

Microstructure and photo-catalytic dye degradation of silver- silica nano composites synthesised by sol-gel method

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ABSTRACT

Sol-gel chemistry has recently attracted a large attention with a view of preparation of silver-silica nano-composites for photo-catalytic applications. This method of synthesis allows glassy materials to be prepared at a much lower temperature than the traditional melt-glass techniques. Moreover, it enables higher doping concentrations and a more uniform distribution of silver in the glass host matrix to be achieved. This method produces large quantities of amorphous gels that are thermal treated in air at the temperature of 500°C for one hour. The silver-silica samples were investigated through X-ray diffraction (XRD) for the determination of their microstructure, phase and compositions. It is found that the microstructure depends closely on the solution pH and the extent of silver-doping. MB dye degradation by undoped and Ag doped SiO₂ was studied under UV and Visible light irradiation. The results are intriguing as the doping by Ag produces opposite effects on photocatalytic degradation rates under the two conditions. Copyright © 2013 VBRI press.

Keywords: Silver; sol-gel, silica; nanocomposite; photo-catalytic.

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Surender Duhan received his Ph.D. in the area of nanomaterials from Guru Jambheshwar University of Science & Tech., Hisar. He has published 30 research papers in reputed International/National Journals and 22 papers in International/National conferences/seminar etc. including several independent research papers. He has authored of five books on Engg. Physics. Dr. Surender Duhan is presently working as Assistant Professor in the Department of Materials Science and

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Introduction

Dispersion-structured nanocomposite materials consist of very small particles of a secondary phase dispersed throughout a host matrix, and are of intense current interest for potential applicability in optical and optoelectronics devices [1-2]. Their use in integrated optics and wave guides [3-5] stems primarily from the greater third order non-linear susceptibility of metal nano-particles [6]. Meanwhile, the use of nanomaterials such as carbon

nanotubes (CNTs) to fabricate matrices for biosensors is one of the most exciting approaches because nanomaterials have unique structures and high surface-to-volume ratio [7]. The surfaces of nanomaterials can also be tailored on the molecular scale in order to achieve various desirable properties such as amperometric, potentiometric, optical, thermal, or piezoelectric behaviors [8]. Moreover, biobased nanomaterials have unique physiochemical properties and are attractive as excellent electroactive, environmental friendly and biocompatible materials [9].

The physical and chemical properties of nanoparticles vary drastically with size and the use of ultrafine particles clearly identifies a major technical area for materials research [10-12]. Among the various nanomaterials, silver nanocomposites have attracted increasing technological and industrial interest [3]. This interest has mainly to do with their novel optical properties, and various desirable biobased properties e.g. it has been found that a change of colour was predominant in humid conditions even at room temperature if the samples were exposed to air for a few days. This indicates that the samples are suitable candidates for making humidity sensors [13-15].

Investigating and understanding these materials are not only of academic interest but also of great technological

and commercial value due to the possibility of wide ranging applications in various fields such as solar materials, sensors, electronic shielding, and environmentally sensitive membranes [9,16-20]. It has been shown that the successful preparation of metal oxides nanoparticles can be achieved by a number of methods - including co-precipitation techniques, solvothermal approach, gas-phase condensation techniques or by colloidal chemical methods, spin coating, dip coating and LB coating methods [21-23]. Among the various methods followed, the sol-gel method has been widely used for the preparation of inorganic oxide, due to its versatility and low cost.

The use of sol-gel derived silica as a glass host for photonics applications requires the fulfilment of several criteria including high density, high mechanical and thermal shock resistance, but the product is sometimes too brittle. Tetraethoxy Silane (TEOS) has been extensively used as a silica precursor for the preparation of various metal-silica composites [9]. In the 1980s, extensive worldwide research was devoted to studying the mechanisms allowing the sol-gel preparation of undoped and metal doped silica matrix. With this method, the synthesis of materials starts from precursors and an oxide network is obtained via hydrolysis, alcohol condensation and water condensation reactions that occur in solution. This method allows the incorporation of different species such as atoms, molecules or ultrafine particles in to dried glass. These species are added in the precursor solutions, producing characteristic properties in solid-glasses afterwards.

