

Research Article

Characterization and Photocatalytic Activity of Enhanced Copper-Silica-Loaded Titania Prepared via Hydrothermal Method

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TiO₂ nanopowder, loaded with SiO₂ and Cu-SiO₂, was prepared under both acidic and basic environments via the hydrothermal method. The morphology and structure of TiO₂ were studied by XRD, TEM, and FT-IR. The photocatalytic activity of samples was studied by monitoring the degradation of methyl orange, using a UV-visible spectrophotometer. The effect of Ti/Si ratio, pH, and Cu²⁺ addition on the formation of TiO₂ and its photocatalytic activity was investigated in detail. The results show that a large surface area and a high surface acidity were important factors to achieve good TiO₂ performance. The presence of Ti-O-Si bonding enhanced surface acidity, which improved its ability to adsorb more hydroxyl radicals and increased its surface area. The addition of 0.1 mol% concentration of Cu²⁺ and 25 mol% SiO₂ in TiO₂ induced the formation of new states close to the conduction band, which narrowed the band gap energy and enhanced the photodegradation efficiency.

1. Introduction

In recent years, cases of air and water pollution have been increasing due to the continuous rise in population and urbanization. Improper waste management has been identified as one of the prime factors that contribute to the pollution. In 2003, the average amount of municipal solid waste (MSW) generated in Malaysia was 0.5–0.8 kg/person/day, which has further increased to 1.7 kg/person/day in major cities [1]. Solid waste management continues to be a major challenge throughout the world, particularly in rapidly growing cities and towns [2].

Land filling and incineration are two of the most common methods of solid waste disposal. Unlike land filling, incineration requires minimum land, reduces the volume of solid waste by half, and can be operated in any weather. Nevertheless, emission of pollutants, especially dioxin and furan, is the major drawback of incineration. Among the various solutions available, photocatalysis is considered to be a green technique that has great potential to decompose

contaminants without leaving harmful intermediates [3–5]. Choi et al. reported that the polychlorinated dibenzo-p-dioxins such as mono-, tetra-, hepta-, and octachlorinated congeners were successfully degraded by a TiO₂ film under UV or solar light irradiation [6].

Titanium dioxide is the most promising photocatalyst due to its superior properties such as low cost, environmental compatibility, and long-term photochemical stability [7–10]. However, its wide band gap energy (3.0 for rutile; 3.2 for anatase) limits its use as a photocatalyst in various applications. The large surface area, high crystallinity, low crystallite size, and crystal structure are important properties that influence the photocatalytic activity of TiO₂. In recent years, much effort has been directed toward TiO₂ modification to enhance its photocatalytic activity [11–15]. For instance, TiO₂ loaded with various secondary oxides, such as ZrO₂ [16], WO₃, MnO₂, CuO, V₂O₅, and Al₂O₃ [17] and transition metals salt such as Cu²⁺ [18] and Fe²⁺ [19, 20], has been reported to be a more efficient photocatalyst than pure TiO₂. The composite TiO₂-SiO₂ has attracted great interest

TABLE 1: Photocatalytic activity of TiO₂ with various SiO₂ content.

Ti/Si ratio (%)	Preparation method	Crystallite size (nm)	Phase structure	Photocatalytic activity (%)
1 : 1 (50%) [18]	Sol-gel (100°C, 1 h)	5–8	A: 100%	90 (MB, 2 h)
1 : 1 (50%) [19]	Sol-gel (100°C, 9 h)	100–120	A: 100%	95 (Rhodamine B, 2 h)
19 : 1 (5%) [20]	Sol-gel (500°C, 1 h)	6.7	A: 100%	73 (MO, 1 h)
3 : 1 (25%) [21]	Sol-gel (550°C, 2 h)	4.5 (A) 9.2 (R)	A: 43.3%	65 (MO, 2 h)
7 : 3 (30%) [22]	Sol-gel (800°C, 2 h)	12	A: 100%	92 (MO, 5 h)
3 : 2 (40%) [23]	Hydrothermal (140°C, 10 h)	7	A: 100%	95 (MB, 1 h)
3 : 1 (25%) [24]	Hydrothermal (200°C, 24 h)	16.3	A: 100%	80 (MB, 8 h)

A: anatase, R: rutile, MB: methyl blue, MO: methyl orange.

