3.1. Introduction

Ag$_2$CO$_3$ is an important narrow band gap semiconductor with plane triangular structure. Ag$_2$CO$_3$ has a band gap of 2.46 eV, and has been recognised as one of the most promising visible-light-driven (VLD) photocatalyst for its excellent and efficient photooxidative capabilities. The incorporation of p-block element carbon into the narrow band gap Ag$_2$O results into the broadening of band gap of Ag$_2$CO$_3$. The top of the valence band (VB) of Ag$_2$CO$_3$ consists of hybridized Ag 4d and O 2p states whereas bottom of conduction band (CB) of Ag$_2$CO$_3$ consists of Ag 5s and Ag 4d states, but Ag 5s states dominate the bottom of conduction band. Further, Ag-Ag bonds in Ag$_2$CO$_3$ are shorter than that in Ag$_2$O suggesting that hybridization takes place between Ag s and Ag s states which results into the more dispersive structure of bottom of CB, which is beneficial for the mobility and migration of photogenerated electrons and holes. This can be the important reason for improved photocatalytic performance of Ag$_2$CO$_3$. It is notable that the hybridization between Ag s states contributes to decrease the effective mass of electrons in favour of transferring electrons, which is also one of the important reasons for improved photocatalytic performance.

However, Ag$_2$CO$_3$ is unstable. The recycle experiments suggested that Ag$_2$CO$_3$ was not stable and displayed photocorrosion which seriously deactivates the photocatalyst. During photochemical oxidation process (PCO), the interstitial Ag$^+$ combines with photogenerated electrons, and hence transformation of Ag$^+$ into Ag takes place which results into the photocorrosion of catalyst in absence of electron acceptors. It is therefore necessary to fabricate the original Ag$_2$CO$_3$, so as to improve its stability, and to further enhance its photocatalytic efficiency.

3.2. Review of Literature

To exploit the solar energy, the development of visible light responsive photocatalysts has become one of the imperative and desired topics in the photocatalytic field. In the past,
attempts of developing visible light responsive photocatalysts were focussed on oxides/composites such as TiO$_2$, 12-14 Ag-TiO$_2$, 15,16 N-TiO$_2$, 17 Nb$_2$O$_5$, 18 Fe$_3$O$_4$/Fe$_2$O$_3$, 19 and sulphides/composite sulphides such as MoS$_2$/MoS$_3$, 20 Cu$_2$ZnSnS$_4$, 21 ZnS, 22 CdS. 23 Recently, silver based compounds, such as AgX (X = Cl, 24,25 Br, 26 I 27), Ag$_2$V$_4$O$_{11}$, 28 AgNbTaO$_3$, 29 Ag$_2$Mo$_3$O$_{11}$, 30 and AgInW$_2$O$_8$ 31,32 were reported to be highly efficient photocatalysts. Among silver based compounds, Ag-based transition metal complex oxide semiconductors possess high photocatalytic activity because of narrow band gap and high mobility of photogenerated electron-hole pairs. For them, the top of the valence band consists of unique hybridized Ag 4d and O2p orbitals which lifts the top position of valence band, and hence narrows the band gap. The bottom of the conduction band for them consists of relatively delocalized s and, or p orbitals which results in significant dispersity so that photogenerated electron-hole pairs display high mobility. 33 Lately, a feasible and highly efficient strategy of incorporating p-block elements into the narrow band gap oxides was used to design new visible-light-driven (VLD) photocatalysts. 34 The reported Ag$_2$O has a narrow band gap of 1.3 eV and hence belongs to narrow band gap semiconductors. 2 It was stated by Ye and co-workers, 34 that for silver based compounds, p-block elements are important ingredients for high photocatalytic activity, however, the focus was on metallic p-block elements. 35 In the context of photocatalysis research, the first example of incorporating non-metallic p-block element phosphorous into Ag$_2$O was reported by Ye and co-workers as Ag$_3$PO$_4$, which displayed strong oxidation power and high quantum yield of O$_2$ generation from water under visible light. 34 The incorporation of p-block elements into the reported Ag$_2$O broadens the narrow band gap of 1.3 eV, 2 and also enhances the oxidative ability and photocatalytic activity of new VLD photocatalysts like Ag$_3$PO$_4$ 34 and AgSbO$_3$. 36 H. Dong et al. 1 reported that incorporation of p-block element carbon into Ag$_2$O results into the broadening of band gap from 1.3 eV to 2.46 eV for Ag$_2$CO$_3$, which is one of the reasons for enhanced oxidation ability of Ag$_2$CO$_3$. However, as stated above, Ag$_2$CO$_3$ is unstable and suffers from photocorrosion during the PCO process. Dai et al. 4 employed a new approach to inhibit the photocorrosion by adding AgNO$_3$ in the reaction system which helps in trapping the electron from conduction band of Ag$_2$CO$_3$, however, this is not the intrinsic property of catalyst itself. Another strategy for improving the stability and catalytic efficiency of Ag$_2$CO$_3$ is to couple it with another semiconductor to form a heterojunction at the interface which will facilitate the separation of photoinduced charge carriers. 37-39 Very recently, Gaopeng et
al.\textsuperscript{40} reported the formation of nanosized Ag\textsubscript{2}CO\textsubscript{3}/reduced graphene oxide photocatalyst with enhanced visible light activity and stability as compared to pure Ag\textsubscript{2}CO\textsubscript{3}. They proposed that under visible light irradiation conducting RGO acts as an effective acceptor of photogenerated electrons form the conduction band of Ag\textsubscript{2}CO\textsubscript{3}, and thus separates and transfers the photogenerated electron-hole pairs effectively. Current literature reports that heterojunctions, such as Ag\textsubscript{2}CO\textsubscript{3}/TiO\textsubscript{2},\textsuperscript{41} g-C\textsubscript{3}N\textsubscript{4}/Ag\textsubscript{2}CO\textsubscript{3},\textsuperscript{42} BN/Ag\textsubscript{2}CO\textsubscript{3},\textsuperscript{43} Ag\textsubscript{2}CO\textsubscript{3}/UiO-66(Zr),\textsuperscript{44} Ag\textsubscript{2}CO\textsubscript{3} modified by graphene oxide,\textsuperscript{45} AgX-loaded Ag\textsubscript{2}CO\textsubscript{3} (X = Cl, I),\textsuperscript{46} nitrogen-doped graphene-Ag\textsubscript{2}CO\textsubscript{3},\textsuperscript{47} etc. could effectively improve the photocatalytic ability and stability of Ag\textsubscript{2}CO\textsubscript{3}.

