Research Article

Enhancement of Photocatalytic Activity of ZnO/SiO₂ by Nanosized Pt for Photocatalytic Degradation of Phenol in Wastewater

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ZnO-SiO₂ nanoparticles were synthesized by a sol-gel technique from Zn(NO₃)₂ · 6H₂O and tetraethyl orthosilicate (TEOS). The synthesized samples were further modified by nanosized Pt from H₂PtCl₆ solution through photoassisted deposition (PAD) and impregnation (Img) routes. The obtained samples were characterized by a series of techniques including X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy, N₂ adsorption, extended X-ray absorption fine structure (EXAFS), and transmission electron microscopy (TEM). The photocatalytic activity of the Pt-ZnO/SiO₂ was evaluated by photocatalytic degradation of phenol in synthetic wastewater under UV-irradiation. Results obtained revealed that the surface area and the photocatalytic activity of the prepared samples were increased in the order ZnO/SiO₂ < PAD: Pt-ZnO/SiO₂ < Img: Pt-ZnO/SiO₂. The surface area decreased from 480 to 460 and 450 m²/g, while the efficiency of the phenol degradation increased from 80 to 85 and 100%, with the ZnO/SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂ samples, respectively.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide direct bandgap of 3.37 eV. Recently, much effort has been devoted to study ZnO as a promising photocatalyst for photocatalytic degradation of water pollutants, owing to its high activity, low cost, and environmentally friendly feature [1–4]. ZnO microcrystal showed also good photocatalytic activity for dye wastewater treatment [5].

However, a major drawback of ZnO is the large bandgap of 3.37 eV; so, wavelengths below 400 nm are necessary for excitation. Another disadvantage of ZnO is that charge carrier recombination of photogenerated electron/hole pairs occurs within nanoseconds and the photocatalytic activity is low [6–9]. Therefore, it is necessary to improve its visible-light activities by extending its absorption threshold from the

UV light region to the visible light region and also reduce the recombination of photogenerated electron/hole. Different works were performed recently to improve the activity of ZnO catalyst. Development of core/shell-structured materials on a nanometer scale has been receiving extensive attention [10, 11]. The shell can alter the charge, functionality, and reactivity of surface or improve the stability and dispersive ability of the core material. Furthermore, catalytic, optical, or magnetic functions can be imparted to the core particles by the shell material. In general, the synthesis of core/shell-structured material has the goal of obtaining a new composite material having synergetic or complementary behaviors between the core and shell materials. Many studies on the synthesis of composites such as NiO [12], V₂O₅ [13], TiO₂ [14], Fe₂O₃ [15], Pt [16], and Ag [17, 18] coated with SiO₂ shells have been reported. SiO₂ is one of the most

studied shell candidates due to its relative ease in preparation, good environmental stability, and compatibility with other materials, which motivated us to prepare the core/shell-structured composite of ZnO and SiO₂ and expected to achieve novel properties resulting from the synergic interaction of these two chemical components. One of the most promising methods to increase the photocatalytic efficiency is surface modification of ZnO, this can be achieved by metal doping into the ZnO catalyst. Dopant can act as a sink to collect photogenerated electrons from the conduction band of the semiconductor. Thus, it hinders the recombination of photogenerated electrons and holes through increasing the charge separation [19–22]. The surface modification of ZnO nanoparticles by preparing charge-transfer catalysts with mixing multicomponent oxides can enhance the surface chemical and physical properties and be considered as the key for the successful photocatalytic applications of such nanoparticles. Several metal ions such as Fe [23] and Ag [24, 25] have been used as dopants for ZnO to improve its photocatalytic activity. Photocatalytic degradation of phenolic compounds with semiconducting oxides holds promise for the purification and treatment of both drinking and industrial wastewater [26–28]. The presence of such organic pollutants in aquatic environments has caused several environmental pollution problems.