because of its ability to prevent the grain growth of TiO₂ particles and enhance the thermal stability for the phase transformation of TiO₂ from anatase to rutile [21–27]. Xu et al. [24] studied the effect of a wide range of SiO₂ levels added to the microstructure and the photocatalytic activity of TiO₂ powder; preparation involved the sol-gel method and calcination at various temperatures. Addition of SiO₂ resulted in a marked reduction in grain size and an increase in the surface area of the catalyst. Results of other studies are summarized in Table 1. Although many reports describe the effect of SiO₂ on the photocatalytic activity of TiO₂, the results do not agree with one another, possibly due to differences in the processing methods or experimental conditions. On the other hand, Chen et al. [18] has been reported that 0.1 wt% of Cu²⁺-doped TiO₂-SiO₂ showed higher photocatalytic activity than that of undoped TiO₂-SiO₂. The effects of pH value on pure TiO₂ formation have been reported by several groups [28, 29]. Yu et al. prepared TiO₂ powder at different pH values through the hydrothermal method [28]. They found that the pH value of the starting solution has a significant effect on the crystallinity, crystallite size, phase structure, and photocatalytic activity of the synthesized TiO₂ powder. They proposed that basic conditions are favorable for the formation of pure anatase. Samples prepared at pH 9 display higher photocatalytic activity. However, this result contradicts those obtained by Karami [29], who concluded that TiO₂ prepared under acidic conditions (pH 3) through the sol-gel method has higher photocatalytic activity.

Although the sol-gel method is widely used due to its simplicity and low cost, calcination in air is required for the formation of the anatase phase from amorphous TiO₂. Li et al. [26] did a comparative study of the sol-gel and hydrothermal methods for the synthesis of TiO₂-SiO₂ composite nanoparticles and found that samples prepared through the hydrothermal route still possess a stable anatase phase, a large specific surface area, a small particle size, and a high photocatalytic activity even when calcined at 1000°C. However, they did not report the effect of pH on the formation of TiO₂-SiO₂ nanoparticles. In the present study, the effect of pH values on photocatalytic activity and the optimum Ti/Si ratio for photocatalytic activity of TiO₂ powder prepared by hydrothermal method were examined. The effect of Cu-SiO₂ addition on the phase structure and the photocatalytic activity of TiO₂ were also studied.

TABLE 2: Crystal properties of TiO₂-SiO₂ oxide powder.

Sample	Ti/Si ratio	SiO ₂ content (%)	Final pH value	Crystallite size/nm (XRD)
SA0	1 : 0	0	3	6.30
SA 5	19 : 1	5	3	6.63
SA10	9 : 1	10	3	7.06
SA16	5 : 1	16.67	3	8.91
SA20	4 : 1	20	3	9.54
SA25	3 : 1	25	3	6.88
SA25-Cu(0.05)	3 : 1	25	3	10.8
SA25-Cu(0.1)	3 : 1	25	3	9.48
SA25-Cu(0.15)	3 : 1	25	3	9.62
SA25-Cu(0.2)	3 : 1	25	3	10.11
SA25-Cu(0.5)	3 : 1	25	3	8.21
SA25-5	3 : 1	25	5	8.63
SN25-7	3 : 1	25	7	9.98
SA30	7 : 3	30	3	11.78
SA50	1 : 1	50	3	11.76
SB0	1 : 0	0	9	3.75
SB16	5 : 1	16.67	9	—
SB20	4 : 1	20	9	—
SB25	3 : 1	25	9	—
SB25-12	3 : 1	25	12	—
SB25-14	3 : 1	25	14	4.57
SB30	7 : 3	30	9	—
SB50	1 : 1	50	9	—

SA: acid, SB: basic, SN: neutral.

2. Experimental Procedure

2.1. Preparation. Initially, the oxide powder TiO₂-SiO₂ with various Ti/Si ratios at pH 3 and 9 were prepared, and the photocatalytic performance was evaluated to select the optimum Ti/Si ratio. The Ti/Si ratios and pH values in the experiment are summarized in Table 2. Tetrabutylorthotitanate (TBOT) with a normal purity of 97% (Aldrich, US) and tetraethylorthosilicate (TEOS) with a normal purity of 98% (Merck, Germany) were used as the source of titanium and silicon, respectively. Both were dissolved in equal volumes of ethanol, after which a few drops of hydrochloric acid were

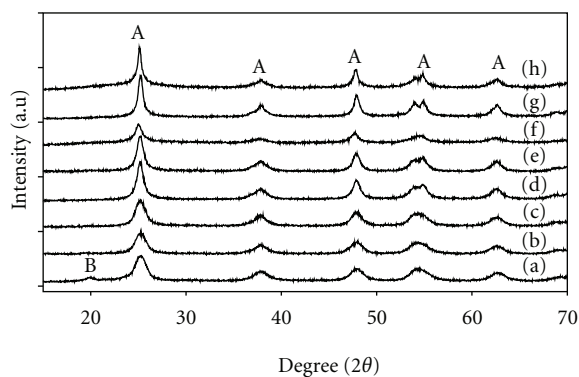


FIGURE 1: XRD patterns of the TiO_2 powder prepared with different amounts of SiO_2 at pH 3: (a) 0 mol%, (b) 5 mol%, (c) 10 mol%, (d) 16 mol%, (e) 20 mol%, (f) 25 mol%, (g) 30 mol%, and (h) 50 mol%. (A: anatase, B: brookite).

added to TEOS as catalyst. Afterward, the mixture was kept in a water bath maintained at 70°C for 2 h. The TEOS and TBOT precursors were then mixed and stirred for 15 minutes before adding the desired amount of copper(II) nitrate. The pH values were adjusted by adding hydrochloric acid for the acidic condition and sodium hydroxide for the basic condition. This solution was stirred for 1 h at room temperature and placed in a Teflon-lined stainless steel autoclave, in which it was heated at 150°C for 24 h, and then cooled to room temperature. The sample obtained was washed and then dried at 100°C . A powder was obtained.