3.3. Present work

It is a well-known fact that light irradiation of silver based compounds results in the decomposition of compound, and generation Ag nanoparticles directly on the surface of the catalyst.\textsuperscript{48,49} The presence of noble Ag nanoparticles on the surface of a catalyst enhances the absorption of visible light, and also helps to trap the photoinduced electrons effectively, e.g. Ag@AgX,\textsuperscript{50-53} Ag\textsubscript{3}VO\textsubscript{4}/AgBr/Ag plasmonic system,\textsuperscript{54} AgBr/Ag\textsubscript{3}PO\textsubscript{4},\textsuperscript{38} and Ag/TiO\textsubscript{2} plasmonic system.\textsuperscript{55} Recently, studies have shown that AgBr can exhibit high stability and photocatalytic activity, when Ag nanoparticles are formed on its surface. The AgBr has therefore been coupled with many semiconductors to improve their photocatalytic performances. For example, Jing \textit{et al.}\textsuperscript{38} reported the formation of AgBr/Ag\textsubscript{3}PO\textsubscript{4} hybrids with enhanced visible light activity and stability. They reported that under visible light irradiation, clusters of Ag nanoparticles are formed on the surface of catalyst, and these Ag nanoparticles play a special role in enhancing the visible light activity and improving the stability of the catalyst.

To the best of our knowledge, no significant attention has been paid to the fabrication of Ag\textsubscript{2}CO\textsubscript{3} with AgX, and the surface plasmon resonance of metal nanoparticles in improving photodecolourization efficiency and stability of the catalyst. Therefore, it was thought to investigate, what special role does Ag nanoparticles play in AgBr/Ag\textsubscript{2}CO\textsubscript{3} system?

Herein, we report a newly constructed AgBr/Ag\textsubscript{2}CO\textsubscript{3} hybrid with different content of AgBr by \textit{in situ} anion exchange method. The anion exchange method was chosen because it helps to grow AgBr shell more effectively with high dispersity on the surface of Ag\textsubscript{2}CO\textsubscript{3}. This novel composite system had some advantages over pure Ag\textsubscript{2}CO\textsubscript{3}. Firstly, it can easily transform to plasmonic Ag@AgBr/Ag\textsubscript{2}CO\textsubscript{3}@Ag system in the early stages of photocatalytic reaction. Secondly, AgBr and Ag\textsubscript{2}CO\textsubscript{3} have matching band potentials.
which facilitate the fast separation and transfer of photoinduced charge carriers. Azo-dye Ponceau BS (PBS) was used as a model pollutant to evaluate the photocatalytic activity under visible light. The photocatalytic experiment was performed in an immersion well reactor. The as-synthesized composite system exhibited very high visible light induced photocatalytic activity. Scavenger experiments and Terephthalic acid fluorescence experiments were carried out to investigate the primary reactive species involved in the photo decolourization of dye. Fluorescence analysis was used to confirm the effective separation of photoinduced charge carriers. The stability of the photocatalyst was investigated by repetition experiments. The used catalyst was analysed with XRD technique to see the visible changes in the catalyst after experiment. The light absorption property of used catalyst was also investigated by diffuse reflectance spectroscopy (DRS) technique. The detailed mechanism of photodecolourization of dye was proposed, and the role played by Ag nanoparticles formed \textit{in situ} on the surface of photocatalyst in enhancing the photocatalytic efficiency and stability of catalyst was discussed in detail.

3.4. Experimental

3.4.1. Preparation of Ag$_2$CO$_3$

The Ag$_2$CO$_3$ samples were synthesized by simple ion exchange reaction between AgNO$_3$ and NaHCO$_3$ aqueous solutions. In a typical synthetic route, AgNO$_3$ (40 mL, 0.2 M) solution was added drop wise into NaHCO$_3$ (40 mL, 0.1 M) solution on ice water bath under vigorous stirring. The yellow green precipitate formed was filtered, and washed several times with deionized water. The product was dried in a vacuum oven at 60 °C for 6 h.

