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Preparation and characterization of nano silver-doped mesoporous titania photocatalysts for dye degradation

N.N. Binitha [a,b,*], Z. Yaakob [b,1], M.R. Reshmi [a], S. Sugunan [c,2], V.K. Ambili [c,2], A.A. Zetty [b,1]

[a] Department of Chemistry, Sree Neelakanta Government Sanskrit College, Pattambi, Palakkad-679306, Kerala, India
[b] Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[c] Department of Applied Chemistry, CUSAT, Cochin 22, Kerala, India

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ABSTRACT

Photodegradation of Methyl orange is done over TiO_2 and nano silver-doped TiO_2. Sol–gel method of preparation is used to get improved structural properties as well as photocatalytic activity for environmental pollutant degradation. Glucose takes the role of the reductant for nano silver preparation together with urea as a stabilizer of nanoparticles. Both of these are working as templates and lead to mesoporous TiO_2 formation. Ag doping is found to be very effective in increasing the photoactivity of TiO_2 in dye degradation. Present work introduces a new route for nano Ag-doped mesoporous TiO_2 preparation which eliminates the presence of sodium which is a catalytic poison. Efficient dispersion of the inserted metal within the TiO_2 matrix is proved from various characterization techniques such as XRD (X-ray Diffraction), TEM (Transmission Electron Microscope), etc.

1. Introduction

Titanium dioxide (TiO_2), the most promising photocatalyst because of its potential application in the decomposition of pollutants in water and air, has attracted much attention for the past few decades. However, the effective photoexcitation of TiO_2 requires the radiation of light with energy higher than the titania band gap energy [1] (3.2 eV for anatase, 3.02 eV for rutile). Consequently, TiO_2 requires UV light with a wavelength of no longer than 387.5 nm to be excited and be capable of photooxidation. This practically rules out the use of sunlight as an energy source for the photoreaction on pure TiO_2. In addition, it has also been known that in TiO_2, there is a high rate of recombination between the excited electron and the positive hole. Therefore, there is an urgent need to develop a new photocatalyst capable of working under sun light/visible light irradiation. Considerable investigations has been focused on improving photocatalytic activity of titania using dopants and surface deposition of noble metals to broaden the absorption of the solar spectrum by TiO_2 and reduce recombination odds of photoexcited carrires.

Doping transition metal ions into TiO_2 is one of the effective methods to control its surface properties by harvesting the visible region of the solar spectrum [2,3]. The effectiveness of titania as a photocatalyst depends on its crystal phase, particle size and crystallinity [4] which are greatly influenced by the preparation methods.

In the present work, Ag-doped TiO_2 photocatalyst was prepared through colloidal sol–gel route. Instead of the routine, generally adapted NaOH mediated nano silver preparation method, we selected glucose as the eco-friendly reducing agent that eliminates the presence of Na which acts as a catalytic poison [5,6]. The properties of the catalysts were characterized and their photocatalytic performance in methyl orange degradation was tested and reported. The use of urea template and glucose reductant leads to well-ordered nano Ag-doped mesoporous titania preparation.

2. Experimental

2.1. Materials and methods

2.1.1. Preparation of nano sliver-doped titania

Titania Sol is prepared via colloidal route from metatitanic acid (M/s Travancore Titanium Products, Trivandrum, India, 99% purity) precursor [7]. Titanyl sulphate is obtained by dissolving the precursor in concentrated sulphuric acid. Ammonia (S.D Fine Chemicals) is added to this until complete precipitation of titanium hydroxide occurs. The sulphate freed precipitate is suspended in hot water and 10% HNO_3 (Merck) is added drop wise until a stable sol is obtained at a pH of around 1.5. After that 2 g glucose (NICE chemicals) is dissolved in 10% urea (NICE chemicals) solution. Then 75 ml 0.01 M silver nitrate (NICE chemicals) is added to this and

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[*] Corresponding author. Tel.: +91 466 2212223.
E-mail addresses: binithann@yahoo.co.in (N.N. Binitha), zahira@eng.ukm.my (Z. Yaakob), resmiraveendran.mr@gmail.com (M.R. Reshmi), ssg@cusat.ac.in (S. Sugunan), ambilivk@yahoo.com (V.K. Ambili), zetty555@yahoo.com (A.A. Zetty).
[1] Tel.: +60 3 8921 6400; fax: +60 3 8921 6148.
[2] Tel.: +91 484 2575804; fax: +91 484 2577595.