In the present report, the microstructure of silver doped silica gel was prepared by the solgel method and the structural and optical characterizations of the samples were carried out post sintering. It was observed that annealing the amorphous structure at high temperatures allows allowing silver to diffuse more freely and therefore to form larger silver particles. The stem of this study is in the results of our earlier report [24], in which we demonstrated the effect of temperature and time on silver particles in similar nanocomposites. The annealing temperature and time dependence of the formation of metal nanocrystallites as well as their distribution in fused silica matrix were measured, and it was found that the average size of the silver nanocrystallites in a silica matrix post annealing was ~15 nm. The X-ray diffraction (XRD) and Ultraviolet spectroscopy data for silver silicates are also presented.

This material system has been under high research interest owing to its various applications. The authors have studied its application for degradation of Methylene Blue dye in this study.

Experimental

Sample preparation

Silver-silica clusters were prepared by the solgel technique. High purity reagents namely, Tetraethoxy silane TEOS (Aldrich 99.999), ethanol (Aldrich 99.9995), and deionized water were used. The molar ratio of the starting solution was taken as 0.38:0.162:0.031 for H₂O: C₂H₅OH: TEOS. Different amounts of silver nitrate were introduced in the pre-hydrolyzed solution under heating at 50 °C. It is worth mentioning here that under our experimental conditions, at longer time irradiations (more than 10 minutes), pH falls by

one to two units. Other authors have reported that the rate of MB degradation is highest around an alkaline pH of 9 [25]. Keeping these observations under consideration, we chose to use borate buffer of pH 9.2 in all the samples under both UV and visible light irradiation. The solution was kept in a drying oven (GFL-7105) at 70°C. It was observed that the gelation starts after a few days. Even after the gelation is complete, the gel was still kept inside the oven for few days for aging. The aging process allows further shrinkage and stiffening of the gel. The dried samples were powdered by Agate pestle and mortar. The powders of this binary system was calcined in a muffle furnace (KSL 1600X, MTI) in air at different heating rates, and the samples were kept inside the furnace at set temperatures for different time durations. Five compositions were synthesized, including the undoped silica glass. Photo-catalytic properties of these materials were studied by means of Methylene Blue (MB) dye photo-oxidation reaction.

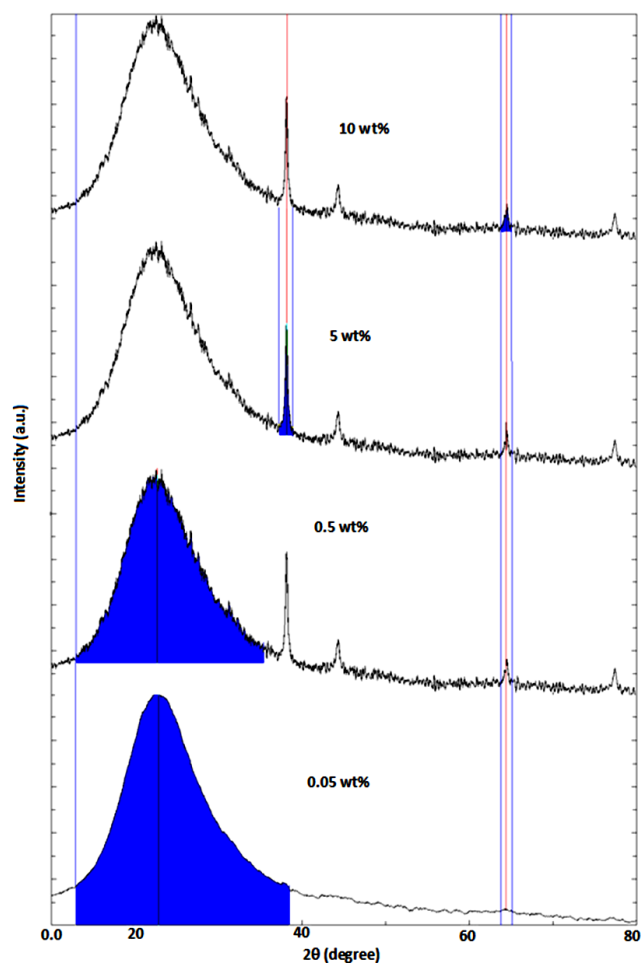


Fig. 1. X-Ray Diffraction (XRD) of (a) 0.05wt% Ag doped SiO₂ (b) 0.5wt% Ag doped SiO₂ (c) 5wt% Ag doped SiO₂ (d) 10wt% Ag doped SiO₂.