2.2. Characterization and Photocatalytic Degradation. The powder samples were characterized by X-ray diffraction (XRD) using a Bruker D8 powder diffractometer employing $\text{Cu K}\alpha$ radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The average crystallite size of the TiO_2 - SiO_2 oxide powder was calculated using X-ray line broadening methods based on the Scherrer formula. Additionally, the morphology of the powder was observed by transmission electron microscopy (TEM) using a Philips 420 T. The chemical structure information of the particles was obtained by Fourier transform infrared spectroscopy (Spectrum One, Perkin Elmer, US). Photocatalytic degradation studies were performed using 30 mg/L methyl orange (MO) solution. A total of 0.1 g TiO_2 - SiO_2 oxide powder was added to 30 mL of MO solution and photoirradiated for 1 h at room temperature using a TUV 18W UV-C Germicidal light. The concentration of the degraded MO was determined using a UV-visible spectrophotometer (Varian, Cary 50 Conc).

3. Results and Discussion

3.1. Effect of SiO_2 Content. XRD was used to analyze the formation of the crystalline phase of the TiO_2 powder prepared with various amounts of SiO_2 in both acidic and basic environments. Figure 1 illustrates the XRD patterns of TiO_2 prepared at pH 3 with various Ti/Si ratios. The TiO_2 prepared at various Ti/Si ratios led to formation of the anatase phase. Patterns of samples without SiO_2 (SA0) shows peak for

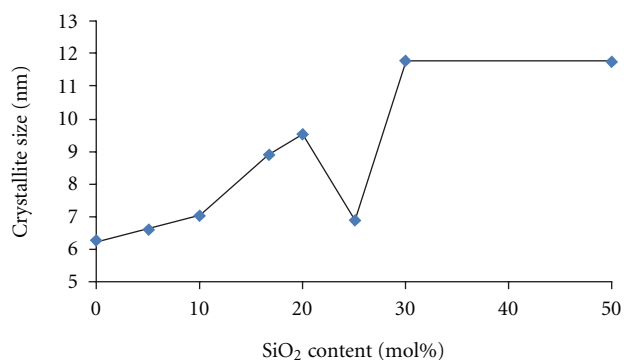


FIGURE 2: Relationship between the crystallite size and amount of SiO_2 on TiO_2 powder prepared at pH 3.

anatase and a small peak for the brookite phase at a diffraction angle of $\sim 20^\circ$. The relative intensities of the anatase diffraction peaks in each sample are different; this suggests that the degree of crystallinity is affected by the SiO_2 content. A high crystallinity of TiO_2 was obtained with addition of 30 mol% SiO_2 (SA30), whereas low crystallinity was observed in samples with 25 mol% SiO_2 (SA25). No SiO_2 crystal phase was identified in all samples. This indicates that SiO_2 existed as an amorphous phase in the TiO_2 - SiO_2 composite.

The formation of brookite phase in sample SA0 (acidic condition) could be explained as follows [28]: $\text{Ti}(\text{OH})_x(\text{OC}_4\text{H}_9)_{4-x}$ forms as a result of hydrolysis reaction between TBOT and HCl, where x was related to the pH value of starting solution. Since the ligand field strength of Cl^- ions was larger than that of butoxy group in HCl solution, thus the Cl^- ions could substitute the butoxy group in the $\text{Ti}(\text{OH})_x(\text{OC}_4\text{H}_9)_{4-x}$ complex and led to the formation of complex $\text{Ti}(\text{OH})_2\text{Cl}_2$. The complex $\text{Ti}(\text{OH})_2\text{Cl}_2$ actually existed in the form of $\text{Ti}(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_2$ in a solution due to the $\text{Ti}(\text{IV})(3d^0)$ complex ions are all octahedrally coordinated in solution and crystal. It is reported that $\text{Ti}(\text{OH})_2\text{Cl}_2(\text{H}_2\text{O})_2$ could be the precursor of brookite. This mechanism was favored to explain the occurrence of brookite in the sample.