In the present work, Pt/ZnO-SiO₂ nanoparticles with large specific surface areas had been synthesized by the application of a photoassisted deposition (PAD) and impregnation (Img) methods, and the properties of the nanoparticles were characterized by XRD, TEM, EXAFS, UV-Vis/DRS, and BET analysis. The photocatalytic activity of the synthesized nanoparticles was evaluated by the photodegradation of phenol (as a model for pollutants in wastewater) under UV irradiation.

2. Experimental Methods

2.1. Chemicals. Zn(NO₃)₂·6H₂O, H₂PtCl₆, and tetraethyl orthosilicate (TEOS) were purchased from Aldrich and selected as the precursors of zinc, platinum, and silica, respectively. Standard grade phenol was purchased from Merck with 99.5% purity. 1 M NaOH and 1 M HCl solutions were used for pH adjustment. All chemicals used in this work were of reagent-grade quality. The water used was deionized water.

2.2. Preparation of ZnO/SiO₂. ZnO/SiO₂ nanoparticles were synthesized via a sol-gel technique and calcination. In a typical procedure, 20 mL TEOS was mixed with ethyl alcohol (C₂H₅OH), ultrapure water (H₂O), and nitric acid (HNO₃) under vigorous stirring for 1 hr. The overall molar ratio of TEOS : C₂H₅OH : H₂O : HNO₃ was 1 : 4 : 8 : 0.02. Subsequently, after 60 min, an aqueous solution of Zn(NO₃)₂·6H₂O was added in to the above solution under vigorous stirring for 60 min. The reaction was performed at room temperature. The prepared samples were aged for 24 h. Finally, the samples were evaporated and dried at 80°C, followed by calcination at 550°C for 3 h in air.

2.3. Preparation of Pt Loaded on ZnO/SiO₂ Using PAD Method. Pt metal (3 wt%) was deposited on ZnO-SiO₂ from aqueous solution of H₂PtCl₆ under UV-light irradiation. The samples were dried at 100°C and reduced by H₂ (20 mL/min) at 350°C for 4 h.

2.4. Preparation of Pt Loaded on ZnO/SiO₂ Using Img Method. In a typical impregnation (Img) method, the 3 wt% of Pt metal was deposited by a simple impregnation of ZnO-SiO₂ in the absence of light with aqueous solution of H₂PtCl₆. The samples were dried at 100°C and reduced by H₂ (20 mL/min) at 350°C for 4 h.

2.5. Characterization Techniques. To determine the crystallite sizes and identities of the Pt loaded on ZnO/SiO₂ nanocomposite photocatalyst, X-ray diffraction (XRD) analysis was carried out at room temperature using Rigaku X-ray diffractometer with Cu K α radiation over a 2 θ collection range of 10–80°. The shape of the samples was tested using Hitachi H-9500 transmission electron microscope (TEM), the prepared samples were prepared by suspending the prepared samples in ethanol, followed by ultrasonication for 30 min, then a small amount of this solution onto a carbon-coated copper grid and drying for TEM. Specific surface area was calculated from measurements of N₂-adsorption using Nova 2000 series chromatech apparatus at 77 K. Prior to the measurements, all samples were treated under vacuum at 200°C for 2 h. The band gap of the samples was identified by UV-visible diffuse reflectance spectra (UV-Vis-DRS) in air at room temperature in the wavelength range of 200–800 nm using Shimadzu UV-2450 spectrophotometer. The extended X-ray absorption fine structure (EXAFS) is performed at BL-7C facility [29] of the Photon Factory at the National Laboratory for High Energy Physics, Tsukuba, Tokyo, Japan. A Si (1 1 1) double-crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The K-edge EXAFS spectra of Fe were measured in the fluorescence mode at 25°C. The Fourier transformation was performed on K³-weighted EXAFS oscillations in effective range from 0–5 Å.