Results and discussion

It was observed that after some days, the percentage of shrinkage of the sample was very low (below 0.1%). It was also noticed that the aged undoped samples were transparent and colorless, while the color of the doped

samples after annealing were glassy yellow due to the presence of silver.

Microstructure: X-Ray diffraction

Fig. 1 shows the XRD patterns of SiO₂, 0.05 wt% Ag-SiO₂, 0.5 wt% Ag-SiO₂, 5 wt% Ag-SiO₂ and 10 wt% Ag-SiO₂ samples. For all samples, the broad diffraction peak matches well with the standard SiO₂ diffraction pattern identified as α -Cristobalite structure with Miller indices (101) and the minor diffraction peaks match well with the standard diffraction pattern identified as structure of metallic Silver for the peaks at $2\theta = 38.3^\circ$, 44.6° and 64.5° silver peaks indexed as (111), (200) and (220) in the samples sintered at 500 °C. These peaks clearly indicate the formation of nanoparticles in the amorphous silica network after sintering. The diffraction peaks became intense and their FWHM turned gradually narrow with increasing temperature indicating an increase in particle size of Ag. The mean size of Ag nanoparticles was estimated by Scherer's equation [9]. Mean Ag particle sizes (diameters) were estimated to vary from about 10 to 25 nm in these composite samples after sintering. The results indicate that with the increase in weight percentage of Ag, the mean size of silver nanoparticles in the amorphous SiO₂ matrix is increased after sintering of samples.

UV-vis spectroscopy: Ultraviolet (UV) irradiation

A setup consisting of MB dye solution (concentration of 1.0×10^{-5} molL⁻¹ in aq.), and powder substrate were exposed to UV light (centered around 350 nm) for photo-oxidation reaction for several time intervals (0, 1, 2, 3, 5, 8, 12 and 20 min. respectively). Un-doped SiO₂ and Ag-doped (0.05, 0.5, 5 and 10 wt %) SiO₂ were tested as photocatalysts, and the results are shown in **Fig. 2** (a-e).

Samples were taken out from the dye-substrate solution undergoing UV irradiation in respective time intervals, and were then centrifuged to separate the catalyst powder. Absorption spectra were recorded for each of these samples. The rate of dye degradation was followed by monitoring the changes in characteristic absorbance corresponding to λ_{\max} (664 nm) pertaining to the MB dye. The rates of reaction are depicted in **Fig. 2** (a-e) for each doping level in SiO₂, and a comparison of different Ag-doped samples' dye degradation efficiency was done. A significant blue shift in the absorption maximum is observed in all Ag-modified SiO₂ (typically 10–12 nm), but no real shift is observed for un-doped SiO₂. These plots reveals the decrease in intensity of characteristic peak of MB dye ($\lambda_{\max} = 664$ nm) with time resulting from dye degradation. A rapid decrease in absorbance results from a fast rate in degradation, and hence it indicates an efficient photo-catalysis activity.

From the **Fig. 2** (a-e), it is clear that reaction/dye degradation increases considerably with irradiation time. With increase in Ag doping concentrations, the rate of reaction further increased. As is evident from figure 3, the activity of the catalyst under ultra violet light is enhanced significantly on addition of silver, with the rate of reaction increasing from 2.9 to 5.42 sec⁻¹ and is the highest for the 5 and 10 wt % Ag-SiO₂ samples (**Table 1**). With such response, we conclude that Ag doped samples are good

catalysts under UV light photocatalysis for MB dye degradation.

