Effect of Low-Doping Concentration on Silver-Doped SnO$_2$ and its Photocatalytic Applications

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Abstract: Stannic Oxide (SnO$_2$) is in the class of metal oxide semiconductors, which is widely employed in a series of applications because of its excellent electrical and optical properties. In this study, we reported the synthesis of undoped and silver (Ag) doped SnO$_2$ via a simple coprecipitation technique to study the photocatalytic activities of Ag/SnO$_2$. Different characterization techniques, such as XRD, SEM, EDX, FTIR, RAMAN, and DRS were used to study the effect of the doping concentration of Ag on the structural, morphological, compositional, and optical properties of SnO$_2$. The XRD spectrum showed the tetragonal structure of SnO$_2$ and Ag/SnO$_2$. The SEM micrographs show the irregular distribution of particles with different shapes and sizes. The EDX results show the incorporation of the Ag element into SnO$_2$. The optical property shows narrowed bandgap energy with Ag content. The photocatalytic activity of the samples was studied by the photocatalytic degradation of Methylene Blue (MB) dye. The photocatalytic activity results reveal that 1wt% of Ag/SnO$_2$ has a better photocatalytic performance of 97.63% when compared to undoped SnO$_2$.

Keywords: silver doping; metal oxide; stannic oxide; coprecipitation; photocatalyst; methylene blue dye.

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1. Introduction

The severity of the persistent increase of organic pollutants that emanates from households and industrial effluents poses a great threat to both aquatic and human life [1–3]. Methylene blue (MB) dye is majorly employed in different industrial applications with core applications in textile industries. MB is mostly used for coloring silk, wood, sticks, paper, and cotton [4]. It has also been used in coloring drugs and cosmetics in aqueous drug solutions. The discharge of these dyes causes effluents to water which is harmful to both domestic and aquatic life [5,6]. Over the last decades, different methods have been established and used to degrade such pollutants from different sources. Most methods employed to purify wastewater are flocculation, coagulation, precipitation,
adsorption, ion exchange, and membrane processing [7,8]. However, numerous progress has been recorded in this field. The majority of these approaches are usually impossible for large-scale applications. Most of these methods are costly and do not degrade the toxic materials completely, hence generating a lesser toxic product [9,10]. To remove organic contaminants from water, a photocatalytic Advanced Oxidation Process (AOP) is used to alleviate major environmental concerns [11,12]. The mechanism of this process is the generation of hydroxyl radicals (OH*) on the surface of the catalyst, which oxidatively degrades the pollutant existing in the sample. Metal oxides semiconductors, such as SnO₂, TiO₂, and ZnO, have been the promising choice of researchers for elementary research and practical applications due to their chemical inertness, high activity, non-toxicity, and low cost [13–19].

Among various metal-oxide-semiconductor that have been employed as a photocatalyst, stannic oxide (SnO₂) nanoparticle, a natural n-type semiconductor with a bandgap of 3.6eV, have been projected to be a strong photocatalyst for the degradation of organic pollutants owing to its unique properties, for instance, high transparency, cost-effectiveness, high photosensitivity and environmental friendliness [20–23]. Compared with other metal oxide semiconductors, the photocatalytic efficiency of SnO₂ is low because of its wide bandgap, limiting its light absorption to irradiation wavelength to the ultraviolet (UV) region of the electromagnetic spectrum but not in the visible region. Consequently, the rapid recombination of generated electron/hole (e⁻/h⁺) pairs is another factor limiting these metal oxide semiconductors in photocatalysis [9,24]. Therefore, there has been much research interest in overcoming these challenges, thereby enhancing the photocatalytic activity of metal oxides. Researchers' efforts have been tailored to develop visible-light-assisted photocatalysts; such methods have been employed to modify SnO₂, such as doping with semiconductors, metal, non-metals, and noble metals. But doping SnO₂ with noble metals shown to be more promising, such as Cu, Au, Ag, etc. [13,25–29]. Doping SnO₂ with a silver (Ag) may hinder recombination of the electron/hole pair and also can be used to reduce the bandgap of undoped SnO₂ [30]. In addition, Ag is more desirable and attractive due to its non-toxicity, cost-effectiveness, and work function Ag aid the formation of a desirable band alignment. Ag-doped photocatalyst has a remarkable photocatalytic performance under solar irradiation, which might be due to the surface plasmon resonance of Ag under visible light irradiation [17,31–33].