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kept at 40 °C. The colour of the solution changes to yellow indicating the formation of nanosized particles of silver. The above solution is then added to the titania sol to get a metal loading of 2 wt.%. After stirring well for 3 h, gelation is done using 1:1 ammonia, filtered and washed the precipitate with distilled water till the filtrate did not answer biuret test in order to ensure complete elimination of urea. It is then dried at 110 °C and calcination is done at 250 °C for 12 h. For comparison of physico-chemical properties and catalytic activity studies, urea template mediated sol–gel titania prepared without adding nano Ag and glucose is also calcined at 250 °C for 12 h. Sol–gel Titania prepared without using urea template same as above method is also used for comparison. Systems are designated as Ag/TiO_2 for nano silver-doped titania, M-TiO_2 for sol–gel titania prepared in the presence of urea template and SG-TiO_2 for sol–gel titania in the absence of template as well as dopant.

2.2. Catalyst characterization

XRD patterns of the samples were recorded for 2θ between 3 and 80° on a Philip diffractometer employing a scanning rate of 0.02°/S with Cu Kα radiation (λ = 1.5418). Nitrogen adsorption measurements were performed at liquid nitrogen temperature with a Micromeritics Tristar 3000 surface area and porosity analyzer. Prior to the measurements, the samples were degassed for half an hour at 90 °C followed by 4 h at 200 °C. Surface area was calculated using the BET (Brunauer–Emmett–Teller) interpretation of the nitrogen adsorption isotherm. Transmission electron microscope, TEM (Philips CM12 operated at 100 kV) was used to examine the size of TiO_2 particles as well as Ag nano particles. The X-ray fluorescence (XRF) (Phillips PW 1480 Spectrometer) technique was used to determine the silver present in the Ag/TiO_2 quantitatively. Diffuse Reflectance Ultraviolet–visible spectroscopy (UV–vis DRS) of powder catalyst samples was carried out at room temperature using a PerkinElmer Lamda-35 spectrophotometer in the range of 200–800 nm.

2.3. Photocatalytic activity

Photocatalytic activity of the specimens was evaluated by measurement of degradation of methyl orange (MO). All solar experiments were carried out in closed Pyrex flasks at room temperature with stirring. Direct sunlight was used in the present study and the irradiation was performed during the sunny days from 11.00 to 14.00 h when solar intensity fluctuations were minimum. The samples were immediately centrifuged and the quantitative determination of MO was performed using *Shimadzu UV–vis spectrophotometer* (UV-1601 A) before and after reaction at 464 nm. Experiments were repeated three times to get better results. Experiments were also conducted under solar irradiation without catalyst to measure any possible direct photolysis of these organics. The pH variation during the course of reaction was not significant. So all runs were conducted at natural condition.

3. Result and discussion

XRD patterns of all the samples show that the titania systems consists of exclusively anatase phase (JCPDS data base 21-1272, Fig. 1) with the major peak manifested by its 101 peak at 2θ = 25.5°. The peak of the 110 peak of rutile at 2θ = 27.5° is found to be absent in all the systems confirming its absence. There is no any diffraction peak corresponding to urea crystals, which has a sharp diffraction peak at 22.2° (JCPDS file no. 89-6731). This confirms complete removal of urea template. The absence of peaks of Ag metal as well as oxides of silver indicates efficient dispersion of nano particles and absence of Ag ions.