2.6. Photocatalytic Activity Measurements. Photodegradation experiments were performed with a photocatalytic reactor system at 25°C. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 1 L. A 150-Watts mercury lamp was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. The photoreactor was filled with 1 L of 100 mg/L aqueous phenol solution with 1 g/L of each of the three prepared nanoparticles samples. The whole reactor was cooled with a water-cooled jacket on its outside to the temperature. Compressed air was purged into the solution by bubbling compressed air from the bottom to maintain an aerobic condition [30]. Magnetic stirrer was also used to keep the solution chemically uniform. The pH of the solutions was adjusted and kept constant at 7 during the experiments by adding NaOH (1 M) and HCl (1 M) using an Orion Model 801 A pH meter. The experiments were carried out for 60 minutes. The liquid samples were filtered for analysis through 0.2 μ m syringe

FIGURE 1: XRD patterns of the (ZnO-SiO₂, Img: Pt-ZnO-SiO₂ and PAD: Pt-ZnO-SiO₂).

filters. The residual phenol was analyzed by the reaction with 4-aminoantipyrine [31]. Diluted sample of phenol was treated with 2 mL of 4 N NH₄OH, 1 mL of 1.5% 4-aminoantipyrine, and 1 mL of 4% K₃ [Fe (CN)₆] and quantitatively diluted to 100 mL with H₂O. After 5 min, the reaction was determined colorimetrically at 510 nm. The photodegradation efficiency of phenol has been calculated applying the following equation:

$$\% \text{ Photodegradation efficiency} = \frac{C_0 - C}{C_0} \times 100, \quad (1)$$

where C_0 is the initial phenol concentration; C is the retained phenol in solution.

3. Results and Discussions

3.1. Phase Analysis. The XRD patterns of the ZnO-SiO₂ and Pt-doped ZnO-SiO₂ nanoparticles prepared by (Img) and (PAD) routes are shown in Figure 1. It can be seen that the diffraction patterns of ZnO-SiO₂ sample and all Pt-doped ZnO-SiO₂ are mainly composed of ZnO phase which still exists after applying both mentioned preparation methods. While in the Pt-doped samples, no diffraction peaks of Pt were observed, this is probably attributed to the low Pt-doping content (ca. 3 wt%). Moreover, it is obvious that Pt is well dispersed over the ZnO-SiO₂ surface.

3.2. Nanostructure Characterization. Figure 2 displays the Fourier transforms of Pt L_{III}-edge EXAFS spectra of the Pt-loaded catalysts. It can be noticed that the presence of the peak assigned to the Pt-Pt bond of Pt metal at around 2.5 Å is an indication of the formation of nanosized Pt metal [32]. In addition, the intensity of the Pt-Pt peak of the PAD: Pt-ZnO-SiO₂ catalyst is smaller than that prepared by impregnation route. Therefore, Pt metal particles formed

FIGURE 2: Fourier transforms of the Pt L_{III}-edge EXAFS spectra for Img: Pt-ZnO-SiO₂ (a) and PAD: Pt-ZnO-SiO₂ (b).

on (PAD: Pt-ZnO-SiO₂) showed smaller particle size than (Img: Pt-ZnO-SiO₂). The grain sizes of PAD: Pt-ZnO-SiO₂ and Img: Pt-ZnO-SiO₂ nanocomposite photocatalysts were displayed in TEM images as shown in Figure 3. The particle size distribution obtained from the analysis of TEM images is shown in Figure 4. The result reveal that the nano-sized Pt metal with a mean diameter (d) of ca. 3 nm having a narrow size distribution was found on the PAD: Pt-ZnO-SiO₂ catalyst, whereas the aggregated Pt metal within various sizes is observed on Img: Pt-ZnO-SiO₂ catalyst (d = 15 nm) which is in agreement with the results of EXAFS measurement. These findings suggest that the size of Pt metal particles depends on the preparation method. Also, TEM micrographs showed the homogenous distribution of Pt over ZnO-SiO₂ matrix which was prepared by PAD method.