The XRD patterns of TiO_2 prepared at pH 9 with various Ti/Si ratios (not shown here) shows samples prepared without SiO_2 (SB0) produced peaks characteristic of anatase at 2θ of 24, 34, 39, and 48° , and the peak of rutile at 28° . However, the peak intensity of this sample is very low compared to those produced by samples prepared under acidic conditions; this indicates that the phase transformation to anatase or rutile was not fully achieved at basic conditions. In contrast, samples prepared with SiO_2 generally showed amorphous TiO_2 . In basic conditions, Na^+ attacks the Ti-O-Ti bond, which results in the formation of a two-dimensional layered structure with dangling bonds that contribute to the formation of the amorphous phase. This is in good agreement with the TEM analysis which is discussed later.

The crystallite size of the TiO_2 - SiO_2 powders prepared in acidic condition was calculated using Scherrer formula and plotted against SiO_2 content. Figure 2 shows a nonlinear relationship between the crystallite size and the amount of added SiO_2 . The trend is contrary to results in the literature wherein

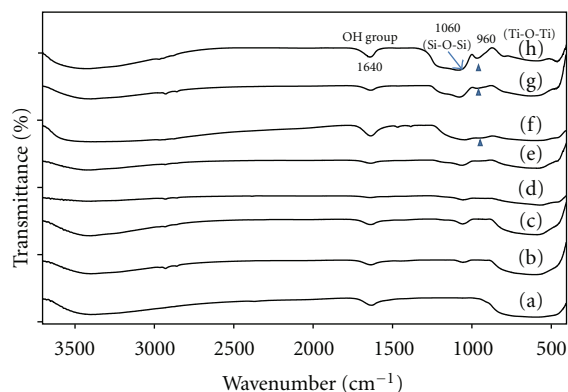


FIGURE 3: FTIR spectra of TiO_2 - SiO_2 oxide powder containing SiO_2 : (a) 0 mol%, (b) 5 mol%, (c) 10 mol%, (d) 16 mol%, (e) 20 mol%, (f) 25 mol%, (g) 30 mol%, and (h) 50 mol%. \blacktriangle indicates absorption bands at 960 cm^{-1} , which is characteristic of Ti-O-Si bonding.

SiO_2 addition was found to retard grain growth of TiO_2 and, therefore, reduce its crystallite size [23, 24, 26]. In the present study, the lowest crystallite size was 6.3 nm for pure TiO_2 (SA0), and increased gradually with further addition of SiO_2 . However, the crystallite size of TiO_2 for sample SA25 decreased drastically as the SiO_2 amount reached 25 mol%; this may be attributed to the large surface area of the sample. Binary metal oxides are known to induce surface acidity [30]. The FTIR spectra of the TiO_2 - SiO_2 powder at various SiO_2 contents are shown in Figure 3. When the SiO_2 content reached 25 mol%, a small peak at 960 cm^{-1} corresponding to the Ti-O-Si bond was observed. The presence of this oxide might have increased the surface acidity of the sample. Higher surface acidity led to a higher degree of adsorption of the OH radicals (1640 cm^{-1}) and resulted in a larger surface area. The surface area was inversely proportional to grain size. The Ti-O-Si band intensity increased with addition of 30–50 mol% SiO_2 , and the intensity of bands for the hydroxyl group decreased. These indicate that large amounts of SiO_2 (30–50 mol%) in TiO_2 cannot effectively improve the surface acidity and prevent the growth of TiO_2 grains. Therefore, in sample SA25, SiO_2 effectively enhanced the surface acidity, suppressed the grain growth of TiO_2 , and produced smaller crystallite size. The peak for the asymmetric stretching of Si-O-Si at 1060 cm^{-1} clearly increased with addition of SiO_2 , whereas the band intensity at $400\text{--}700\text{ cm}^{-1}$ (vibration of Ti-O bonds in Ti-O-Ti bonding) decreased. Therefore, the intensity of the peak for the Si-O-Si bond was inversely proportional to the intensity of the peak for the Ti-O-Ti bond.

3.2. Effect of pH Value. Figure 4 shows the XRD pattern of TiO_2 powder with 25 mol% SiO_2 (TiO_2 -25mol% SiO_2) at various levels of pH. In the presence of SiO_2 , an acidic condition was favorable to form anatase structure. As the system is shifted from acidic to neutral, the intensity of the anatase peak ($2\theta = 25^\circ$) and the crystallite size increased. Thus, pH value also affected the degree of crystallinity despite the presence of SiO_2 . At pH 12, the crystal structure of sample SB25-12 could not correspond to anatase, rutile, or brookite.

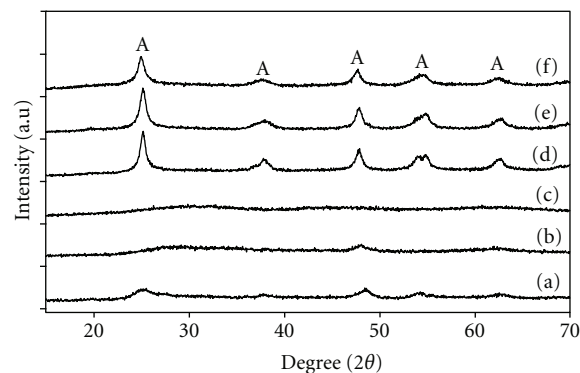


FIGURE 4: XRD pattern of 25 mol% SiO_2 -loaded TiO_2 powder at various pH values: (a) pH 14, (b) pH 12, (c) pH 9, (d) pH 7, (e) pH 5, and (f) pH 3. (A: anatase).

