Nanostructured AgBr loaded TiO₂: An efficient sunlight active photocatalyst for degradation of Reactive Red 120

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Abstract
The AgBr loaded TiO₂ catalyst was prepared by a feasible approach with AgBr and tetraisopropyl orthotitanate and characterized by BET surface area measurement, diffuse reflectance spectra (DRS), scanning electron microscope (SEM), energy dispersive spectra (EDS), X-ray diffraction (XRD), transmission electron microscope (TEM) and atomic force microscope (AFM) analysis. The results of characterization reveal that AgBr loaded TiO₂ has a nanostructure. Formation of the nanostructure in AgBr loaded TiO₂ results in substantial shifting of the absorption edge of TiO₂ to red and enhancement of visible light absorption. Electrochemical impedance spectroscopy measurements reveal that AgBr loaded TiO₂ has a higher photoconductivity than prepared TiO₂ due to higher separation efficiency of electron-hole pairs. Cyclic voltammetric studies reveal enhanced conductivity in AgBr loaded TiO₂, which causes an increase in its photocatalytic activity. AgBr loaded TiO₂ exhibited a higher photocatalytic activity than TiO₂-P25 and prepared TiO₂ in the photodegradation of Reactive Red 120 (RR 120).

1. Background
Azo dyes, which contain one or more azo bonds, are the most widely used synthetic dyes and generally are major pollutants in dye wastewater. Due to their toxicity and slow degradation, these dyes are classified as environmentally hazardous materials. Advanced oxidation technologies (AOTs) are widely used for environmental remediation of toxic organic pollutants from the domestic use and industrial activities [1-4]. AOT is characterized by the generation of highly reactive radicals which can initiate the oxidative degradation of organic pollutants. TiO₂ is the most widely studied photocatalyst due to its efficiency, low cost, non-toxicity and high stability [5]. But ultraviolet (UV) light (l < 385 nm) is required to overcome the band gap of TiO₂ to produce electron (-)/hole (+) pairs. Since the generation of UV photons is relatively expensive and requires special equipment, it is advantageous to use solar radiation as an abundant and inexpensive light source for photocatalysis. In solar spectrum, UV radiation accounts for about 4%, compared to more than 50% for the visible light. Nowadays research is focused on the development of visible light active catalysts [6-9]. Silver halides are known as visible light sensitive materials and are widely used in photographic films. Absorption of a photon by silver halides liberates an electron and a positive hole. The electrons will combine with mobile interstitial silver ions, leading to separation of a silver atom. If the photographic process is inhibited, the photogenerated electron and hole could be used in the photocatalytic process [10]. AgBr is one of the primary materials used in the photographic industry and its photographic processes are given in equations 1-3 [11].

\[ \text{AgBr} + h\nu \rightarrow \text{AgBr} \left( h^+ + e^- \right) \]  
\[ e^- + Ag^+ \rightarrow Ag^0 \ (Ag^+ : \text{interstitial silver ions}) \]  
\[ \text{AgBr} \xrightarrow{h\nu} \text{Ag} + \frac{1}{2} \text{Br}_2 \]

However, AgBr could maintain its stability and photocatalytic activity if it is well dispersed on support materials. Al-MCM-41 [12] (Aluminium loaded Mobile Crystalline Material) and titanium dioxide (TiO₂) [13] were used as the support to deposit AgBr and these...
catalysts were active and stable while applied in gas phase or aqueous solution under UV or visible irradiation for the degradation of organic compounds.

In this study, we report the synthesis of AgBr loaded TiO$_2$ photocatalyst without using any surfactant or solvent at moderate temperature and its characterization. Reactive Red 120 (RR 120) was chosen as the model pollutant to evaluate the photoactivity and stability of the synthesized catalyst under direct sunlight. RR 120 is one of the most widely used synthetic azo dye in textile industries. Direct sunlight was employed to illustrate the possibility of solar energy utilization.

2. Results and discussion

2.1 Characterization of AgBr loaded TiO$_2$ photocatalyst

2.1.1 XRD analysis

In order to confirm the crystalline structure of prepared AgBr loaded TiO$_2$ catalyst, powder XRD study was carried out. Figure 1 displays the XRD pattern of AgBr loaded TiO$_2$ (a), prepared TiO$_2$ (b) and AgBr (c). In AgBr loaded TiO$_2$ system there are two well defined peaks with 2$\theta$ values of 30.9° and 44.3° corresponding to (200) and (220) crystal planes of cubic AgBr (JCPDS No.79-0149), respectively (Figure 1a). Moreover, the diffraction peak at 64.4° assigned to metal Ag is also displayed in AgBr loaded TiO$_2$ system [14,15]. The crystalline size of both prepared TiO$_2$ and AgBr loaded TiO$_2$ were determined using Debye-Scherrer equation (4).