Recently, Ag/SnO₂ has been successfully synthesized and employed as a photocatalyst in removing organic pollutants using different synthesis methods. However, most of the reported work centered on the higher doping concentration of Ag [7,11,13,15,22]. Hence it is essential to study the effect of the lower doping concentration of Ag on SnO₂ and its efficacy as a photocatalyst for the degradation of Methylene Blue (MB) dye. In addition, different methods have been adopted for the synthesis of Ag/ SnO₂, such as hydrothermal, solvothermal, sol-gel, coprecipitation, thermal evaporation methods, among others [17,31,34–37]. But coprecipitation is proven relatively simple and effective owing to its advantages of easy and rapid synthesis seamless control of particle size, composition, and morphology [38,39].

This study synthesized undoped and Ag-doped SnO₂ using the coprecipitation technique. The photocatalytic activities of the synthesized samples were investigated and compared. In addition, the effect of low concentration Ag doping on the photocatalyst was investigated.
2. Materials and Methods

Tin (II) chloride dehydrate (SnCl₂·H₂O), and silver nitrate (AgNO₃) procured from Sigma Aldrich and Merck Chemicals, India, were used as sources of tin and silver, respectively. Distilled water was used as a solvent for synthesis. Ammonia was used as a precipitate agent to get the desired pH value. All the chemicals and solvents used are analytical grade.

2.1. Preparation of SnO₂ and Ag-doped SnO₂.

Ag/SnO₂ was prepared by dissolving 5.21g (0.077M) of Tin (II) chloride dihydrate in 300ml of distilled water. The solution was stirred in a magnetic stirrer for 20 minutes to obtain a homogeneous solution. Concentration of AgNO₃ at different atomic ratio (0.25, 0.50, 0.75 and 1 %) were added to the solution. Consequently, aqueous ammonia as a precipitate agent dropped wisely added to the solution under vigorous stirring until a pH of 12 is attained. The precipitate formed was centrifuged for 10 minutes at 2000 rpm to completely remove organic materials (Cl⁻ and NO₃⁻) ions at the surface; the sediment was washed with distilled water and soaked in ethanol for 2 hours, and then centrifuged for 10 minutes to remove the ethanol. The precipitate obtained was dried for 4 hours at a temperature of 80°C, and after grinding, the powder was annealed for 2 hours at 500°C; a yellowish-colored powder was obtained. The above procedure was repeated to prepare the pure SnO₂ without adding AgNO₃, which resulted in a white powdered SnO₂.

2.2. Characterization of the samples.

The samples' grain size and crystallography were studied using a powdered X-ray technique by Rigaku X-ray diffractometer with monochromatic Cu Kβ with wavelength (λ= 1.5406 Å) at 40kV and 30mA. The scanning speed of all samples was 2.0156° at the scanning range of 10° - 80°. The morphological and elemental composition analysis was obtained in (FESEM) model 6340F (JEOL Japan) coupled with (EDX Model INCA 200 (UK)) at 20 keV. The organic, inorganic, and polymeric nature of the samples were studied using a PerkinElmer FTIR spectrometer. The Raman spectra were recorded using an (STR 500 Cornes Technology) Raman spectroscopy machine (Japan) having 100x objective of the microscope at an excitation wavelength of 514.5 nm. Iron (Fe) green laser was used to excite the samples at approximately 50 mW. The Raman signal was collected in the spectral interval of 150 cm⁻¹ until 3500 cm⁻¹. The Raman shift and intensities of the scattered light were compared with reference data. The diffuse absorbance and reflectance spectra were obtained using Ocean Optics USB 4000 in the range of 200-900 nm. The DRS spectrum was used to calculate the energy bandgap using the Kubelka-Munk relation, as shown in equation 1.

\[ F(R) = \frac{(1-R)^2}{2R} \]  
where R is the reflectance, F(R) is proportional to the extinction coefficient (α).