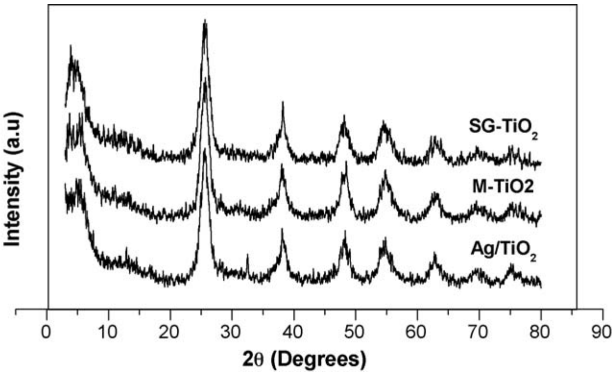

Fig. 1. XRD patterns of photocatalysts Ag/TiO_2, M-TiO_2 and SG-TiO_2.

Table 1 shows the results of N_2-adsorption/desorption measurements. This technique was performed to determine specific surface area and average pore size of the different systems. Fig. 2 shows the N_2-sorption hysteresis of the photocatalysts which is in agreement with the mesoporous nature. The details of adsorption desorption data of sol–gel titania and urea template mediated titania is already reported from this lab [8]. We are using the same data for comparison with nano silver-doped system. The systems show type IV isotherms with H2 hysteresis, which shows mesoporous nature with cage like or ink in a bottle type pores. The specific surface area measurement was based on the BET model**.** In sample SG-TiO_2, there are two types of hysteresis loops as mentioned in our earlier paper [8]. Presence of H2-hysterisis loop indicates cage-like/ink bottle shaped pore structure whereas the type H4 loop appears to be associated with narrow slit-like pores. SG-TiO_2 also contains low pressure hysteresis (indicates micropores), extending to the lowest attainable pressures. This phenomenon is thought to be associated with the swelling of a non-rigid porous structure or with the irreversible uptake of molecules in pores (or through pore entrances) of about the same width as that of the adsorbate molecule [9]. This is not favourable for a catalyst where adsorption must be reversible. Sol–gel titania prepared without using template shows pores with irregular shapes and different range of dimensions. But urea mediated mesoporous titania as well as nano Ag-doped one shows single type pores and absence of micropores.

The pore size distribution determined by the BJH method is shown in Fig. 3. The average pore diameter of each system is given in the Table 1. The results showed that the pore size of all samples were uniform in the main range of 2.0–6.0 nm with a maximum portion at about 4–5 nm. The pore size distribution is narrowest in the case of Ag/TiO_2 and widest for SG-TiO_2. Presence of urea template creates more ordered pores when compared to sol–gel titania prepared without the presence of any template. In the nano Ag-doped system, in addition to urea; glucose may also acts as a template to create well-ordered pores. In this case the average pore diameter is also found to be least. The presence of both urea as well as glucose creates more number of well-ordered pores and that may be one of the reasons for slight increase in the surface area of Ag-doped system.

XRF Spectral analysis shows that the amount of Ag incoporated is 1.4%. We tried to incorporate 2 wt.% Ag per TiO_2 and the slight

Table 1
Surface area, porevolume and average pore size of the prepared systems.

Catalyst	BET Surface area (m^3/g)	Pore volume (cm^3/g)	Pore size (Å)
Ag/TiO_2	238.01	0.3369	40.89
M-TiO_2	234.87	0.3214	44.13
SG-TiO_2	227.71	0.2923	44.88