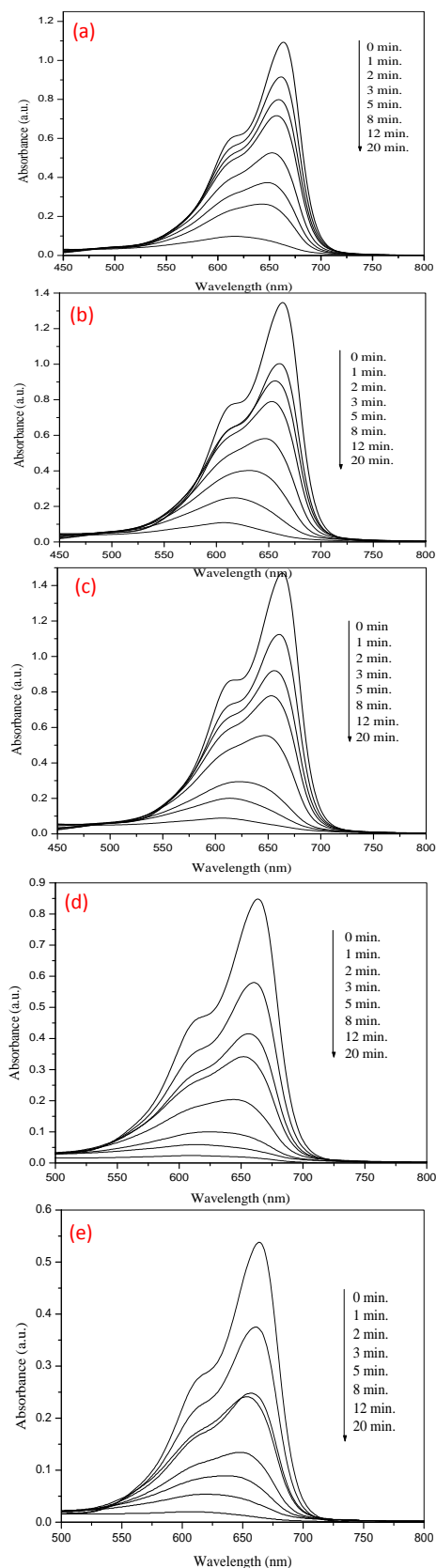


Fig. 2. UV-Vis absorption spectra of degradation of MB dye under UV light using (a) Bare SiO₂ as a catalyst, (b) 0.05 wt % Ag SiO₂ as catalyst, (c) 0.5 wt % Ag SiO₂ as catalyst, (d) 5 wt % Ag SiO₂ as catalyst and (e) 10 wt % Ag SiO₂ as catalyst.

Table 1. shows rate of reaction using different wt% Ag-doped SiO₂ as a catalyst under UV light.

Concentration of Ag (in wt%)	Rate of reaction (R _i) (10 ⁻⁸ mol.dm ⁻³ .sec ⁻¹)
0	2.9
0.05	3.9
0.5	4.2
5	5.39
10	5.42

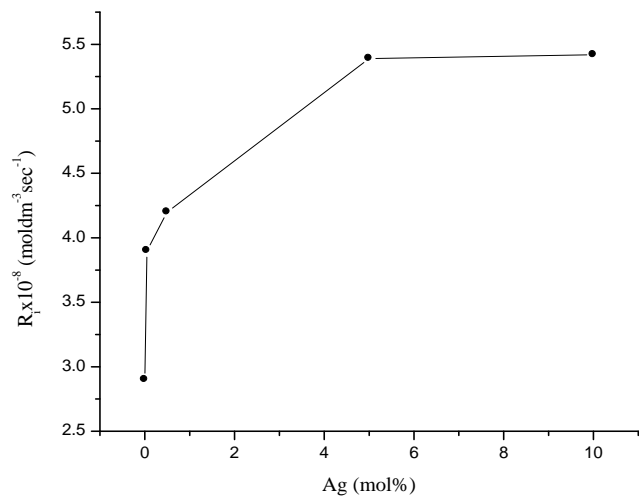


Fig. 3. Plot of Initial rate of reaction (R_i) against amount of Ag (mol %) doping in SiO₂ under UV light photocatalysis.