2.3. Photocatalytic activity.

Photocatalytic activity of the synthesized nanoparticles was conducted to degrade a modeled methylene blue (MB) dye in the presence of sunlight. The solar spectrum measured on
an experimental day with a Lux meter was 90,000lux. At a neutral pH, 2.5mol/L of the dye solution was prepared in a volumetric flask. 25mL of the dye solution was measured in a 250mL flask. To every 25 mL of dye solution, 15 mg photocatalyst was added and stirred for 20 minutes to achieve the adsorption/desorption equilibrium and later exposed to solar irradiation for 120 mins. At specified time intervals (0 min, 15min, 30 min, 45 min, 60 min, 75min, 90 min, 105 min, and 120 min) 2 ml of the samples was extracted and centrifuged for 5 minutes to remove the photocatalyst. The supernatant was studied by a UV-visible spectrophotometer to monitor changes in the absorbance peaks for calculating the degradation percentages using Beer's Lambert equation as shown in equation 2.0.

\[
\text{% Degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) is the initial concentration of MB dye and \(C_t\) is the concentration of dye solution after exposure time (t) to solar light.

3. Results and Discussions

3.1. X-ray diffraction analysis of SnO\(_2\) and Ag/SnO\(_2\).

The crystal structure of the synthesized samples via coprecipitation techniques was analyzed by the XRD spectrum of SnO\(_2\) and Ag/SnO\(_2\). As shown in figure 1, the undoped SnO\(_2\) exhibits a well-defined tetragonal structure at the diffraction peaks at 26.51°, 34.56°, 38.62°, 52.82°, 55.81°, 58.62°, 62.03°, 64.71°, 65.84°, 71.24°, 78.22° with diffraction plane (110), (101), (200), (211), (220), (002), (310), (112), (301), (202) and (321) matched with JCPDS card number (No: 41-1445). A notable peak of low intensity at 33.54° 2theta degree matched with JCPDS card number (No: 07-0483) was observed, which increases as the concentration of the dopant increases.

![Figure 1. (a) XRD spectrum of pure SnO\(_2\), 0.25, 0.5, 0.75 and 1.0 at% Ag/ SnO\(_2\).](https://doi.org/10.33263/BRIAC132.165)

The incorporation of Ag nanoparticles gradually shifts the most intense peak (110) towards a higher 2theta degree. However, the shift is inconsistence, 0.25 and 0.5% Ag/SnO\(_2\) nanoparticles shifted to a higher 2theta degree, but 0.75% Ag/ SnO\(_2\) shifted back to a lower 2theta degree while 1% Ag/SnO\(_2\) nanoparticles shifted to a higher 2theta degree as it was observed in the XRD pattern.
revealed in Figure 2a. This confirms that Ag is successfully loaded into the SnO2 lattice. The crystallite of the samples was calculated using Scherer's equation, as shown in equation 3. Where D is crystallite size, β is full width at half maxima (FWHM), θ is the glancing angle, and 0.98 is the shape factor.

\[
D = \frac{0.98\lambda}{\beta \cos \theta}
\]

Figure 2b shows the mean crystalline size are in the range 9.08, 8.47, 9.57, 12.65, and 19.95 nm respectively for undoped SnO2 and Ag/ SnO2 concentration at 0.25, 0.5, 0.7%, and 1%. The increase in the crystallite sizes of 1% Ag doped SnO2 might be a result of the segregation of Ag ions in the SnO2 boundaries.