3.3. Surface Area Analysis. Specific surface area (S_{BET}) of ZnO/SiO₂, PAD: Pt-ZnO-SiO₂, and Img: Pt-ZnO-SiO₂ powder samples were determined. The S_{BET} values were 480, 460, and 450 m²/g for the ZnO-SiO₂, PAD: Pt-ZnO-SiO₂, and Img: Pt-ZnO-SiO₂, respectively. The parameters of surface area and the data calculated from the t -plot are collected in Table 1. Furthermore, the total pore volume of Pt-ZnO-SiO₂ is higher than that of ZnO-SiO₂. The values of S_{BET} and S_t are generally close in most samples indicating the presence of mesopores. The values of S_{micro} are high compared to that of S_{meso} implying that the main surface is mesoporous solid. The surface texture data are correlated with the catalytic activity as will be mentioned later on. The N₂ adsorption-desorption isotherm of the prepared samples is shown in Figure 5. It is clear that the isotherm shows a typical type IV sorption behavior, which confirms the presence of mesoporous form.

3.4. Band-Gap Analysis (UV-Vis-DRS). Study of the UV-visible radiation absorption is an important tool for evaluating the changes in the absorbance spectra of the prepared semiconductor materials. This is expressed by the band-gap

FIGURE 3: The TEM images of the Img: Pt-ZnO-SiO₂ (a) and PAD: Pt-ZnO-SiO₂ (b) catalysts.

FIGURE 4: Size distribution diagrams of Pt metal obtained from the TEM images of the Img: Pt-ZnO-SiO₂ (a) and PAD: Pt-ZnO-SiO₂ (b) catalysts.

(E_g) measurement which can be altered by different parameters. For instance, E_g value for pure ZnO phase is usually reported 3.37 [7]; however, these values are influenced by the synthesis method, and also affected by the existence of impurities doping the crystalline network and also the average crystal size of the semiconductor. In a previous study, different methods for calculating the E_g from the UV-Vis reflectance spectra were used. For example, some authors calculated the E_g values by a direct extrapolation of the $F(R)$ spectrum, whereas others reported the wavelength corresponding to the maximum absorption [33]. As a consequence, quite different E_g values for ZnO samples are found in the literature. For instance, threshold wavelength values of 240 nm [34], 290 nm [35], and 360 nm [36] correspond to bandgaps 5.15, 4.28, and 3.45, respectively. Figure 6 gives UV-Vis-DRS of (ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and

PAD: Pt-ZnO-SiO₂). The results showed an increase in the absorbance in the visible light region with the Pt doping. The values of E_g for the synthesized semiconductors can be derived from the spectra by plotting $(F(R) \cdot h\nu)^{1/2}$ against $h\nu$ [37, 38] as shown in Figure 7 and tabulated as shown in Table 2. The results revealed that the calculated values of E_g for (ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂) were 3.4, 3.25, and 3.05 eV, respectively. This indicates shifting the spectra of the PAD: Pt-ZnO-SiO₂ sample to the visible light area.

3.5. Evaluation of Photocatalytic Activity. The photocatalytic activity of the synthesized nanoparticles samples was evaluated by degradation of phenol in solution under UV light. Figure 8 displays the photocatalytic degradation of

TABLE 1: Texture parameters of ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂.

Sample	S_{BET} (m ² /g)	S_t (m ² /g)	S_{micro} (cm ² /g)	S_{ext} (cm ² /g)	V_p (cm ³ /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	r (Å)
ZnO-SiO ₂	480	485	380	100	0.866	0.069	0.803	38.00
Img: Pt-ZnO-SiO ₂	450	455	500	365	0.726	0.022	0.704	36.00
PAD: Pt-ZnO-SiO ₂	460	465	650	385	0.668	0.066	0.602	34.00

Note: (S_{BET}) BET-Surface area, (S_t) surface area derived from V_{t-t} plots, (S_{mic}) surface area of micropores, (S_{ext}) external surface area, (V_p) total pore volume, (V_{mic}) pore volume of micropores, (V_{meso}) pore volume of mesopores, and (r) mean pore radius.

