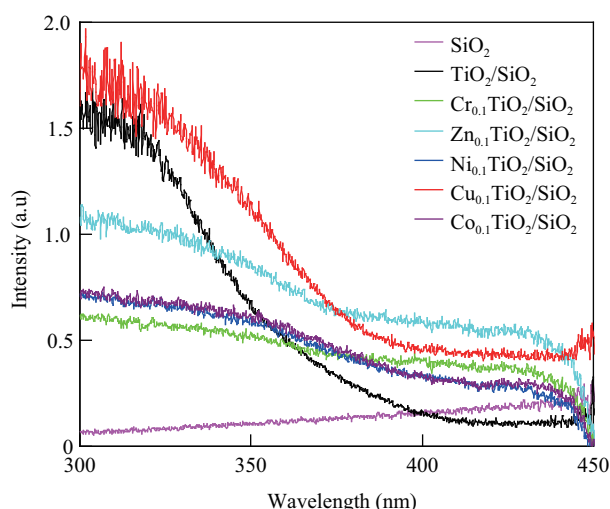


Fig. 3 UV-Vis absorption spectra of SiO_2 , $\text{TiO}_2/\text{SiO}_2$, and 0.1 mol% metal doped $\text{TiO}_2/\text{SiO}_2$.

2.2 Catalytic activity

2.2.1 Effect of metal-dopant concentration

Figure 4 shows the reaction time profiles of the photocatalytic degradation of 5 mg/L phenol under illumination of black light by $\text{TiO}_2/\text{SiO}_2$ and Cu-doped $\text{TiO}_2/\text{SiO}_2$ in various concentrations. The negative time region shows the adsorption equilibrium in the absence of illumination. There was only slight loss of phenol due to adsorption when the irradiation was not carried out. The phenol concentration rapidly decreases after irradiation of black light and was completely removed within 120 min in all cases.

Figure 4 shows that the phenol degradation increases upon doping 0.1 mol% Cu to $\text{TiO}_2/\text{SiO}_2$ photocatalyst but the activity of photocatalyst decreases with increasing doped Cu amount. Similar trend was obtained for other metal-doped $\text{TiO}_2/\text{SiO}_2$ as well (figure not shown).

Transition metal elements has many valences and trace

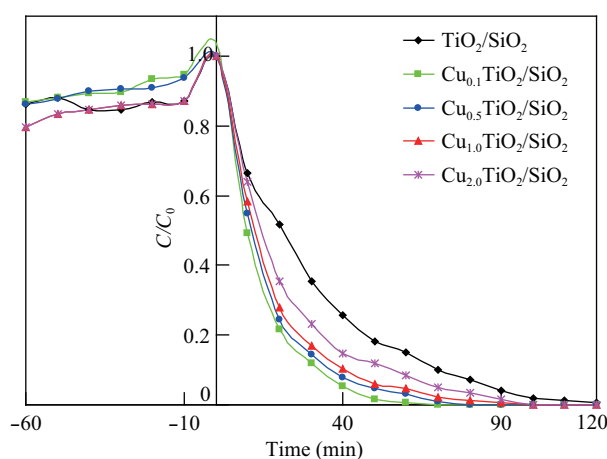


Fig. 4 Effect of Cu-dopant concentration on photocatalytic degradation of phenol. Experimental conditions: initial phenol concentration 5 mg/L; flow rate 100 mL/min; and total volume of solution 200 mL.

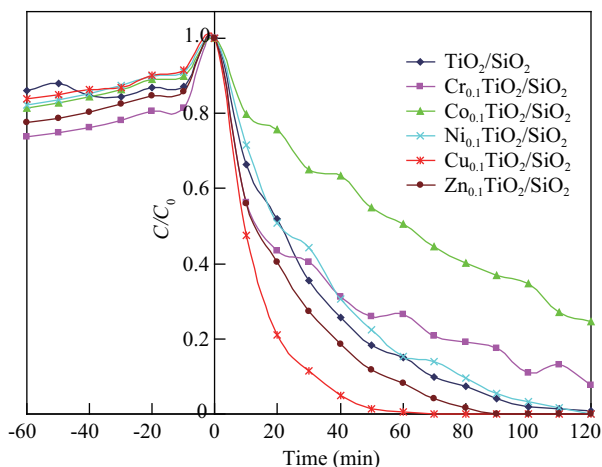


Fig. 5 Effect of metal dopant on photocatalytic degradation of phenol. Experimental conditions: initial phenol concentration 5 mg/L; flow rate 100 mL/min, and calcination temperature 500°C.

transition metal ions doped in the TiO₂ matrix could be superficial potential trap of photogenerated electron-hole pairs, which lengthened the lifetime of electrons and holes and increase photocatalytic activity. However, at a high dopant concentration, the dopant again becomes recombination center for photogenerated electron-hole pairs. Due to which there is an optimal metal dopant concentration for highest activity for the metal doped photocatalyst (Srinivasan et al., 2006; Jing et al., 2005; Anpo and Takeuchi, 2003). The 0.1 mol% metal-doping with respect to Ti was considered as the optimum doping concentration in this case.

2.2.2 Photocatalytic activity of different metal doped catalysts

The conversion of phenol over metal doped TiO₂/SiO₂ under illumination with black light is shown in **Fig. 5**. It shows that Cu- and Zn-doping could improve the photocatalytic degradation of phenol. The best photocatalytic activity was obtained with Cu-doping. The effects of Cr, Co, and Ni-doping are also shown in **Fig. 5**. The results indicated that photocatalytic activity of the Ni-doped photocatalyst was not much affected after Ni-doping but the photocatalytic activity of Cr and Co-doped photocatalyst decreased remarkably compared with original TiO₂/SiO₂ photocatalyst.