$$D = \frac{K \lambda}{\beta \cos \theta}$$  \hspace{1cm} (4)

where D is the crystal size of the catalyst, $K$ is dimensionless constant (0.9), $\lambda$ is the wavelength of X-ray, $\beta$ is the full width at half-maximum (FWHM) of the diffraction peak and $\theta$ is the diffraction angle. The average crystalline size of AgBr loaded TiO$_2$ is found to be 31.8 nm which is less than the size of prepared TiO$_2$ (34.7 nm).

2.1.2 BET surface area analysis

In general the surface area of the catalysts is the most important factor influencing the catalytic activity. The BET surface area of AgBr loaded TiO$_2$ is given in Table 1. BET surface area of AgBr loaded TiO$_2$ (55.4 m$^2$ g$^{-1}$) is higher than the commercial TiO$_2$-P25 (50.0 m$^2$ g$^{-1}$). The N$_2$ adsorption/desorption isotherms of the synthesized AgBr loaded TiO$_2$ exhibited typical IUPAC type IV pattern with the presence of hysteresis loop as exemplified in Figure 2 for the sample calcined at 450°C for 2 h. This catalyst provided the highest photocatalytic degradation of Reactive Red 120 dye (based on 200 mg of AgBr loaded TiO$_2$) as discussed later. A clear hysteresis at high relative pressure is observed, which is related to capillary condensation associated with large pore channels. Average pore diameter of AgBr loaded TiO$_2$ is shown in the inset of Figure 2 is 37.2 Å (3.72 nm). The pore size distribution of the AgBr loaded TiO$_2$ samples thus confirm the mesoporosity. As illustrated in the inset in Figure 2 the pore size distribution calculated by BJH (Barret-Joyner-Halenda) method of samples obtained from this deposition precipitation method is quite narrow, verifying good quality of the samples [16].

2.1.3 SEM and EDS analysis

The texture and morphology of prepared TiO$_2$ and AgBr loaded TiO$_2$ samples are very important parameters and might influence the photocatalytic activity. The SEM images of AgBr loaded TiO$_2$ and prepared TiO$_2$ are shown in Figures 3a and 3b. The SEM image of prepared TiO$_2$ (Figure 3b) depicts that the particles are in the form of aggregates and the surface of the prepared TiO$_2$ is irregular and not spherical. In the case of

| Properties               | Values       |
|-------------------------|--------------|
| BET surface area        | 55.4 (m$^2$ g$^{-1}$) |
| Total pore volume (single point) | 0.146 (cm$^3$ g$^{-1}$) |
| BJH desorption average pore diameter (2 V/A) | 3.72 nm |
| Median pore width       | 12.54 nm     |

Table 1 Surface properties of AgBr loaded TiO$_2$.
AgBr loaded TiO$_2$ composite material, distribution of smaller size AgBr particles on the TiO$_2$ particles could be seen (Figure 3a). Because of the smaller size, several AgBr particles are capable of interacting with a single TiO$_2$ particle. The grape bunch-type clusters in AgBr loaded TiO$_2$ create nanostructured pores of various dimensions within the surface. Such a direct contact between the two particles may be crucial for improving the photocatalytic activity of the composite semiconductor materials [17].

The EDS of AgBr loaded TiO$_2$ and prepared TiO$_2$ are displayed in Figures 4a and 4b. The EDS of AgBr loaded TiO$_2$ (Figure 4a) shows the presence of Ag and Br in the catalyst. The weight percentages of Ag and Br in 42.4 wt% AgBr loaded TiO$_2$ at a particular region are 11.63 and 12.53, respectively (Table, in inset Figure 4a).

### 2.1.4 TEM analysis of AgBr loaded TiO$_2$

Figure 5 shows the typical bright-field TEM image of the 42.4 wt% AgBr loaded TiO$_2$ powder. TEM image reveals the presence of highly crystalline AgBr loaded TiO$_2$ nanoparticles with a few aggregations and also the presence of AgBr as dark spots on TiO$_2$. The size of the TiO$_2$ nanoparticles is in the range of 10 to 50 nm, which is consistent with the average crystallite size (31.8 nm) estimated from XRD analysis.