FIGURE 5: N₂ sorption isotherms of ZnO-SiO₂, PAD-Pt/ZnO-SiO₂, and Img-Pt/ZnO-SiO₂.TABLE 2: The calculated band gap energy of ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂.

Sample	Band gap energy (eV)
ZnO-SiO ₂	3.40
Img: Pt-ZnO-SiO ₂	3.25
PAD: Pt-ZnO-SiO ₂	3.05

100 mg/L phenol pertaining to (ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂) at solution pH 7 for different time intervals. It can be seen that the rate of phenol photodegradation increased gradually with time reaching maximum efficiency values of 80, 85, and 99.9% after 1 h with parent ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂ samples, respectively. Considering that the pure Pt oxides have no photocatalytic oxidation properties, such change in the photodegradation activity may be explained in terms of the differences in interaction between Pt and ZnO-SiO₂ that led to several modifications in physical properties such as bandgap, particle size, and surface texture. Also, one could observe that the catalytic activity of ZnO-SiO₂ generally increased with the addition of Pt promoters. Figure 9 shows the good correlation between the physical

FIGURE 6: Diffuse reflectance UV-Vis absorption spectra of ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂.

properties of the synthesized samples, such as bandgap, surface area, and pore volume, with their catalytic activity. It was obvious that the photodegradation activity was gradually increased with the decrease of bandgap and the increase of the surface area and pore volume. The maximum photocatalytic degradation of phenol was achieved in the case of PAD: Pt-ZnO-SiO₂ in which the surface area and pore volume were maximum with lower bandgap value. It is believed that the lack of electron scavengers (surface Zn²⁺) and hole traps (surface hydroxyl groups) is responsible for the rapid recombination rate of e⁻/h⁺, which leads to lower photocatalytic activity with the parent ZnO-SiO₂ sample [6–9]. The photocatalytic activities of the Pt-doped ZnO-SiO₂ nanoparticles increased due to that Pt plays two important roles; noble metal incorporation into TiO₂ dielectric provides an absorption feature due to the surface plasmon resonance (SPR) occurring over the visible range of the spectrum. In particular, Ag, Pt, and Au metals are the most popular materials due to the strong SPR character [39, 40]. On the other hand, the superior driven photocatalytic efficiency of the Pt/TiO₂ nanocomposite photocatalyst can be ascribed to the high efficiency of charge-pair separation due to the presence of deposited Pt serving as electron sinks to retard the rapid e⁻-h⁺ couple recombination, the good photoabsorption capacity in the visible light region, and the higher concentration of surface hydroxyl groups, which are able to effectively scavenge photogenerated valence band holes [41].

FIGURE 7: Bandgap calculated from the DR-UV-Vis spectra of ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂.

FIGURE 8: Photocatalytic degradation of phenol (%) for ZnO-SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂. (a) PAD: Pt-ZnO-SiO₂, (b) Img: Pt-ZnO-SiO₂, and (c) ZnO-SiO₂.

Accordingly, the highest activity was more clear in the PAD: Pt-ZnO-SiO₂ sample in which the Pt diffuses in the lattice of the semiconductor. Thus, it lowered both the bandgap (as confirmed from the UV-Vis-DRS spectra analysis) and particle size (as confirmed from the TEM analysis). This resulted in increase in the surface area and pore volume, and consequently showed the best photoactivity with phenol degradation.

4. Conclusions

Pt doping, through photoassisted deposition (PAD) and impregnation (Img) routes, can greatly enhance the performance of ZnO-SiO₂ as a photocatalyst. The nano-sized

FIGURE 9: Effect of physical parameters of the materials on their photocatalytic activity.