It was similar to that of $\text{Na}_2\text{O}_7\text{Ti}_3$ [31], $\text{H}_2\text{O}_{24}\text{Si}_3\text{Ti}_4$, and $\text{H}_4\text{Na}_4\text{O}_{16}\text{Si}_4\text{Ti}_2$ probably due to their same layered titanate family [32]. Further increase in basic condition (pH 14) resulted in formation of the partial anatase phase, as seen in the TEM images of TiO_2 -25 mol% SiO_2 powders prepared at various pH values in Figure 5. Spherical like particles (Figures 5(a) and 5(b)) were observed in samples prepared in acidic and neutral conditions. At pH 12, a lamellar structure (two-dimensional layered structures) formed as a result of the reaction between the sample and NaOH (Figure 5(c)), which involved attack of Na^+ on the Ti-O-Ti bond. The edges of the lamellar structure might have many atoms with dangling bonds with enough energy to destabilize the two-dimensional structures [33]. As the system shifted toward high pH, the lamellar TiO_2 deformed to saturate the dangling bonds. At pH 14, the transition three \rightarrow two \rightarrow one dimension was almost complete, while the lamellar structure formed tubes (Figure 5(d)); this resulted in a partial anatase phase. Thus, the pH appeared to have a significant effect on TiO_2 phase structure and morphology.

Figure 6 illustrates the FTIR transmission spectra of TiO_2 -25 mol% SiO_2 powder prepared at various pH values and autoclaved at 150°C for 24 h. The spectrum of pure TiO_2 is also included as reference. The broad peaks at 3400 cm^{-1} and the peaks at 1640 cm^{-1} in all spectra are attributed to surface-adsorbed water and the bending mode of hydroxyl groups. The surface-adsorbed water and hydroxyl group decreased slightly as the pH increased; this is possibly due to the reduction in surface area of the sample, which prevented further water vapor absorption. This is consistent with the results wherein samples prepared at pH 3 had higher photocatalytic activity compared with those prepared at pH 7. The peaks, which were absent in pure TiO_2 , appeared at 960 cm^{-1} and $1040\text{--}1070\text{ cm}^{-1}$ due to the Ti-O-Si stretching and the asymmetric stretching vibration of Si-O-Si, respectively. These peaks gradually decreased and eventually disappeared at higher pH. This implies that the Ti-O-Si bonds weakened as the pH increased. The stretching vibration of Ti-O bonds in Ti-O-Ti can be observed at $400\text{--}700\text{ cm}^{-1}$. Peaks related to carboxyl groups were observed at the $1340\text{--}1470\text{ cm}^{-1}$ range. The carboxyl groups might be a result of oxidation