### 2.1.5 AFM analysis of AgBr loaded TiO$_2$

The striking differences in morphology of the prepared TiO$_2$ and AgBr loaded TiO$_2$ become very clear in their AFM images. The existence of nano sized particles in the AgBr loaded TiO$_2$ nanocomposite is more clearly reflected in its 3D AFM image (Figure 6a) which is characterized by a wave type projection in the z direction (uniform array). Interestingly, one can notice the AgBr loaded TiO$_2$ composite in the form of uniform assembled entities and fine crystals. On the other hand, these features are completely absent in the 3D image of the prepared TiO$_2$ (Figure 6b), which in fact shows an random array of cluster like nodules (cloud assembled entities) projection in the z direction. Film imperfections in the form of large aggregation and scratches can also be noticed in the case of prepared TiO$_2$. The fine surface and small crystalline size of AgBr loaded TiO$_2$ may enhance the photocatalytic activity [18]. Thus the AFM results confirm the structural differences in the surface morphology of the prepared TiO$_2$ and AgBr loaded TiO$_2$.

### 2.1.6 DRS analysis

Optical absorption spectra of prepared TiO$_2$ and 42.4 wt % AgBr loaded TiO$_2$ are shown in Figure 7. It can be seen from the Figure 7b that the absorption onset is
around 400 nm for prepared TiO$_2$. This absorption extends into the visible region (510 nm) for AgBr loaded TiO$_2$. The band gap energy value of corresponding spectrum was calculated using the equation $E_{bg} = \frac{1239.8}{\lambda}$ nm [19]. The band gap energy value of AgBr loaded TiO$_2$ is 2.47 eV, which is smaller than that of prepared TiO$_2$ (3.1 eV). Thus AgBr loading causes the adsorption edge of TiO$_2$ to shift to the lower energy region. This extended absorption may be due to the band gap of AgBr - TiO$_2$ nanojunction.

2.1.7 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a relatively new and powerful tool to probe the electrical properties of semiconductors. As a widely used electrochemical method, EIS is very effective to investigate the properties of the electron-transfer process across the TiO$_2$-electrolyte interfaces under light [20-22]. It is well established that of EIS Nyquist plots are associated with the charge transfer resistance and the separation efficiency of the photohole-electron pairs [23]. Figure 8b shows the Nyquist plot of the prepared TiO$_2$ catalyst material and the frequency for EIS measurement is scanned from 0 to 120000 Hz. A large circular radius usually shows a higher charge transfer resistance indicating the lower conductivity of TiO$_2$. Therefore pure
TiO₂ has a lower separation efficiency of the electron-hole pairs. Nyquist plot of AgBr-TiO₂ (Figure 8a) is scanned from 400-800 Hz. Enlarged Nyquist plot of AgBr-TiO₂ (inset of Figure 8a) shows a small circular radius indicating lower charge transfer resistance. Hence AgBr-TiO₂ has higher separation efficiency. This increases the photoconductivity and photocatalytic activity of AgBr loaded TiO₂. Equivalent circuit model used for analyzing the EIS is given in Figure 9. ([-] unknown resistance, [Q] Known resistance).

2.1.8 Cyclic voltammetry analysis
CV of the reversible redox pair [Fe(CN)₆]⁴⁻/³⁻ is a valuable method to monitor the properties of the modified electrode [24]. Prepared TiO₂/GCE composite electrode was initially cycled with 3 mM Fe(CN)₆⁴⁻/³⁻ in 0.1 M KCl electrolyte solution giving a working potential window from -0.4 V to +1.0 V versus a Ag/AgCl reference electrode, as shown in curve (b) of Figure 10. This large 1.4 V potential window demonstrated that prepared TiO₂ is unable to induce either oxidation or reduction of ferro/ferri cyanide. The AgBr loaded TiO₂/GCE nanocomposite electrode was tested for detection of 3 mM Fe(CN)₆⁴⁻/³⁻ in 0.1 M KCl. The peak to-peak separation (ΔEp) is 309 mV (Figure 10a) indicating a quasi-reversible redox reaction at the electrode [25]. The AgBr loaded TiO₂ electrode shows a reversible peak current ratio, Ip, red/Ip, ox, of ~1.13 which approaches the limit for a reversible one electron transfer. This ideal reversible behavior of a fully conductive electrode indicates the presence of AgBr in TiO₂.