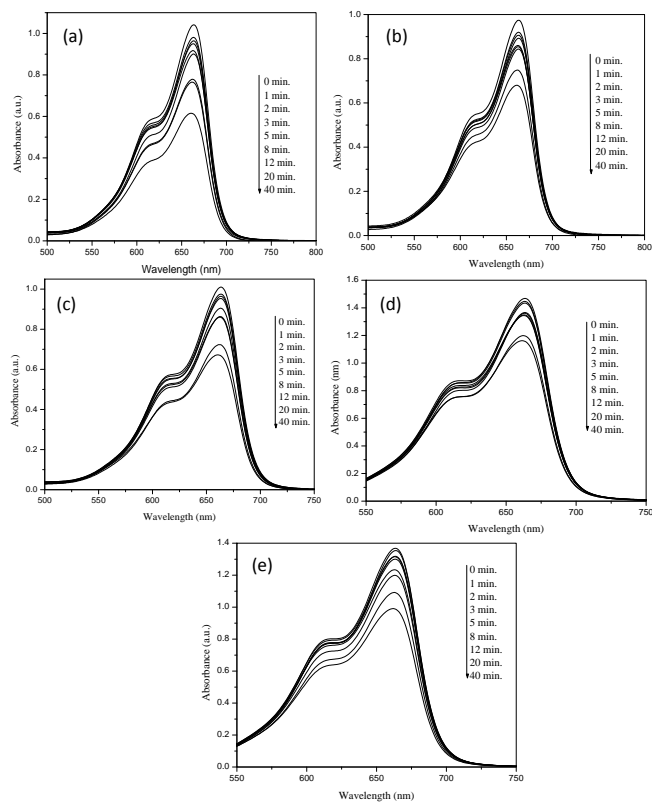


Fig. 4. UV-Vis absorption spectra of degradation of MB dye under visible light using (a) Bare SiO₂ as catalyst, (b) 0.05 wt % Ag SiO₂ as catalyst, (c) 0.5 wt % Ag SiO₂ as catalyst, (d) 5 wt % Ag SiO₂ as catalyst and (e) 10 wt % Ag SiO₂ as catalyst.

Visible light irradiation

A solution containing of MB dye (concentration of 1.0 x 10⁻⁵ molL⁻¹ in aqueous) and powder substrate was exposed to visible light (centered on 550 nm) for photo-oxidation reaction at various time intervals (0, 1, 2, 3, 5, 8, 12, 20 and 40 min. respectively). The undoped SiO₂ and Ag doped (0.05, 0.5, 5 and 10 wt %) SiO₂ as photocatalysts are shown in **Fig. 4 (a-e)**. Samples were taken out during irradiation in respective time periods, and then centrifuged to separate the powder catalyst. The absorption spectra were measured for each of these samples. The rate of dye degradation was followed by monitoring the changes in characteristic absorbance corresponding to λ_{max} (664 nm) pertaining to MB dye. The rate of reaction is depicted in **Fig. 4 (a-e)** for each doping in SiO₂ and these show the comparative behaviours of different Ag doped samples. It is clear that under visible light the photo-oxidation/degradation of MB dye does occur. However the rate of reaction seems to occur at a considerably slower rate probably due to increase in band gap of SiO₂ as the result of Ag doping. This observation is under further investigation and will be reported later. The results of photocatalysis are reported as the % degradation of MB dye for each time intervals.

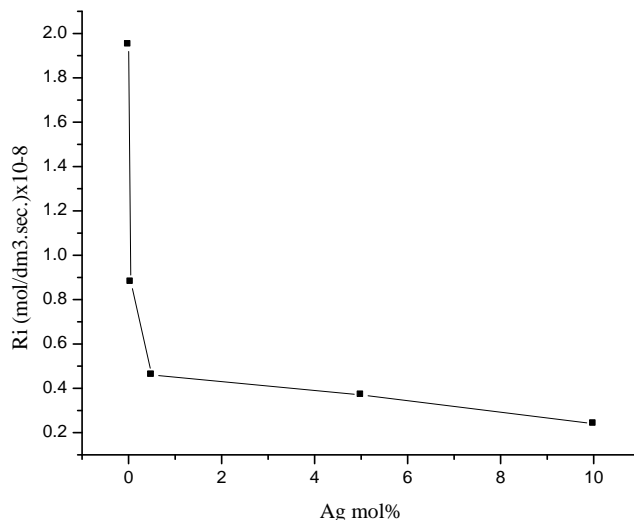


Fig. 5. Plot of rate of reaction (R_i) against amount of Ag (mol %) doping in SiO₂ under visible light photocatalysis.

From **Fig. 5**, we note that the activity of the catalyst decreases the reaction rate under visible light photocatalysis on addition of silver, with the rate of reaction decreasing from 1.95 to 0.24 sec⁻¹ as tabulated in **Table 2**. Hence under visible light photocatalysis Ag doped SiO₂ shows an opposite response than as shown in UV light.

Table 2. It shows rate of reaction using different wt % Ag doped SiO₂ as a catalyst under visible light.