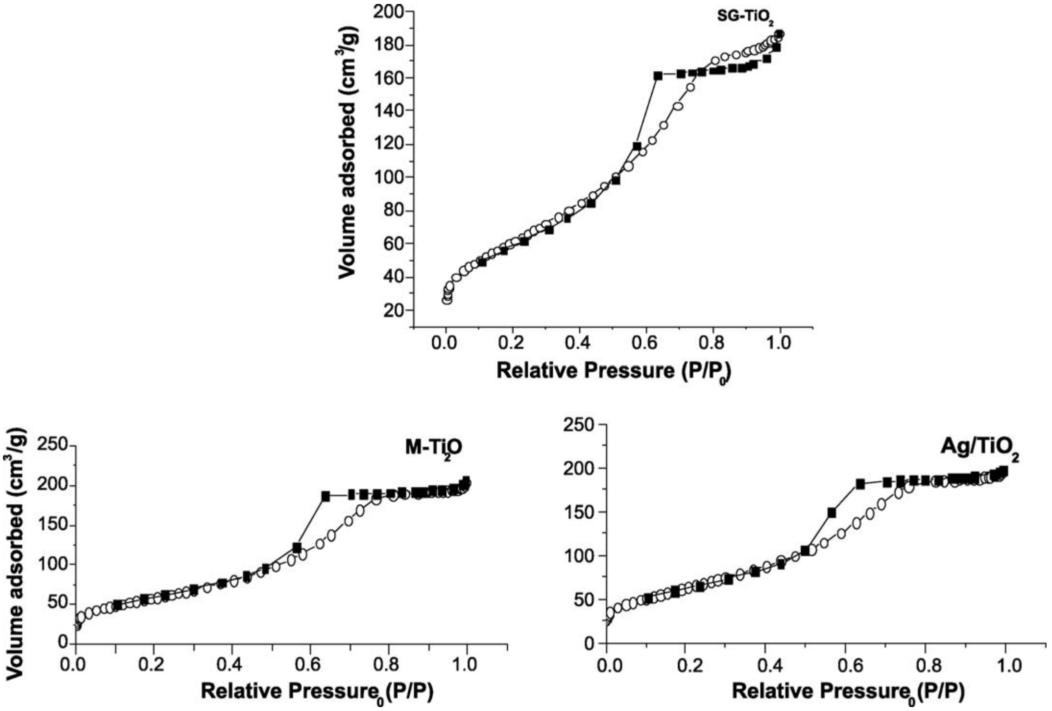

Fig. 2. Nitrogen adsorption–desorption isotherms for titania samples Ag/TiO_2, M-TiO_2 and SG-TiO_2.

decrease in the metal content after doping is due to leaching out of nano Ag during washing. UV–vis light excitation creates photogenerated electrons and holes. Information about the absorptive properties of metal oxides can be obtained from diffuse reflectance UV–vis spectroscopy. This is very important for catalysts for photocatalytic applications since it gives information about the band gap of semiconductors. Characteristic band for octahedrally coordinated titanium appear at about 300–400 nm [10]. The absorption is associated to the $O^{2-} \rightarrow Ti^{4+}$ charge transfer corresponding to electronic excitation from the valence band to the conduction band. It is clear that upon Ag doping the band width shifts to higher wavelengths. Urea assisted sol–gel method without metal incorporation also shows slight shift towards the visible region when compared to the non-templated sol–gel route. The derivative plots of the spectra indicating the maximum absorption in UV region are shown in Fig. 4.

TEM photographs of the systems are shown in Fig. 5. The particle size of TiO_2 is found to be in the range of 8–12 nm which is found to be suitable for efficient photocatalysis. In the Ag-doped system, a uniform distribution of Ag nanoparticles are seen and size is found to be 4–5 nm. The uniform distribution of nano particles and small particles size indicates the efficiency of the present preparation method. The smaller size for the particles could be attributed to an increase in the thermal stability and the