Pt metal with a mean diameter (d) of ca. 3 nm having a narrow size distribution was found on the PAD: Pt-ZnO-SiO₂ catalyst, whereas the aggregated Pt metal with various sizes is observed on Img: Pt-ZnO-SiO₂ catalyst ($d = 15$ nm). The surface area of the synthesized samples was decreased from 480 to 460 and 450 m²/g with ZnO-SiO₂, PAD: Pt-ZnO-SiO₂, and Img: Pt-ZnO-SiO₂, respectively. The UV-Vis-DRS spectra analysis confirmed the lowest bandgap of PAD: Pt-ZnO-SiO₂ with a value of 3.05, comparing to 3.25 and 3.4 with Img: Pt-ZnO-SiO₂ and ZnO-SiO₂, respectively. The photocatalytic degradation of phenol in synthetic wastewater solution was found to be much more effective in the PAD: Pt-ZnO-SiO₂. The degradation efficiency increased from 80 to 85 and 99.9%, with the ZnO/SiO₂, Img: Pt-ZnO-SiO₂, and PAD: Pt-ZnO-SiO₂ samples, respectively. The smallest particle size and lowest bandgap of the PAD: Pt-ZnO-SiO₂ sample resulted in a high increase in the surface area and pore volume and consequently showed the best photoactivity with phenol degradation.