The reaction time profiles data of TiO₂/SiO₂, Cu_{0.1}TiO₂/SiO₂, and Zn_{0.1}TiO₂/SiO₂ was fitted with first order kinetic equation (Eligwe and Okolue, 1994):

$$\log C_e = -kt/2.303 + \log C_0 \quad (1)$$

where, C_e is equilibrium phenol concentration at time t , C_0 is initial phenol concentration, and k is the rate constant. The experimental data is well fitted to first order reaction equation as shown by high correlation coefficients (R^2) in **Table 2**. The rate constant for phenol degradation using TiO₂/SiO₂ as photocatalyst was $3.96 \times 10^{-2} \text{ min}^{-1}$. The rate of phenol degradation increases by 2.15 times upon

Table 2 Estimated rate constant using first order rate equation for phenol degradation

Photocatalyst	R^2	$k \text{ (min}^{-1}\text{)}$
TiO ₂ /SiO ₂	0.978	3.96×10^{-2}
Cu _{0.1} TiO ₂ /SiO ₂	0.990	8.52×10^{-2}
Zn _{0.1} TiO ₂ /SiO ₂	0.993	4.28×10^{-2}

doping 0.1 mol% Cu and the rate constant became $8.52 \times 10^{-2} \text{ min}^{-1}$. The increment in rate constant was very less upon doping zinc ion.

The different photoreactivity can be attributed to the different ionic radii of the dopants. As the radius of metal ion becomes much smaller or larger than that of Ti⁴⁺, it would be difficult for metal ion to replace a Ti⁴⁺ site. If the size is very similar it is very likely that metal ion enters into the interstitial site of the TiO₂ crystal. The doping metal ions located mainly on the shallow surface of TiO₂ can induce defects. The defects could become the centers of shallow electrons or holes traps, which would efficiently improve separation of electron-hole pair. Hence the photocatalyst will have a high photocatalytic activity. The doping ion in the deep bulk is also detrimental (Peng et al., 2007).

The ionic radii of the metal ions are: Cr³⁺ = 0.061 nm, Co²⁺ = 0.074 nm, Ni²⁺ = 0.069 nm, Cu²⁺ = 0.072 nm, and Zn²⁺ = 0.074 nm. The ionic radius of Ti⁴⁺ is 0.068 nm (Nistora et al., 2009; Ma and Du, 1993; Mazen et al., 1996; De Araujo et al., 2010). The ionic radii are in the order of Cr³⁺ < Ti⁴⁺ < Ni²⁺ < Cu²⁺ < Zn²⁺ = Co²⁺. The size of Cr³⁺ is much smaller than Ti⁴⁺. Thus, Cr³⁺ can enter into deep bulk when calcination was done at high temperature due to which the result can be detrimental (Li et al., 2007). We also found similar result where the photocatalytic activity decreases upon Cr³⁺-doping. Beside the smaller ionic radius, photocorrosion also play a role for decrease in photocatalytic activity upon Cr³⁺-doping as observed by the change in color to yellowish after Cr³⁺-doping which turns into black after photocatalytic treatment.

The ionic radius of Ni²⁺ (0.069 nm) is comparable to Ti⁴⁺ (0.068 nm). However, the photocatalytic beads color changes to yellowish after Ni²⁺-doping which turned into black after using it for photocatalytic treatment of aqueous phenol solution. Thus, photocorrosion of catalyst is the reason for decrease in photocatalytic activity upon Ni doping.

The ionic radii of Cu²⁺, Zn²⁺, and Co²⁺ (0.072, 0.074 and 0.074 nm, respectively) are slightly bigger than Ti⁴⁺. When calcination was done at high temperature they may enter the interstitial site of TiO₂ crystal and can create crystal defect. Thus should increase the photocatalytic activity. As expected the Cu²⁺ and Zn²⁺-doping increases the photoactivity where the increase in photoactivity by Cu²⁺-doping is higher than Zn²⁺-doping. However, Co²⁺-doping decreases the photoactivity which was due to

photocorrosion effect as observed in case of Ni²⁺-doping.

3 Conclusions

The TiO₂/SiO₂ was modified by doping transition metal ions (Cr, Co, Ni, Cu, and Zn) under reducing calcination atmosphere. Non-doped TiO₂/SiO₂ and doped TiO₂/SiO₂ were characterized by XRD, SEM-EDAX, and UV-Vis. From the characterization results, it was revealed that after metal doping, the structure (anatase phase) still remained and the extension of the spectral response into the visible region was noted. Photocatalytic activity for the decomposition of phenol was investigated. The obtained results showed that Cu- and Zn-doping enhances the photocatalytic activity under black-light illumination. The enhancement was maximum upon doping copper ion which can be attributed to Cu-ion participating in lengthening of electron-hole pair recombination time and the improvement of light absorption. The different photoreactivity was ascribed to the different ionic radii and photocorrosion tendency of the dopants. The slightly bigger ionic radius of doped metal ion than Ti⁴⁺ is suitable to increase the photoactivity of TiO₂ photocatalyst. However, if the doped metal ions are unstable the phenol degradation must compete with the photocorrosion which will suppress the reaction rate.

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