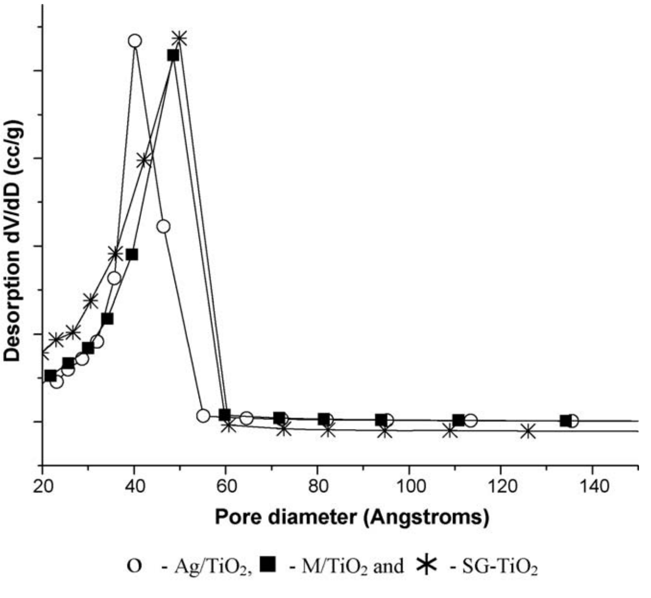

Fig. 3. Pore size distribution curves of prepared systems Ag/TiO_2, M-TiO_2 and SG-TiO_2.

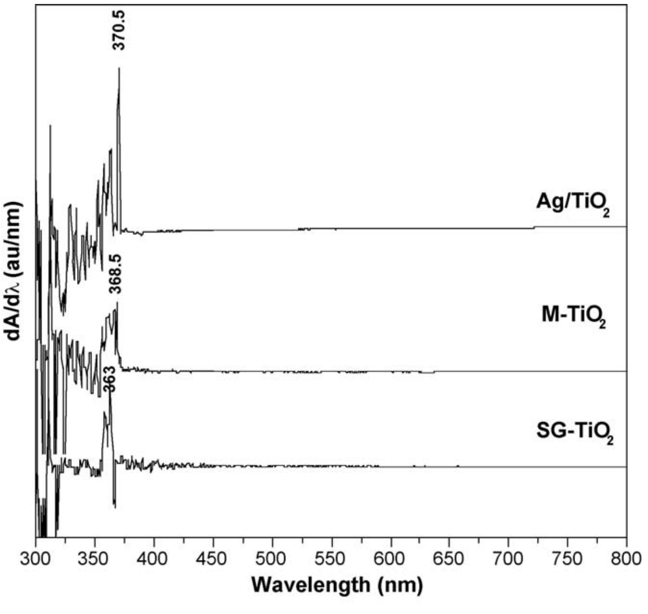

Fig. 4. UV–vis DRS of samples Ag/TiO_2, M-TiO_2 and SG-TiO_2.