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References

- [1] C. Hariharan, "Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: revisited," *Applied Catalysis A*, vol. 304, no. 1-2, pp. 55-61, 2006.
- [2] M. Mrowetz and E. Selli, "Photocatalytic degradation of formic and benzoic acids and hydrogen peroxide evolution in TiO₂ and ZnO water suspensions," *Journal of Photochemistry and Photobiology A*, vol. 180, no. 1-2, pp. 15-22, 2006.
- [3] T. Pauporté and J. Rathouský, "Electrodeposited mesoporous ZnO thin films as efficient photocatalysts for the degradation of dye pollutants," *Journal of Physical Chemistry C*, vol. 111, no. 21, pp. 7639-7644, 2007.
- [4] J. Yu and X. Yu, "Hydrothermal synthesis and photocatalytic activity of zinc oxide hollow spheres," *Environmental Science and Technology*, vol. 42, no. 13, pp. 4902-4907, 2008.
- [5] J. H. Sun, S. Y. Dong, Y. K. Wang, and S. P. Sun, "Preparation and photocatalytic property of a novel dumbbell-shaped ZnO microcrystal photocatalyst," *Journal of Hazardous Materials*, vol. 172, no. 2-3, pp. 1520-1526, 2009.
- [6] M. Zhou, J. Yu, and B. Cheng, *Journal of Hazardous Materials*, vol. 137, 2006.
- [7] C. F. Klingshirn, "ZnO: material, physics and applications," *ChemPhysChem*, vol. 8, no. 6, pp. 782-803, 2007.
- [8] A. Singhal, S. N. Achary, A. K. Tyagi, P. K. Manna, and S. M. Yusuf, "Colloidal Fe-doped ZnO nanocrystals: facile low temperature synthesis, characterization and properties," *Materials Science and Engineering B*, vol. 153, no. 1-3, pp. 47-52, 2008.
- [9] C. R. Estrellan, C. Salim, and H. Hinode, "Photocatalytic activity of sol-gel derived TiO₂ co-doped with iron and niobium," *Reaction Kinetics and Catalysis Letters*, vol. 98, no. 1, pp. 187-192, 2009.
- [10] J. J. Schneider, "Magnetic core/shell and quantum-confined semiconductor nanoparticles via chimie douce organometallic synthesis," *Advanced Materials*, vol. 13, no. 7, pp. 529-533, 2001.
- [11] H. B. Lee, Y. M. Yoo, and Y. H. Han, "Characteristic optical properties and synthesis of gold-silica core-shell colloids," *Scripta Materialia*, vol. 55, no. 12, pp. 1127-1129, 2006.
- [12] R. M. Mohamed and E. S. Azam, "Photocatalytic oxidation of carbon monoxide over NiO/SnO₂ nanocomposites under UV irradiation," *Journal of Nanotechnology*, vol. 2012, Article ID 794874, 9 pages, 2012.
- [13] A. A. Ismail, I. A. Ibrahim, and R. M. Mohamed, "Sol-gel synthesis of vanadia-silica for photocatalytic degradation of cyanide," *Applied Catalysis B*, vol. 45, no. 2, pp. 161-166, 2003.
- [14] J. Zhang, Z. Liu, B. Han et al., "Preparation of silica and TiO₂-SiO₂ core-shell nanoparticles in water-in-oil microemulsion using compressed CO₂ as reactant and antisolvent," *Journal of Supercritical Fluids*, vol. 36, no. 3, pp. 194-201, 2006.
- [15] V. Maurice, T. Georgelin, J. M. Siaugue, and V. Cabuil, "Synthesis and characterization of functionalized core-shell γ -Fe₂O₃-SiO₂ nanoparticles," *Journal of Magnetism and Magnetic Materials*, vol. 321, no. 10, pp. 1408-1413, 2009.
- [16] R. M. Mohamed, "Characterization and catalytic properties of nano-sized Pt metal catalyst on TiO₂-SiO₂ synthesized by photo-assisted deposition and impregnation methods," *Journal of Materials Processing Technology*, vol. 209, no. 1, pp. 577-583, 2009.
- [17] K. S. Chou and C. C. Chen, "Fabrication and characterization of silver core and porous silica shell nanocomposite particles," *Microporous and Mesoporous Materials*, vol. 98, no. 1-3, pp. 208-213, 2007.
- [18] R. M. Mohamed and I. A. Mkhallid, "Characterization and catalytic properties of nano-sized Ag metal catalyst on TiO₂-SiO₂ synthesized by photo-assisted deposition and impregnation methods," *Journal of Alloys and Compounds*, vol. 501, no. 2, pp. 301-306, 2010.
- [19] M. J. Height, S. E. Pratsinis, O. Mekasuwandumrong, and P. Praserttham, "Ag-ZnO catalysts for UV-photodegradation of methylene blue," *Applied Catalysis B*, vol. 63, no. 3-4, pp. 305-312, 2006.
- [20] T.-Y. Han, C.-F. Wu, and C.-T. Hsieh, "Hydrothermal synthesis and visible light photocatalysis of metal-doped titania nanoparticles," *Journal of Vacuum Science and Technology B*, vol. 25, no. 2, article 430, 6 pages, 2007.
- [21] R. Ullah and J. Dutta, "Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles," *Journal of Hazardous Materials*, vol. 156, no. 1-3, pp. 194-200, 2008.
- [22] R. Slama, F. Ghribi, A. Houas, C. Barthou, and L. El Mir, *International Journal of Nanoelectronics and Materials*, vol. 3, p. 133, 2010.
- [23] R. M. Mohamed, M. A. Al-Rayyani, E. S. Baeissa, and I. A. Mkhallid, "Nano-sized Fe-metal catalyst on ZnO-SiO₂: (photo-assisted deposition and impregnation) Synthesis routes and nanostructure characterization," *Journal of Alloys and Compounds*, vol. 509, no. 24, pp. 6824-6828, 2011.
- [24] C. Ren, B. Yang, M. Wu et al., "Synthesis of Ag/ZnO nanorods array with enhanced photocatalytic performance," *Journal of Hazardous Materials*, vol. 182, no. 1-3, pp. 123-129, 2010.
- [25] Y. Lai, M. Meng, and Y. Yu, "One-step synthesis, characterizations and mechanistic study of nanosheets-constructed fluffy ZnO and Ag/ZnO spheres used for Rhodamine B photodegradation," *Applied Catalysis B*, vol. 100, no. 3-4, pp. 491-501, 2010.
- [26] M. A. Barakat, H. Schaeffer, G. Hayes, and S. Ismat-Shah, "Photocatalytic degradation of 2-chlorophenol by Co-doped TiO₂ nanoparticles," *Applied Catalysis B*, vol. 57, no. 1, pp. 23-30, 2005.
- [27] M. A. Barakat, J. M. Tseng, and C. P. Huang, "Hydrogen peroxide-assisted photocatalytic oxidation of phenolic compounds," *Applied Catalysis B*, vol. 59, no. 1-2, pp. 99-104, 2005.
- [28] A. Abdel Aal, M. A. Barakat, and R. M. Mohamed, "Electrophoretic Zn-TiO₂-ZnO nanocomposite coating films for photocatalytic degradation of 2-chlorophenol," *Applied Surface Science*, vol. 254, no. 15, pp. 4577-4583, 2008.
- [29] M. Nomura and A. Koyama, "Design of an XAFS beamline at the photon factory: possibilities of bent conical mirrors," *Journal of Synchrotron Radiation*, vol. 6, no. 3, pp. 182-184, 1999.
- [30] M. A. Barakat, Y. T. Chen, and C. P. Huang, "Removal of toxic cyanide and Cu(II) Ions from water by illuminated TiO₂ catalyst," *Applied Catalysis B*, vol. 53, no. 1, pp. 13-20, 2004.
- [31] J. R. Pemberton, "Retention of preservative levels of formaldehyde in desiccated biological products," *Journal of Clinical Microbiology*, vol. 2, no. 2, pp. 144-146, 1975.
- [32] A. Caballero, F. Villain, H. Dexpert, F. Lepeltier, B. Didillon, and J. Lynch, "In situ EXAFS studies of modifications to supported metallic catalysts under reactive atmospheres," *Catalysis Letters*, vol. 20, no. 1-2, pp. 1-13, 1993.
- [33] R. J. Davis and Z. Liu, "Titania-silica: a model binary oxide catalyst system," *Chemistry of Materials*, vol. 9, no. 11, pp. 2311-2324, 1997.