Concentration of Ag (in wt%)	Rate of Reaction (mol.dm ⁻³ .sec ⁻¹) x 10 ⁻⁸
0	1.95
0.05	0.88
0.5	0.46
5	0.37
10	0.24

Percentage degradation during the course of irradiation was evaluated using the following formula.

$$\% \text{ Degradation} = \frac{(A_0 - A)}{A_0} \times 100$$

where A_0 and A depict the absorbance of non-irradiated (0 min.) and irradiated (at the specific time interval) samples. The results are displayed in form of histograms in Fig. 6 (a-d) which show the percentage degradation of the MB dye under UV and Visible light irradiations, using undoped SiO_2 , and Ag-doped SiO_2 at various time intervals.

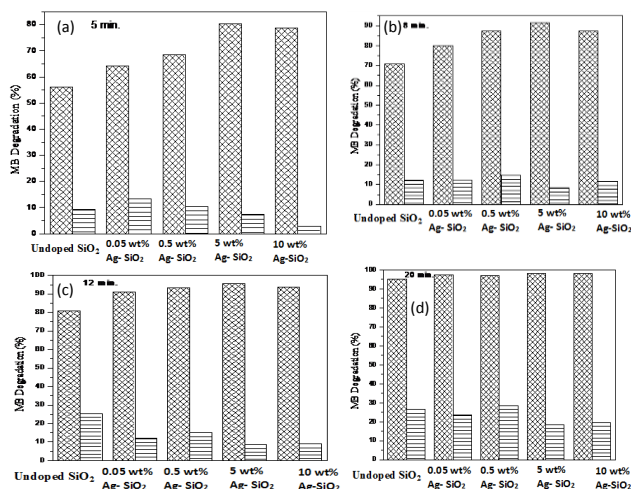


Fig. 6. Percentage degradation of MB dye (a) upon 5 min. irradiation under UV (▨) and Visible (▨) light using Bare and Ag doped SiO_2 as a photocatalyst, (b) upon 8 min. irradiation under UV (▨) and Visible (▨) light using Bare and Ag doped SiO_2 as a photocatalyst, (c) upon 12 min. irradiation under UV (▨) and Visible (▨) light using Bare and Ag doped SiO_2 as a photocatalyst and (d) upon 20 min. irradiation under UV (▨) and Visible (▨) light using Bare and Ag doped SiO_2 as a photocatalyst.

From these Fig. 6 (a-d) and the data depicted within, the photocatalysis rate enhancement involving UV light is considerable as compared to visible light irradiation, where the reaction rate is lowered on addition of Ag – both in comparison to undoped SiO_2 . This data clearly shows that the effect of Ag doping as compared to undoped SiO_2 is that the rate of degradation increases under UV light whereas it decreases under visible light irradiation. Within 8 min. of UV irradiation, the 5 wt% Ag doping could effectively degrade 90 % of MB dye, and upon longer irradiation of 12 minutes, this degradation was almost complete. Within 20 minutes of UV irradiation, under all dopant concentrations, the dye was completely degraded.

Conclusion

The photocatalytic degradation of sol-gel derived SiO_2 with various amounts of doping by silver has resulted has been studied. The doping with low concentration of silver (0.05 wt % and 0.5 wt %), resulted in a slight decrease in average crystallite size (from 13.51 nm to 12.75 nm) but as we increased the concentration of silver to 5 wt % and 10 wt % average crystallite size increased to 15.07 nm and 21.04

nm respectively, as calculated from X-ray diffraction data. These results indicate that with the increase in weight percentage of Ag, the mean size of silver nanoparticles in the amorphous SiO_2 matrix is increased after sintering of samples. The Ag- SiO_2 photocatalyst with appropriate content of Ag (5 wt %) perhaps possess abundant electron/hole traps and favors the transfer of the electrons to the surface. As a result, the recombination of photo-induced charge carriers can effectively be inhibited. In addition, the behaviors of the materials in photocatalytic decomposition of MB under both UV and visible light irradiation were studied as a function of crystallite size, and it was found that under UV light, while the photo-activity of our undoped SiO_2 sample was good with increasing irradiation time, the Ag-doped catalysts showed considerably faster degradation of MB dye. Under visible light photocatalysis, however, the Ag-doped SiO_2 shows an opposite response than what is shown in UV light. For UV irradiation, a significant blue shift in the absorption maximum is observed in all Ag-modified SiO_2 (typically 10–12 nm), but no real shift is observed for undoped SiO_2 .

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