2.2 Photodegradability of RR 120
Experiments were carried out to test the photocatalytic activity of by AgBr loaded TiO₂ catalyst and to compare its efficiency with prepared TiO₂ and TiO₂-P25. The results are presented in Figure 11. Prior to irradiation, the dispersions were air purged in the dark for 30 min to achieve the adsorption-desorption equilibrium between AgBr loaded TiO₂ and RR 120. In the presence of AgBr loaded TiO₂ the adsorption of RR 120 was 35.6% which is slightly higher than the adsorption of...
The dye is not degradable by direct photolysis and by AgBr loaded TiO₂ in dark. However, a rapid degradation of RR 120 occurred by irradiation in the presence of AgBr loaded TiO₂. In the presence of AgBr loaded TiO₂ 98.0% degradation of RR 120 was achieved in 40 min whereas 60.1 and 75.0% degradations were observed with prepared TiO₂ and TiO₂-P25 respectively in 40 min. Higher degradation efficiency of AgBr loaded TiO₂ is due to its higher separation efficiency of electron-hole pair as revealed by Nyquist plot of AgBr-TiO₂ (Figure 8a).

Degradation efficiency of AgBr-TiO₂ was also tested with a colorless toxic chemical 4-nitrophenol. It was found that 83.0% degradation occurred with UV light where as only 66% degradation was observed with solar light in 60 min. Higher efficiency in solar light for dye degradation reveals the presence of dye sensitization mechanism along with Ag-Br-TiO₂ sensitization. Since this dye sensitization is common for AgBr-TiO₂, TiO₂-P25 and prepared TiO₂, higher efficiency of AgBr-TiO₂ may be due to the plasmonic photocatalytic mechanism reported for AgCl-TiO₂ system [26]. Further work in the study of mechanism is in progress.

2.3 Catalyst recyclability

The stability of synthesized catalysts was investigated by the repeated use of the catalyst for four runs under the same conditions. After each run, the catalyst was separated by centrifugation and dried at 110°C for 12 h. The results are displayed in Figure 12. Although the degradation efficiency of RR 120 decreased after each run, the catalyst exhibited significant activity after four successive cycles under the natural sunlight irradiation. To
test the effect of annealing the catalyst after the 4th run was calcined at 500°C for 3 h and used for the degrada-
tion. In this case, it was found that degradation effi-
ciency increased to 26.4% when compared with 4th
This may be due to the formation of metallic sil-
ver during calcination [27]. These results indicated that
AgBr loaded TiO2 catalyst remained effective and stable
under successive sunlight illumination if calcinated at
500° for 3 h.

3. Conclusions
Nanostructured AgBr loaded TiO2 catalyst has been
prepared at room temperature by the facile deposition-
precipitation method. The UV-Vis spectra indicate that
the range of visible-light photosresponse of AgBr loaded
TiO2 system is broadened increasing its visible-light-
driven photocatalytic activity. The formation of AgBr
loaded TiO2 nanocluster has been revealed by the
XRD, SEM, TEM and AFM analysis. Electron-hole
recombination in TiO2 is reduced by AgBr loading as
revealed by Nyquest plots of Electrochemical Imped-
ance Spectroscopy. Cyclic voltammetric studies reveal
enhanced conductivity in AgBr loaded TiO2. The
increase of electro conductivity of AgBr loaded TiO2
enhances its photocatalytic activity. Nano AgBr loaded
TiO2 is found to be more efficient than prepared TiO2
and TiO2-P25 for degradation of RR 120. Nano AgBr
loaded TiO2 is found to be a stable, recyclable and effi-
cient photocatalyst at pH 5, for the degradation of RR
120 under solar light.

4. Experimental
4.1 Materials
A gift sample of TiO2-P25 (80:20 mixture of anatase and
rutile) was obtained from Degussa (Germany). It has the
particle size of 30 nm and BET specific surface area of
50 m² g⁻¹. Titaniumisopropoxide (Himedia), sodium
bromide (99.0%) and silver nitrate (99.5%) analytical
grade from Merck were used as received. The model
pollutant, azo dye (Reactive Red 120), obtained from
Balaji Colour Chem, Chennai, was used without further
purification. Double distilled water was used for all the
experiments.

4.2 Irradiation experiments
All photocatalytic experiments were carried out under
similar conditions on sunny days of April-May 2010
between 11 am and 2 pm. An open borosilicate glass
tube of 50 mL capacity, 40 cm height and 20 mm di-
ameter was used as the reaction vessel. The suspensions
were magnetically stirred in the dark for 30 min to
attain adsorption-desorption equilibrium between dye
AgBr loaded TiO2. Irradiation was carried out in the
open-air condition. Fifty mL of dye solution with
AgBr loaded TiO2 was continuously aerated by a pump
to provide oxygen and for the complete mixing of reac-
tion solution. During the illumination time no volatility
of the solvent was observed.

After dark adsorption the first sample was taken. At
specific time intervals 2-3 mL of the sample was with-
drawn and centrifuged to separate the catalyst. One mL
of the centrifugate was diluted to 10 mL and its absorb-
bance 285 nm was measured. The absorbance at 285
nm represents the aromatic content of RR 120 and its
decrease indicates the degradation of dye.