3.4.2. Synthesis of AgBr/Ag$_2$CO$_3$ hybrids

AgBr/Ag$_2$CO$_3$ hybrids were obtained through an \textit{in situ} anion exchange method in dark conditions at room temperature. The obtained Ag$_2$CO$_3$ (1.0 g) powder was dispersed in 50 mL of distilled water, and suspension was ultra-sonicated for 20 min. Subsequently, different stoichiometric amounts of NaBr solutions were added drop wise into the above Ag$_2$CO$_3$ suspension with constant stirring. The obtained suspension was vigorously stirred for 4 h. The samples containing different theoretical molar percentages of added Br/original C were noted as 10% AgBr/Ag$_2$CO$_3$, 30% AgBr/Ag$_2$CO$_3$, 50% AgBr/Ag$_2$CO$_3$, and 70% AgBr/Ag$_2$CO$_3$. The precipitates were collected, washed with deionized water several times, and finally dried at 60 °C for 24 h. The pure AgBr sample was obtained by a simple precipitation method for comparison.
3.4.3. **Characterization of AgBr/Ag\(_2\)CO\(_3\) photocatalyst**

X-ray diffraction pattern of as prepared samples was carried out at room temperature with Shimadzu XRD-6100 X-ray diffractometer. The morphology was probed by scanning electron microscopy (SEM, JEOL), on which elemental analysis was also probed using EDS attachment. A UV-vis-NIR spectrophotometer (PerkinElmer) equipped with an integrating sphere assembly was used to obtain DRS of the samples in the region of 300-800 nm. The fluorescence emission spectra were recorded over a wavelength range of 420-650 nm on Shimadzu Spectrofluorometer 5000 using 260 nm excitation source.

3.4.4. **Evaluation of photocatalytic activity**

The visible light photocatalytic activity of pure Ag\(_2\)CO\(_3\), AgBr, and the hybrids was evaluated by studying the decolourization of an azo-dye Ponceau BS (PBS). The photocatalytic tests were performed in an immersion well photoreactor (consisting of inner and outer jacket) made of pyrex glass equipped with a magnetic bar, a water circulating jacket, and an opening for molecular oxygen. Irradiations were carried out using a visible light halogen linear lamp (500 W, 9500 Lumens). The reaction temperature was kept constant at 20 ± 0.3 °C using refrigerated circulating liquid bath. Prior to the illumination, 180 mL of the dye solution (0.1mM) containing appropriate quantity of the catalyst (1 gL\(^{-1}\)) was magnetically stirred while the solution was purged continuously with atmospheric air for at least 30 minutes in the dark to attain adsorption–desorption equilibrium between dye and catalyst surface. Aliquots (5ml) were collected at 2 min interval, and centrifuged to remove the catalyst particles. The catalyst free dye solution was then analysed with (Shimadzu UV-vis 1601) spectrophotometer. The change in absorbance of the dye was followed at its \(\lambda_{\text{max}}\) (505 nm) as a function of irradiation time. The observed absorbance is proportional to Beer-Lambert Law in the range of studied dye concentration. The concentration of dye was calculated by standard calibration curve obtained from the absorbance of the dye at different known concentrations.

To determine the effect of reactive oxygen species, various quenchers of species were introduced in the reaction system in a manner similar to the photocatalytic experiment. The dosage of quenchers was referred to the previous studies.\(^{57,58}\) To further investigate the formation of ·OH on the surface of catalyst under visible light irradiation, photo luminescence (PL) technique with Terephthalic acid (TA) as a probe molecule was used. The experimental procedure was referred to the previous studies.\(^{39}\)
3.5. Results and discussion

3.5.1. XRD analysis

Fig. 3.1 presents the XRD patterns of as prepared samples. It was observed that diffraction peaks of Ag$_2$CO$_3$ (Fig. 3.1 (a)) are in good agreement with those of monoclinic structure of Ag$_2$CO$_3$. The main diffraction peak corresponding to lattice plane (130) is centred at 2θ = 33.5°. For AgBr (Fig. 3.1 (f)), diffraction peaks with 2θ values of 31.0°, 44.3°, and 55.0° are assigned to (200), (220), and (222) crystal planes of cubic structure.

The AgBr/Ag$_2$CO$_3$ hybrids (Fig. 3.1 (b-e)) exhibit coexistence of AgBr and Ag$_2$CO$_3$ phases with peaks at 2θ values corresponding to both Ag$_2$CO$_3$ and AgBr indicating the formation of AgBr crystals. Further, with increasing AgBr content the intensity of diffraction peaks of AgBr increase, whereas those of Ag$_2$CO$_3$ decrease simultaneously.