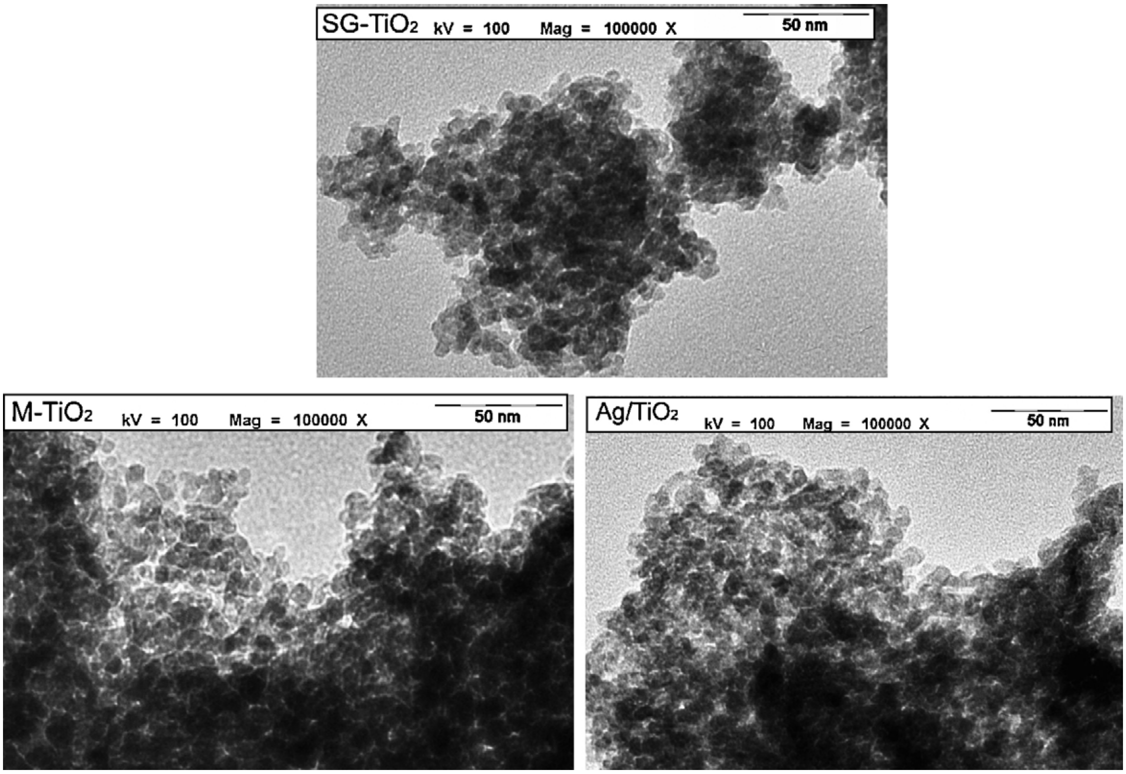

Fig. 5. TEM photographs of titania based systems Ag/TiO_2, M-TiO_2 and SG-TiO_2.

resistance to sintering [11]. This indicates the effectiveness of sol–gel titania preparation through colloidal route adopted in this study.

Photo degradation of organic and inorganic pollutants on semiconductor TiO_2 is a current topic of research. As the international environmental standards are becoming more stringent, many research studies have been focused on the treatments of coloured waste water. The heterogeneous photocatalytic degradation of a large number of dyes over titania is studied and is found to be cost effective. To check the photo degradability of present titania systems degradation of methyl orange (MO) is done under solar irradiation. The solar spectrum (sea level) contains ca 5% of UV radiation. So the activity may be either due to that UV or visible light present under sunlight. The activity is compared at a methyl orange molar concentration of 10^{-5}, after 1 h irradiation using 0.2 g of the catalysts. The MO degradation rate of blank test without any photocatalysts was zero. Activity in dark is also found to be zero confirming the photodegradation of pollutant in the presence of photocatalyst titania. The results are shown in Table 2. The activity is also compared with commercially available non-porous anatse Titania (Qualigens fine chemicals). The present systems are found to be promising photocatalysts, where Ag doping shows maximum photodegradation of MO. Template assisted preparation leads to increase in surface area as well as catalytic activity when compared to the non-templated sol–gel titania.

Table 2
Photodegradation data of MO over present titania samples and commercial anatase titania.

Catalyst	Degradation (mol%)
Ag/TiO_2	93.89
M-TiO_2	81.48
SG-TiO_2	73.52
Anatase TiO_2	68.25

The dispersion stability, improved by incorporation of metals would expose more TiO_2 surface to methyl orange. Thus the dispersion stability may be the reason for improved methyl orange degradation over nano silver-doped TiO_2. In the case of urea mediated method, the increased surface area adds the activity. A very good correlation is obtained between the λ_{max} and the percentage degradation of MO over these systems. Since the λ_{max} is still in the UV region, the present systems can be very effective in photodegradation of pollutants even with the presence of low intensity of UV light in the sunlight.

4. Conclusions

$TiO_{2,}$ urea template mediated TiO_2 and nano Ag-doped TiO_2 were prepared using sol–gel method in mild conditions. Present method uses eco-friendly method for nano Ag preparation and cheap colloidal route without any organic solvent for sol–gel titania preparation. The nano Ag incorporated TiO_2 exhibited higher sunlight absorption and was responsible for the sloar activity. The presence of nano silver dopant increased wavelength of absorption of titania and improved the photocatalytic activity. Here we introduce an efficient method for the homogeneous distribution of nano Ag over mesoporous sol–gel titania. Glucose reductant together with urea stabilizer makes size of silver particles low in the range of 4–5 nm for better catalytic activity.

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