Solar light intensity was measured for every 30 min
and the average light intensity over the duration of each
experiment was calculated. The sensor was always set in
the position of maximum intensity. The intensity of
solar light was measured using LT Lutron LX-10/A
Digital Lux meter and the intensity was 1250 × 100 ±
100 lux. The intensity was nearly constant during the
experiments.

4.3 Preparation of photocatalyst
AgBr loaded TiO2 was prepared by the deposition-preci-
ipation method [14]. NaBr-ethanol solution was obtained by dissolving 0.1028 g of NaBr in 4 mL of
ethanol. AgNO3-ethanol solution was obtained by dis-
solving 0.1690 g of AgNO3 in 15 mL of ethanol by soni-
cation. The NaBr solution was mixed with the AgNO3
solution under magnetic stirring. AgBr formed was
added to a mixture of 10 mL of Ti(OBu)₄, 80 mL of 2-
propanol and 10 mL water under magnetic stirring. Pale
yellow precipitate was obtained and it was filtered,
washed thoroughly with distilled water and then with
acetone, dried in air oven for 5 h at 90°C and then cal-
cined in muffle furnace at 450°C for 2 h. AgBr loaded
TiO2 was formed as a greenish yellow powder. This cat-
alyt contained 42.4 wt% of AgBr. Pure titania (TiO2)
was prepared by a similar procedure without the addi-
tion of AgBr.

4.4 Analytical methods
The specific surface areas of the samples were deter-
mined through nitrogen adsorption at 77 K on the basis
of BET equation using a micrometrics ASAP 2020
V3.00 H. Scanning electron microscope (SEM) analysis
was performed on gold coated samples using a JEOL-
JSM 5610 LV, equipped with OXFORD energy disper-
sive X-ray microanalysis (EDS). A quantity of AgBr
loaded TiO2 suspensions were dropped onto copper
grids with holey carbon film. The grids were dried
under natural conditions and examined using a TEM
Hitachi H-7500. The surface morphology and particle
shape were obtained from atomic force microscope
(AFM, JSPM-5200TM, JEOL). Powder X-ray diffraction
patterns of AgBr loaded TiO2 catalyst was obtained.
using X’Per PRO diffractometer equipped with a CuKα radiation (wavelength 1.5406 Å) at 2.2 kW Max. Peak positions were compared with the standard files to identify the crystalline phase. Diffuse reflectance spectra were recorded using Shimadzu UV-2450. The solution containing beaker was then kept in sonication bath (33 KHz, 350 W) at room temperature. UV spectral measurements were done using Hitachi-U-2001 spectrometer. The pH of the solution was measured by using ELICO (LI-10T model) digital pH meter.

4.5 Electrochemical impedance spectroscopy analysis

The values of bulk electrical resistance (Rb) of all the synthesized samples were estimated from the complex impedance data collected in the temperature range 298-363 K using a computer-controlled Hewlett-Packard Model HP 4284A Precision LCR Meter over the frequency range 1MHz-20Hz and at an applied potential difference of 500 mV. The complex impedance data were obtained for prepared TiO2 and AgBr loaded TiO2 by employing a specially designed conductivity cell having a fixed sample thickness of 2 mm. As AgBr is an electroactive material AgBr-TiO2 acts as a solid electrolyte. The samples were effectively held between a pair of cylindrical silver non-blocking electrodes in conjunction with a teflon spacer and suitably placed in a temperature controlled oven. The electrical conductivity (σ) values of individual catalyst specimens were evaluated using the eqn. 5.

\[ \sigma = \frac{1}{R_b} \frac{A}{t} \]  

(5)

where A is the area of cross section, t is the thickness of the sample, σ is conductivity and Rb is resistance of the catalyst material.

4.6 Preparation of AgBr loaded TiO2 nanocomposite electrode for cyclic voltammetry study

A predetermined amount of AgBr loaded TiO2 was dispersed in 0.1% nafion in ethanol solution for 1 h in an ultrasonic bath to form a stable suspension. In this case, a uniformly dispersible solution containing up to 1.0 mg/1 mL (AgBr loaded TiO2 solution) is stable. AgBr loaded TiO2 nanocomposite was deposited on the glassy carbon electrode by droplet evaporation for 15 min and then drying in nitrogen atmosphere for 20 minutes. Finally the electrodes were washed with water, before use. For comparison experiments, Prepared TiO2/GCE electrode was prepared, using the the same procedure.



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