![Fig. 3.1: XRD patterns of: (a) Ag$_2$CO$_3$, (b) 10% AgBr/Ag$_2$CO$_3$, (c) 30% AgBr/Ag$_2$CO$_3$, (d) 50% AgBr/Ag$_2$CO$_3$, (e) 70% AgBr/Ag$_2$CO$_3$, and (f) AgBr.](image)

The crystallite sizes of Ag$_2$CO$_3$ and AgBr in Ag$_2$CO$_3$/AgBr composites were calculated by the Scherer formula$^{39}$: $D = K \lambda / \beta \cos \theta_B$, where $D$ is taken as crystallite size, $K$ is a constant, $\beta$ is the FWHM measured in radians on the 2θ scale, $\theta_B$ is the Bragg angle for diffraction peaks. The crystallite sizes of Ag$_2$CO$_3$ and AgBr/Ag$_2$CO$_3$ hybrids are given in Table 3.1. The crystallite size of Ag$_2$CO$_3$ in the heterojunctions decrease with increase in
AgBr loading up to 50 %, suggesting high dispersity of AgBr in the hybrids. **Fig. 3.2** displays the XRD patterns of used 50% AgBr/Ag$_2$CO$_3$ catalyst after 1 and 5 recycling runs. As can be seen, the used 50% AgBr/Ag$_2$CO$_3$ samples after 1 (**Fig. 3.2 (b)**) and 5 (**Fig. 3.2 (c)**) recycling runs display diffraction peaks assigned to Ag metal$^{51}$ at 38.06°. Moreover, the used AgBr/Ag$_2$CO$_3$ hybrids turned little dark compared to fresh hybrids and this is attributed to the formation of Ag° nanoparticles on the catalyst surface.

**Table 3.1.** Crystallite size of pure samples and AgBr/Ag$_2$CO$_3$ hybrids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size (nm)</th>
<th>Ag$_2$CO$_3$</th>
<th>AgBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$CO$_3$</td>
<td>49.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td>53.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% AgBr/Ag$_2$CO$_3$</td>
<td>47.87</td>
<td>42.26</td>
<td></td>
</tr>
<tr>
<td>30% AgBr/Ag$_2$CO$_3$</td>
<td>47.30</td>
<td>49.31</td>
<td></td>
</tr>
<tr>
<td>50% AgBr/Ag$_2$CO$_3$</td>
<td>42.53</td>
<td>49.61</td>
<td></td>
</tr>
<tr>
<td>70% AgBr/Ag$_2$CO$_3$</td>
<td>48.10</td>
<td>51.71</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 3.2:** XRD patterns of: (a) Fresh 50% AgBr/Ag$_2$CO$_3$, (b) used 50% AgBr/Ag$_2$CO$_3$ after 1 recycling run, and (c) used 50% AgBr/Ag$_2$CO$_3$ after 5 recycling runs.
3.5.2. **SEM and EDS analysis**

The SEM images of pure Ag$_2$CO$_3$, AgBr, and hybrids are presented in Fig. 3.3, and the corresponding EDS results are shown in Fig. 3.4-3.8. **Fig. 3.3 (a)** shows that Ag$_2$CO$_3$ particles have polyhedral rod like morphology with homogenous distribution and smooth surfaces, a factor which enhances the dye adsorption, and improves the electron migration. **Fig. 3.3 (b-e)** presents the SEM micrographs of AgBr/Ag$_2$CO$_3$ hybrids. The formation of hybrids is obvious from these figures which show the irregular cubic shape of AgBr particles (bright spots).

**Fig. 3.3:** SEM images of: (a) Ag$_2$CO$_3$, (b) 10% AgBr/Ag$_2$CO$_3$, (c) 30% AgBr/Ag$_2$CO$_3$, (d) 50% AgBr/Ag$_2$CO$_3$, and (e) 70% AgBr/Ag$_2$CO$_3$. 

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Fig. 3.4-3.8 shows the energy dispersive X-ray spectrum (EDS) and EDS elemental mapping for pure Ag$_2$CO$_3$ and the hybrids. The EDS analysis demonstrate that the pure Ag$_2$CO$_3$ (Fig. 3.4) is composed of Ag, C, and O elements whereas AgBr/Ag$_2$CO$_3$ hybrids (Fig. 3.5-3.8) are consisted of Ag, C, O, and Br. Further, with increase in AgBr content, the percentage of Br detected by EDS also increase. All these results clearly prove the formation of AgBr. The EDS elemental mapping clearly shows that the bromine is highly dispersed in the AgBr/Ag$_2$CO$_3$ hybrids indicating the high dispersity of AgBr in all hybrids. It can be seen from the figure that the dispersity of Br⁻ in hybrids increases with increase in its content. This clearly proves that AgBr does not merely happen to be on the surface of Ag$_2$CO$_3$ but small AgBr nanoparticles are highly dispersed in the hybrids.

Fig. 3.4: EDS and elemental mapping of Ag$_2$CO$_3$. 
Fig. 3.5: EDS and elemental mapping of 10% AgBr/Ag$_2$CO$_3$. 
Fig. 3.6: EDS and elemental mapping of 30% AgBr/Ag₂CO₃.
Fig. 3.7: EDS and elemental mapping of 50% AgBr/Ag₂CO₃.
TEM analysis was used to further investigate the structure and morphology of Ag₂CO₃ and hybrids. The TEM image of pure Ag₂CO₃ (Fig. 3.9 (a)) displays the rod like structure with smooth surface, whereas the AgBr/Ag₂CO₃ hybrids (Fig. 3.9 (b-d)) depict the formation of small AgBr nanoparticles on the surface of Ag₂CO₃ crystal. The EDS
mapping and TEM results clearly prove the formation of small AgBr nanoparticles which are in direct contact with smooth surface of Ag$_2$CO$_3$.