- [34] H. Yoshida, T. Shimizu, C. Murata, and T. Hattori, "Highly dispersed zinc oxide species on silica as active sites for photoepoxidation of propene by molecular oxygen," *Journal of Catalysis*, vol. 220, no. 1, pp. 226–232, 2003.
- [35] M. Huang, P. E. J. Rivera-Díaz-Del-Castillo, O. Bouaziz, and S. Van Der Zwaag, "Irreversible thermodynamics modelling of plastic deformation of metals," *Materials Science and Technology*, vol. 24, no. 4, pp. 495–500, 2008.
- [36] G. D. Mihai, V. Meynen, M. Mertens, N. Bilba, P. Cool, and E. F. Vansant, "ZnO nanoparticles supported on mesoporous MCM-41 and SBA-15: a comparative physicochemical and photocatalytic study," *Journal of Materials Science*, vol. 45, no. 21, pp. 5786–5794, 2010.
- [37] M. Anpo and M. Che, "Applications of photoluminescence techniques to the characterization of solid surfaces in relation to adsorption, catalysis, and photocatalysis," *Advances in Catalysis*, vol. 44, pp. 119–257, 1999.
- [38] G. Lassaletta, A. Fernández, J. P. Espinós, and A. R. González-Elipe, "Spectroscopic characterization of quantum-sized TiO_2 supported on silica: influence of size and TiO_2 - SiO_2 interface composition," *Journal of Physical Chemistry*, vol. 99, no. 5, pp. 1484–1490, 1995.
- [39] J. F. Rivadulla, M. C. Vergara, M. C. Blanco, M. A. López-Quintela, and J. Rivas, "Optical properties of platinum particles synthesized in microemulsions," *Journal of Physical Chemistry B*, vol. 101, no. 44, pp. 8997–9004, 1997.
- [40] N. A. M. Barakat, K. D. Woo, M. A. Kanjwal, K. E. Choi, M. S. Khil, and H. Y. Kim, "Surface plasmon resonances, optical properties, and electrical conductivity thermal hysteresis of silver nanofibers produced by the electrospinning technique," *Langmuir*, vol. 24, no. 20, pp. 11982–11987, 2008.
- [41] D. Zhang, "Visible light-induced photocatalysis through surface plasmon excitation of platinum-metallized titania for photocatalytic bleaching of rhodamine B," *Monatshefte für Chemie*, vol. 143, no. 5, pp. 729–738, 2012.