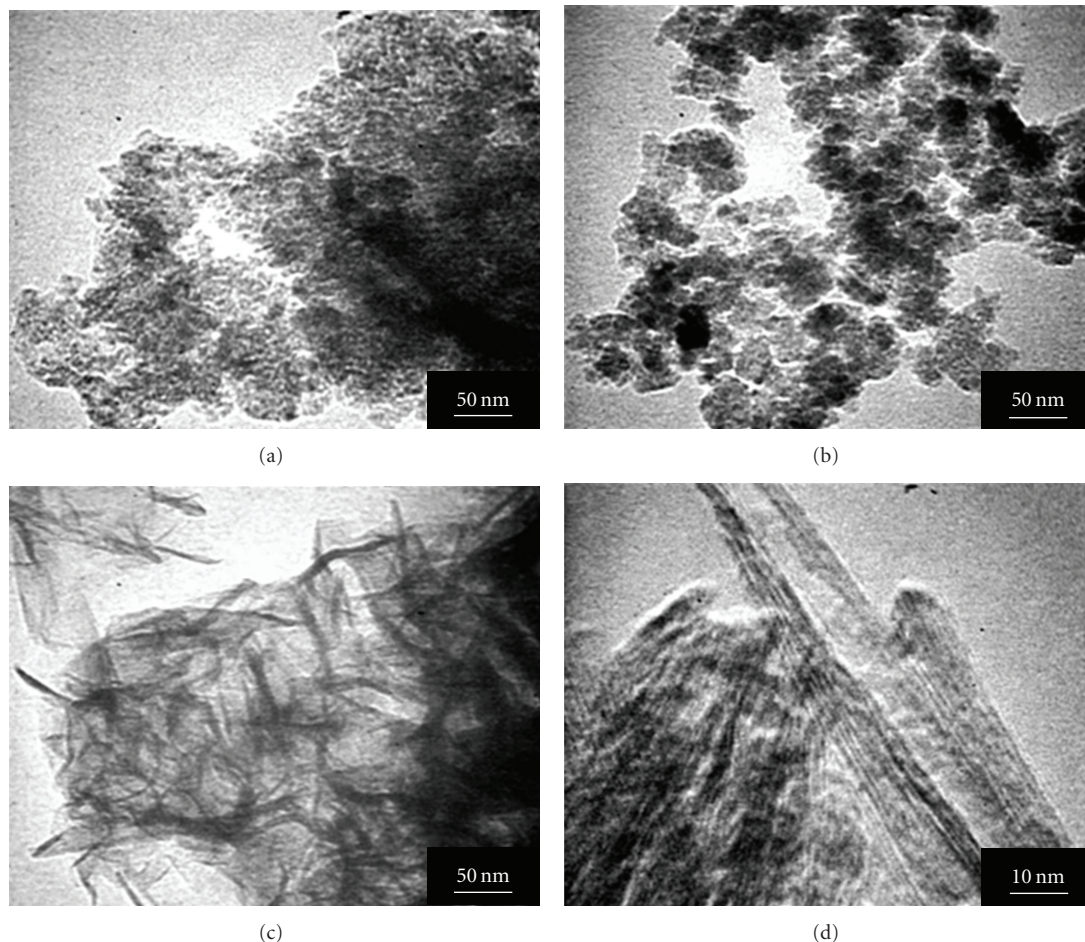


FIGURE 5: TEM images of TiO_2 -25% SiO_2 oxide powder prepared at various pH values: (a) pH 3, (b) pH 7, (c) pH 12, and (d) pH 14.

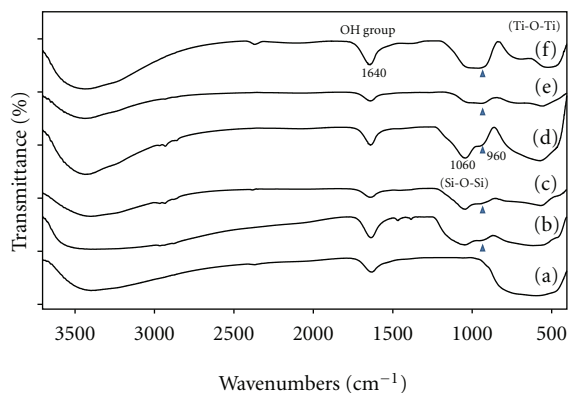


FIGURE 6: FTIR spectra of TiO_2 -25% SiO_2 oxide powder prepared at various pH values: (a) pure TiO_2 (pH 3), (b) pH 3, (c) pH 5, (d) pH 7, (e) pH 9, and (f) pH 12. \blacktriangle indicates absorption bands at 960 cm^{-1} , which is characteristic of Ti-O-Si bonding.

of organic species during hydrothermal treatment [28]. As the preparation conditions shifted from acidic to basic, the oxidation process was inhibited; this caused the peaks to disappear completely.

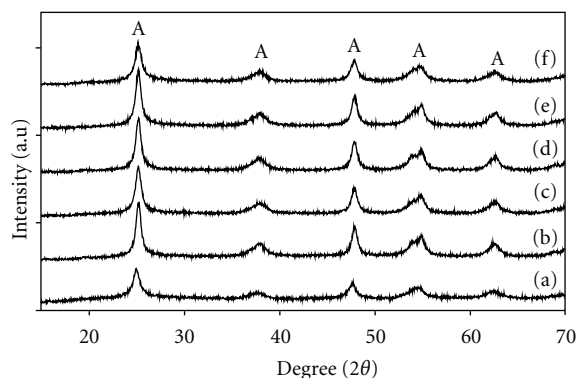


FIGURE 7: XRD pattern of 25% SiO_2 -loaded TiO_2 powder with various copper contents: (a) 0 mol%, (b) 0.05 mol%, (c) 0.1 mol%, (d) 0.15 mol%, (e) 0.2 mol%, and (f) 0.5 mol%. (A: anatase).

3.3. Effect of Cu^{2+} Addition in TiO_2 - SiO_2 Powder. The XRD patterns of Cu^{2+} -loaded TiO_2 - SiO_2 are shown in Figure 7. The TiO_2 - SiO_2 loaded with various amounts of Cu^{2+} , maintained an anatase phase. The presence of Cu^{2+} was hardly detected by XRD due to its low content. However, the relative intensities of the anatase peak vary among samples.