**Fig. 3.9:** TEM images of: (a) Ag$_2$CO$_3$, (b, c, and d) 50% AgBr/Ag$_2$CO$_3$.

### 3.5.3. DRS analysis

The optical absorbance of obtained samples was measured by UV-visible diffuse reflectance spectra (DRS). As shown in the **Fig. 3.10 (a)**, Ag$_2$CO$_3$ has an absorption edge around 466 nm, while AgBr has an absorption edge around 480 nm suggesting that both have strong absorption in the visible light region. As can be seen from the **Fig. 3.10 (a)**, the AgBr/Ag$_2$CO$_3$ hybrids exhibit mixed absorption property in between 400-500 nm.

**Fig. 3.10 (b)** shows the extended and enhanced absorption of used 50% AgBr/Ag$_2$CO$_3$ after 1 and 5 recycling runs in the visible region compared to fresh 50% AgBr/Ag$_2$CO$_3$. This is because of the SPR effect of Ag$^0$ deposited directly on the surface of AgBr$^{48-54}$ and Ag$_2$CO$_3$.$^4$
Fig. 3.10: (a) DRS of AgBr, Ag$_2$CO$_3$ and AgBr/Ag$_2$CO$_3$ hybrids, (b) DRS of Fresh 50% AgBr/Ag$_2$CO$_3$ hybrid and used 50% AgBr/Ag$_2$CO$_3$ after 1 and 5 recycling runs.

The band gap energy of the semiconductor was determined by the following expression (Equation 3.1).\textsuperscript{59}

\[(h\nu \alpha) = (A\nu - E_g)^{n/2}\]  \[3.1\]

Since $\alpha$ is proportional to kubelka-munk function $F(R)$, the expression becomes

\[h\nu \cdot F(R) = (A\nu - E_g)^{n/2}\]  \[3.2\]

where $h$ is planck’s constant, $\nu$ is the light frequency, $F(R)$ is the kubelka-munk function, $A$ is the proportional constant, and $E_g$ is the Band gap energy. The value of ‘$n$’ is
determined by the type of optical transition \((n=1\) for direct transition and \(n = 4\) for indirect transition). For AgBr the value of ‘\(n\)’ is 4\(^9\) and for \(\text{Ag}_2\text{CO}_3\) the value of ‘\(n\)’ is also 4.\(^1\) The \(E_g\) of \(\text{Ag}_2\text{CO}_3\) was determined from the plot of \((F(R), hv)\)\(^{1/2}\) vs. \(hv\) (Fig. 3.11) and was elicited to be 2.46 eV. Accordingly, the \(E_g\) of AgBr was found to be 2.48 eV from the plot of \((F(R), hv)\)\(^{1/2}\) vs. \(hv\) (Fig. 3.11).

The VB and CB edge potentials of a semiconductor at the point of zero charge were calculated using the empirical formula in Equation 3.3.\(^{60}\)

\[
E_{\text{VB}} = X - E^\text{e} + 0.5E_g \\
[3.3]
\]

Where \(E_{\text{VB}}\) is the energy of VB edge potential, \(X\) is the electronegativity of semiconductor, and \(E^\text{e}\) is the energy of free electrons on hydrogen scale (4.5 eV). The top of the valence band \(E_{\text{VB}}\) of \(\text{Ag}_2\text{CO}_3\) and AgBr were calculated to be 2.75 eV/NHE and 2.55 eV/NHE, respectively. Moreover, conduction band edge potential \(E_{\text{CB}}\) can be determined by Equation 3.4.

\[
E_{\text{CB}} = E_{\text{VB}} - E_g \\
[3.4]
\]

Thus \(E_{\text{CB}}\) for \(\text{Ag}_2\text{CO}_3\) and AgBr were elicited as 0.29 eV/NHE and 0.07 eV/NHE, respectively.
3.5.4. Photocatalytic properties

The photocatalytic activity and stability of the as prepared AgBr/Ag₂CO₃ photocatalysts was evaluated by the degradation of Azo dye Ponceau BS (PBS) under visible light irradiation. For comparison, photocatalytic activity of pure AgBr and Ag₂CO₃ samples, and direct photolysis of PBS in absence of photocatalyst was also investigated. **Fig. 3.12 (a)** shows the decolourization of PBS solution in the presence of pure AgBr, Ag₂CO₃, and AgBr/Ag₂CO₃ hybrids. The dark adsorption of PBS over each sample is insignificant and can be neglected. **Fig. 3.12 (a)** shows that under visible light irradiation, all AgBr/Ag₂CO₃ hybrids demonstrate efficient photocatalytic activity compared to pure AgBr and Ag₂CO₃, while PBS could hardly be decolourized in the absence of catalyst indicating that photolysis of PBS can be neglected. Among the heterojunctions, 50% AgBr/Ag₂CO₃ exhibits highest photocatalytic activity with approximately 90% decolourization of PBS compared to pure Ag₂CO₃ (9%) and pure AgBr (38%) within 10 minutes of irradiation in visible light. It is worthwhile to mention here that the photocatalytic activity of the hybrids is related to the content of AgBr loading, and the activity sequence is in the order as follows: AgBr (50%) > AgBr (70%) > AgBr (30%) > AgBr (10%). These results suggest that the optimum content of AgBr in AgBr/Ag₂CO₃ hybrid is 50% i.e. the Br/C molar ratio is 0.50. The more likely factor for the enhancement of the photocatalytic activity is the formation of heterojunction between AgBr and Ag₂CO₃ which effectively separates the photoinduced charge carriers, and thus enhances the photocatalytic activity. Another possibility for improved activity is the presence of Ag⁰ particles, *in situ* formed on the surface of catalyst during PCO process.⁴⁻⁸⁻⁵³ These Ag⁰ particles trap the excited electrons, and hence facilitate the separation of photoinduced charge carriers.⁶¹,⁶² The decrease in photocatalytic activity with increase in Br content above optimum value is attributed to decrease in heterojunction interface, and increase in Ag⁰ clusters. Although Ag⁰ clusters can effectively trap the photoinduced electrons,⁶¹⁻⁶⁴ but with increase in the size of Ag⁰ clusters, the capability of accepting photoinduced holes also increases, and the Ag⁰ clusters become centres for recombination of electrons and holes,⁶⁵,⁶⁶ which counteracts the improvement in activity. **Fig. 3.12 (b)** shows decrease in absorption intensity of PBS at its λₘₐₓ 505 nm as a function of irradiation time in the presence of 50% AgBr/Ag₂CO₃ hybrid. The inset shows the corresponding colour changes of the PBS solution at different irradiation times.
Fig. 3.12: (a) Photocatalytic activities of Ag$_2$CO$_3$ and AgBr/Ag$_2$CO$_3$ hybrids on the decolourization of PBS under visible light ($\lambda > 400$ nm), (b) UV-vis spectra of PBS in aqueous suspension of 50% AgBr/Ag$_2$CO$_3$ at different irradiation times. *Inset:* Colour change of the PBS solution at different irradiation times.
It is well known that photocatalytic decolourization of most dyes follows pseudo-first-order kinetics model.\textsuperscript{6}\textsuperscript{7} For our experimental conditions, data are in good agreement with pseudo first-order reaction as depicted by plotting \( \ln \left( \frac{C_0}{C_t} \right) \) versus irradiation time (Figure not shown). The correlation constant for the fitted lines was calculated to be \( R^2 \geq 0.99 \) for all experiments. The values of apparent pseudo first-order rate constant (\( k_{\text{app}} \)) are given in Table 3.2.

**Table 3.2.** Pseudo-first order rate constants (\( k_{\text{app}} \)) of different photocatalysts for the decolourization of PBS calculated from the plots of \( \ln \left( \frac{C_0}{C_t} \right) \) versus irradiation time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k_{\text{app}} ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(_2)CO(_3)</td>
<td>0.0095</td>
</tr>
<tr>
<td>AgBr</td>
<td>0.0492</td>
</tr>
<tr>
<td>10% AgBr/Ag(_2)CO(_3)</td>
<td>0.1983</td>
</tr>
<tr>
<td>30% AgBr/Ag(_2)CO(_3)</td>
<td>0.2125</td>
</tr>
<tr>
<td>50% AgBr/Ag(_2)CO(_3)</td>
<td>0.2620</td>
</tr>
<tr>
<td>70% AgBr/Ag(_2)CO(_3)</td>
<td>0.2346</td>
</tr>
</tbody>
</table>

**3.5.5. Discussion of degradation mechanism**

**3.5.5.1. Formation of reactive species**

During the PCO process, large number of reactive species including \( ^\cdot \text{OH} \), \( h^+ \), \( \text{H}_2\text{O}_2 \), and \( ^\cdot \text{O}_2^- \) are produced. To investigate the underlying mechanism of photodecolourization of PBS, various scavengers of reactive species were added to the reaction system, and their effect on the overall photodecolourisation efficiency was examined. Isopropyl alcohol (IPA) was added to the system to quench \( ^\cdot \text{OH} \)\textsuperscript{57,68} whereas benzoquinone (BQ),\textsuperscript{57, 69} catalase (CAT),\textsuperscript{57} and ammonium oxalate (AO)\textsuperscript{58} were added as \( ^\cdot \text{O}_2^- \), \( \text{H}_2\text{O}_2 \), and \( h^+ \) scavengers respectively. The results are shown in Fig. 3.13 (a). As clear from the Fig. 3.13 (a), BQ and catalase exhibit weaker effect on the photocatalytic decolourisation efficiency indicating that \( ^\cdot \text{O}_2^- \) and \( \text{H}_2\text{O}_2 \) are not primary reactive species in the PCO process, and thus play minor role. The addition of IPA or AO has a significant effect on \( k_{\text{app}} \) of PBS decolourisation compared with no scavenger under same conditions indicating the main role of \( ^\cdot \text{OH} \) and \( h^+ \) in PCO process. With the addition of IPA or AO, the \( k_{\text{app}} \) value decreases significantly indicating that \( ^\cdot \text{OH} \) and \( h^+ \) are primary reactive species.
To further confirm the existence of $^\cdot$OH, terephthalic acid-photoluminescence (TA-PL) technique was used to detect the $^\cdot$OH on the surface of catalyst.\textsuperscript{70, 71} The PL spectral changes observed during the irradiation of AgBr/Ag$_2$CO$_3$ in TA solution (excitation 315nm) are exhibited in Fig. 3.13 (b). As shown in Fig. 3.13 (b), PL signal at 425 nm is observed for all hybrids with maximum PL intensity for 50\% AgBr/Ag$_2$CO$_3$ hybrid. It clearly indicates that $^\cdot$OH is formed in the photocatalytic reaction which causes fluorescence by undergoing chemical reactions with TA.\textsuperscript{70,71} Hence in AgBr/Ag$_2$CO$_3$ hybrids the main reactive oxygen species is $^\cdot$OH.
3.5.5.2. Origin of reactive species
Two possible reaction mechanisms may exist for the origin of reactive species including dye photosensitization and photocatalytic mechanism. TiO$_2$ being visible light inactive has been used in most of the previous studies as a typical catalyst probe to study the photosensitization.\textsuperscript{72} As can be seen from the Fig. 3.12 (a), the degradation of PBS in the presence of TiO$_2$ (Degussa P25) can be neglected indicating that photosensitization process can be ignored. It is therefore, clear that the reactive species originate from the photocatalytic process of AgBr/Ag$_2$CO$_3$ in which electron-hole pairs are directly produced by photocatalyst after illumination. These photoinduced charge carriers then lead to the formation of other reactive species. Further discussion regarding the formation of reactive species will be carried out in section 3.5.5.4