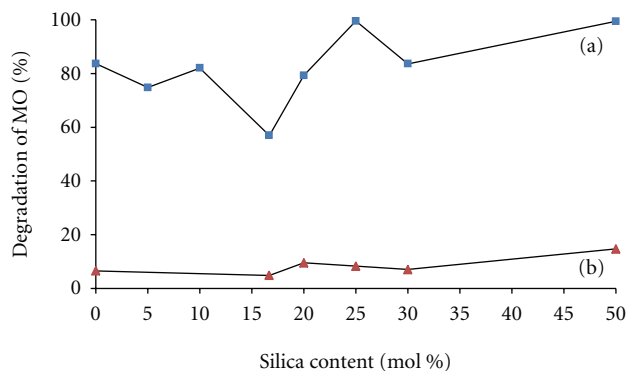


FIGURE 8: Photodegradation of MO (1 hr) on TiO_2 - SiO_2 powder prepared at (a) pH 3 and (b) pH 9.

High TiO_2 crystallinity was obtained with the addition of 0.2 mol% Cu^{2+} and lower degrees of crystallinity were observed in samples containing 0.5 mol% copper, which were due to the poor distribution of Cu^{2+} in the TiO_2 matrix. The TiO_2 without Cu^{2+} produced relatively small diffraction peaks of anatase at 25° (101), in contrast to the patterns of the samples with Cu^{2+} . Therefore, phase transformation was not fully achieved without Cu^{2+} , as the TiO_2 retained portions of the inactive amorphous phase.

3.4. Photocatalytic Activity. The photocatalytic activity of the TiO_2 - SiO_2 powder, prepared under acidic and basic conditions was evaluated through the degradation of methyl orange (MO) under ultraviolet light irradiation for 1 h at room temperature. Evaluation was repeated for 3 times, and average values were plotted. Samples prepared in acidic conditions displayed photocatalytic activity higher than that of samples prepared in basic conditions (Figure 8). This is attributed to the presence of anatase in the samples prepared under acidic conditions. Photocatalytic activities of the samples with different Ti/Si ratio vary. Pure TiO_2 (SA0) prepared in acidic conditions resulted in high photocatalytic activity. However, addition of 25 and 50 mol% of SiO_2 in TiO_2 produced the highest photocatalytic activity compared with pure TiO_2 . Thus, the presence of SiO_2 was essential to higher photocatalytic activity. As the SiO_2 present in TiO_2 promoted a high degree of anatase crystallinity, a lower crystallite size was produced due to suppression of TiO_2 grain growth. This might have contributed to the larger surface area of the TiO_2 particles. The addition of SiO_2 in TiO_2 also enhanced the acidity of the binary oxide. A model has been proposed to explain this increase in acidity [34]. In this model, the silicon cation enters the lattice of the host oxide, TiO_2 , and retains its original coordination number. Since the silicon cation is still bonded to the same number of oxygen atoms despite coordination changes in the oxygen atoms, a charge imbalance is created. The charge imbalance must be satisfied. Thus, Lewis sites are expected to form due to the positive charge in the TiO_2 - SiO_2 . The surface with improved acidity can adsorb more OH radicals, thus resulted in a larger surface area. This might enhanced the photocatalytic activity and led to complete degradation of MO. This is consistent with

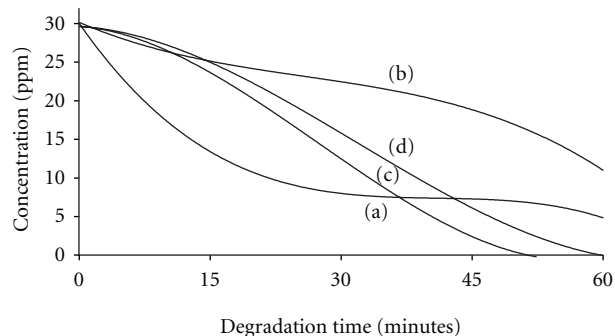


FIGURE 9: Photodegradation of MO on TiO_2 - SiO_2 with various Si content, prepared at pH 3: (a) 0% Si, (b) 16% Si, (c) 25% Si, and (d) 50% Si.

the FTIR results of the sample (pH 3) possessed high intensity of hydroxyl group. The result also indicates that samples prepared at basic conditions showed the poor MO degradation, which is in agreement with the observations of Yu et al. [23]. They revealed that amorphous TiO_2 has a lower photocatalytic activity compared with crystalline TiO_2 . Hence, SiO_2 -loaded TiO_2 powder prepared under basic conditions is inefficient for high photodegradation.

To understand the degradation of MO with time, samples were irradiated and collected every 15 min. Pure TiO_2 showed rapid degradation at the beginning, which eventually remained constant after 15 min (Figure 9). This is due to the low anatase concentration of TiO_2 and its inherent structure and low surface area. The TiO_2 with 25 and 50 mol% SiO_2 had low degradation rate during the first 15 min. Afterward, degradation markedly increased; both samples completely degraded MO within 1 h. It is worth while to note that the complete mineralization of MO in sample SA25 was faster than that of sample SA50. The TiO_2 with 25 mol% SiO_2 exhibited the highest photocatalytic activity, which can be attributed to the combination of several factors including large surface area, high degree of anatase crystallinity, and improved surface acidity. Hence, an optimum amount of SiO_2 (25 mol%) added to TiO_2 systems may be essential to enhance the photocatalytic activity.