3.5.5.3. Fluorescence emission spectra
The photocatalytic activity of a photocatalyst is largely affected by the recombination of photoinduced electrons and holes.\textsuperscript{9} The electron-hole recombination dissipates energy in the form of fluorescence emission whose intensity is directly proportional to the recombination rate.\textsuperscript{74} Fig. 3.14 presents the fluorescence emission spectra of the pure and hybrid samples with an excitation wavelength of 260 nm. As clear from the Fig. 3.14, the intensity of the fluorescence emission for pure Ag$_2$CO$_3$ and AgBr samples is higher than those of hybrid samples. This clearly indicates the higher electron-hole recombination rate in pure samples because of their narrow band gaps. In case of hybrid samples due to matching band potentials of Ag$_2$CO$_3$ and AgBr, the photoinduced charge carriers migrate between Ag$_2$CO$_3$ and AgBr, and therefore, reduce the electron-hole recombination. As can be seen from the Fig. 3.14, the fluorescence intensity of the hybrid samples decreases from 10% to 50%, and then again increases in case of 70% hybrid. The lowest fluorescent emission intensity in case of 50% hybrid suggests lower electron-hole recombination. These results exhibit that AgBr/Ag$_2$CO$_3$ heterojunction is helpful in reducing the electron-hole recombination, and improving the photocatalytic activity.
3.5.5.4. Possible activity enhancement mechanism

Based on the above discussions and DRS results, following mechanism may be proposed for the decolourization of PBS as described in the Equations 3.5-3.15.

Under visible light irradiation, both AgBr and Ag₂CO₃ are simultaneously excited and generate electron-hole pairs. The photo excited electrons on less positive conduction band of AgBr (0.07 eV) will prefer to flow down to the more positive conduction band of Ag₂CO₃ (0.29 eV), while the photogenerated holes will flow from more positive valence band of Ag₂CO₃ (2.75 eV) to less positive valence band of AgBr (2.55 eV). From the photochemistry point of view, it is not possible to reduce O₂ to •O₂⁻, \((E^0(O_2/\cdot O_2^-) = -0.33\text{V/NHE})\) through one electron reduction process because sufficient potential cannot be generated due to the lower \(E_{CB}\) values of Ag₂CO₃ and AgBr. However, the valence band edge potentials of Ag₂CO₃ and AgBr are more positive than \(E^\circ (\cdot OH/H_2O) = +2.27\text{ eV}\),\(^{77}\) this demonstrates that sufficient potential can be generated by \(h^+\) to oxidize H₂O to •OH, which is a very strong oxidant for the decolourization of organic pollutants. It is important to mention here that in AgBr, some of the interstitial Ag⁺ ions are squeezed into the gap positions created because of the difference in the radius of Ag⁺ ion and Br⁻ ion.\(^{77}\) These Ag⁺ ions are prone to reduction, and get easily converted into Ag₀ particles by trapping an electron, if available. Under visible light irradiation, some of the photoexcited
electrons on AgBr surface are trapped by these interstitial Ag\textsubscript{i} ions present on the lattice gaps of AgBr. This results in the formation of Ag\textsuperscript{0} particles on AgBr surface, and eventually transform the AgBr/Ag\textsubscript{2}CO\textsubscript{3} into Ag@AgBr/Ag\textsubscript{2}CO\textsubscript{3}@Ag\textsuperscript{38,53} in the early stages of photocatalytic reaction. These Ag\textsuperscript{0} particles act as excellent electron traps,\textsuperscript{59,60} which further facilitates the separation of photoinduced charge carriers, and improves the stability of catalyst significantly. The Ag\textsuperscript{0} clusters may also act as centres for two electron reduction process of O\textsubscript{2}\textsuperscript{37,76,78-80} (E\textsubscript{o}O\textsubscript{2}/H\textsubscript{2}O\textsubscript{2} = +0.695V/NHE)\textsuperscript{76} to form H\textsubscript{2}O\textsubscript{2} which may combine with an electron to form "OH. The in situ formation of Ag\textsuperscript{0} on the surface of catalyst during PCO process is confirmed by the XRD analysis of used 50% AgBr/Ag\textsubscript{2}CO\textsubscript{3} after 1 and 5 recycling runs (Fig. 3.2 (b-c)). The enhanced visible light absorption of used 50% AgBr/Ag\textsubscript{2}CO\textsubscript{3} after 1 and 5 recycling runs (Fig. 3.10 (b)) compared to fresh 50% AgBr/Ag\textsubscript{2}CO\textsubscript{3} also confirms the increased amount of Ag\textsuperscript{0} metal.

In conclusion, the photogenerated electrons and holes can be effectively separated through the formation of heterojunction and efficient trapping of electrons by Ag\textsuperscript{0} nanoparticles.

\[
\begin{align*}
\text{AgBr} + \text{hv} & \rightarrow \text{AgBr} (e^- + h^+) \quad (3.5) \\
\text{Ag}_2\text{CO}_3 + \text{hv} & \rightarrow \text{Ag}_2\text{CO}_3 (e^- + h^+) \quad (3.6) \\
\text{AgBr} (e^-_{\text{CB}}) + \text{Ag}_2\text{CO}_3 & \rightarrow \text{Ag}_2\text{CO}_3 (e^-_{\text{CB}}) \quad (3.7) \\
\text{Ag}_2\text{CO}_3 (h^+) + \text{AgBr} & \rightarrow \text{AgBr} (h^+) \quad (3.8) \\
h^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{OH} \quad (3.9) \\
\text{Simultaneously} & \\
\text{Ag}_i (\text{AgBr}) + e^- & \rightarrow \text{Ag}^0 \quad (3.10) \\
\text{Ag}_2\text{CO}_3 (e^-_{\text{CB}}) + \text{Ag}^0 & \rightarrow \text{Ag}^0 (e^-) + \text{Ag}_2\text{CO}_3 \quad (3.11) \\
\text{AgBr} (e^-_{\text{CB}}) + \text{Ag}^0 & \rightarrow \text{Ag}^0 (e^-) + \text{AgBr} \quad (3.12) \\
\text{O}_2 + 2\text{H}^+ + 2e^- (\text{Ag}^0) & \rightarrow \text{H}_2\text{O}_2 \quad (3.12) \\
\text{H}_2\text{O}_2 + e^- & \rightarrow ^\cdot \text{OH} + \text{OH}^- \quad (3.14) \\
\text{Photocatalytic reaction} & \\
^\cdot \text{OH} + h^+ \quad \text{FBS} & \rightarrow \text{Products} \quad (3.15)
\end{align*}
\]
The pictorial representation of the mechanism is given in **Scheme 3.1**.

**Scheme 3.1:** Schematic diagram of electron-hole pair separation and the possible reaction mechanism over AgBr /Ag₂CO₃ photocatalyst under visible light irradiation.

### 3.5.6. Stability of the Catalyst

Since Ag₂CO₃ is unstable and can be easily decomposed by light irradiation because of reduction of Ag⁺ into Ag⁰ metal by electrons,⁴ therefore its stability is of vital consideration. However, after the formation of heterojunction with AgBr, the stability of the catalyst improves significantly. As shown in the **Fig. 3.15**, during the re-cycle experiments, the photocatalytic activity of the catalyst is maintained except for the 6.6% decrease suggesting that the AgBr/Ag₂CO₃ hybrid has high stability. Under visible light irradiation, as the PCO process proceeds, the AgBr/Ag₂CO₃ transforms into Ag@AgBr/Ag₂CO₃@Ag plasmonic system³⁸,⁵³ in the early stages of photocatalytic reaction. The Ag⁰ nanoparticles on the surface of catalyst act as excellent electron traps and trap the photoexcited electrons⁵⁹,⁶⁰ efficiently from either of the conduction bands of heterojunction, and therefore serve as centres for two electron reduction process of
This also prevents the coupling of electrons with the interstitial Ag\(^+\) and thereby prevents the photocorrosion of catalyst. Thus, effective separation of electrons and holes by heterojunctions, and subsequent trapping of electrons by Ag\(^0\) nanoparticles \textit{in situ} formed on the surface of catalyst helps the catalyst to retain its activity effectively after the initial reaction process.

![Fig. 3.15: Cycling runs of 50% AgBr/Ag\(_2\)CO\(_3\) for decolourization of PBS under visible light.](image)

3.6. Conclusion

An efficient stable photocatalyst with double visible light active components was synthesized using an \textit{in situ} anion exchange method. The AgBr/Ag\(_2\)CO\(_3\) hybrids displayed enhanced photocatalytic activity for the decolourization of Azo dye PBS compared to the single AgBr and Ag\(_2\)CO\(_3\) under visible light (\(\lambda >420\) nm). Even after recycling runs the photocatalytic activity did not show any significant decrease except for the 6.6 %. On the basis of experimental and theoretically calculated results, the photocatalytic mechanism for the decolourization of PBS over AgBr/Ag\(_2\)CO\(_3\) under visible light was suggested to be via \(\cdot\)OH and h\(^+\) oxidation mechanism. It was shown that the two factors i.e. heterojunction formed between AgBr and Ag\(_2\)CO\(_3\), and the efficient electron trapping by Ag\(^0\) nanoparticles were responsible for enhanced activity and
improved stability of the as obtained hybrids. Therefore, this may provide promising way to construct AgX/Ag₂CO₃ heterojunction photocatalysts, and would provide another approach to understand the role of Ag⁰ nanoparticles in improving stability of the catalyst.
References:

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