Since SA25 was found to be the best sample for MO degradation, this was used to investigate the effect of pH on photocatalytic activity. The TiO_2 - SiO_2 powder prepared at pH 3 and pH 5 showed the highest photocatalytic activity (Figure 10). Rapid degradation rates were observed and resulted in nearly 100% degradation of MO. In contrast, the photocatalytic activity of samples prepared at pH 7, 9, and 12 were very low. Samples from neutral conditions (pH 7) had the anatase structure and high crystallinity but showed lower photocatalytic activity. As the pH increased from 3 to 7, the crystallite size increased, while the surface area decreased, which resulted in lower photocatalytic activity. These observations also indicate that a neutral environment for the synthesis could not enhance the photocatalytic activity. Overall, TiO_2 powder loaded with 25 mol% SiO_2 prepared at pH 3 was the sample with the highest photocatalytic activity.

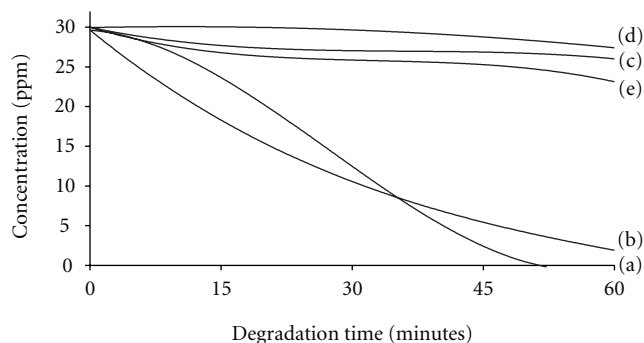


FIGURE 10: Photodegradation of MO on TiO₂-25 mol% SiO₂ powder prepared at various pH values: (a) pH 3, (b) pH 5, (c) pH 7, (d) pH 9, and (e) pH 12.

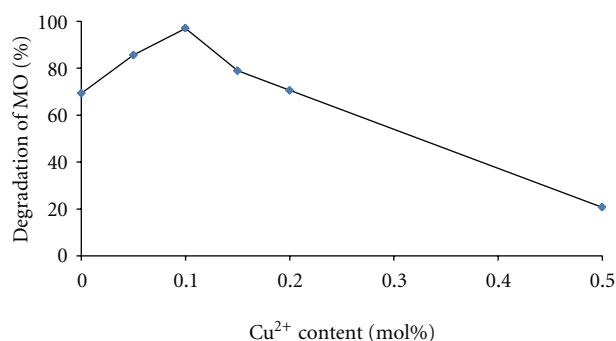


FIGURE 11: Photodegradation of MO (1 h) on Cu²⁺-loaded TiO₂-25 mol% SiO₂ powder prepared at pH 3.

To investigate the effect of Cu²⁺ on photocatalytic activity, SA25 was loaded with varying amounts of Cu²⁺. The photocatalytic activity was markedly enhanced in the presence of Cu²⁺ (Figure 11). About 97% of MO was mineralized with the addition of 0.1 mol% of Cu²⁺. This is mainly due to the high degree of crystallinity of the samples and the capability of Cu²⁺ to induce the formation of new states close to the conduction band, which leads to reduction of the band gap energy and an increase in the photodegradation efficiency. However, as the Cu²⁺ increased, the photocatalytic activity decreased rapidly. The photocatalytic activity dropped to ~21% when the Cu²⁺ content reached 0.5 mol%. This may be attributed to the low crystallinity and the behavior of Cu²⁺ at high concentrations, wherein it becomes a recombination center for the photo-induced electrons and holes thereby inhibits photocatalysis [20]. Hence, an optimum amount of Cu²⁺ in TiO₂-SiO₂ is essential to improve its photodegradation efficiency.

4. Conclusion

The effect of SiO₂ content and pH value on the TiO₂ photocatalytic activity was investigated. The addition of SiO₂ into the TiO₂ strongly affected the degree of crystallinity of the composite. The phase structure was dependent on pH value in the presence of SiO₂. An acidic environment led to anatase phase formation, and samples prepared in

basic conditions exhibited the amorphous phase. Addition of SiO₂ improved the surface area of TiO₂ particles by enhancing the surface acidity; this led to high photocatalytic activity compared with pure TiO₂. A higher degree of MO degradation was produced by TiO₂ samples with 25 mol% SiO₂ prepared at pH 3. The TiO₂ loaded with 0.1 mol% Cu²⁺ and 25 mol% SiO₂ exhibited photocatalytic activity higher than that without Cu²⁺. Therefore, the optimum amount of SiO₂ and Cu²⁺ and the pH during preparation were essential to achieving high photocatalytic TiO₂ activity.

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