### 3.2. Structural and morphological analysis of the samples.

Field Emission Scanning Electron Microscope (FESEM) has been used to investigate the effect of Ag doping on SnO2. Figure 3(a-c) below shows the morphological images of undoped SnO2, 0.5 and 1.0 at% Ag/SnO2 photocatalyst. The FESEM micrograph shows that the particles are irregularly distributed, and they vary in size and occur as the tetragonal structure of SnO2 [40]. The tetragonal structure of the particle is in good agreement with the XRD result.

| Samples        | Elements | Atomic % | Weight % | Kev |
|----------------|----------|----------|----------|-----|
| SnO2           | Sn       | 78.97    | 66.39    | 3.6 |
|                | O        | 21.03    | 33.61    | 0.8 |
| 0.5% Ag/SnO2   | Sn       | 19.15    | 62.99    | 3.6 |
|                | O        | 80.39    | 35.65    | 0.6 |
|                | Ag       | 0.46     | 1.37     | 2.7 |
| 1% Ag/SnO2     | Sn       | 25.55    | 70.24    | 3.6 |
|                | O        | 73.43    | 27.21    | 0.6 |
|                | Ag       | 1.02     | 2.54     | 2.6 |

The micrograph distinctly specifies the occurrence of agglomeration and also affirms that the morphology of the undoped SnO2 and Ag/SnO2 are similar. The elemental composition of the
selected samples as shown by the EDX spectra in Figure 3(d-f), the pattern in Figure 3(d) reveal that the undoped SnO\textsubscript{2} sample consists of Sn and O atoms only, the absence of no other element revealed the purity of the synthesized sample.

Figure 3. SEM and EDX spectrum of (a & d) Undoped SnO\textsubscript{2} (b & e) 0.5 Ag/ SnO\textsubscript{2} (c & f) 1.0 Ag/ SnO\textsubscript{2}

Figure 3(e and f) are the EDX spectra of 0.5 and 1 % of Ag/SnO\textsubscript{2}, and they contain Sn, O, and Ag, respectively, which implies that Ag is successfully incorporated into SnO\textsubscript{2}. The absence of any other element confirms the purity of the synthesized samples. The weight and atomic percentage of those samples, as revealed by the EDX analysis, are shown in Table 1.

3.3. Optical characteristics of SnO\textsubscript{2} and Ag/ SnO\textsubscript{2}.

The optical characteristic of the undoped SnO\textsubscript{2} and Ag-doped SnO\textsubscript{2} as revealed by diffuse reflectance scattering (DRS) in the scanning range of 200-900nm is shown in Figure 4. In Figure 4a, the absorbances spectra for the undoped SnO\textsubscript{2} appeared at 302.3 nm.

Table 2. Absorption maxima, energy band gap and crystallite size of the undoped and Ag doped SnO\textsubscript{2} NPs.

| Name of Sample | Undoped SnO\textsubscript{2} | 0.25% Ag/SnO\textsubscript{2} | 0.5% Ag/SnO\textsubscript{2} | 0.75% Ag/SnO\textsubscript{2} | 1% Ag/SnO\textsubscript{2} |
|----------------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------------|
| Absorption maxima (nm) | 302.3 | 299.2 | 301.0 | 301.8 | 292.8 |
| Energy band gap E\textsubscript{g} (eV) | 3.36 | 3.25 | 3.19 | 3.10 | 3.05 |
| Crystallite Size (nm) | 9.08 | 8.47 | 9.57 | 12.65 | 19.95 |

As the doping concentration increases (i.e. 0.25, 0.5, 0.75, and 1.0%) the absorption peaks also have a blue shift to 299.2, 301.0, 301.8 and 292.8nm respectively. The addition of Ag content could be responsible for the blue shift in the absorbance spectra, which correlates with the report of Yakout's works [41]. Figure 4b is the reflectance spectra of the synthesized samples; there is a redshift with the addition of a dopant. The optical band gap calculation was determined by the Kubelka-Munk relation. The graph of \((F(R)hv)^2\) was plotted against the photon energy, and the intercepts of the graph give the bandgap energy. The bandgap energy was found to be 3.36, 3.25,
3.18, 3.10, and 3.05 for the undoped and 0.25, 0.5, 0.75, and 1.0% Ag doped SnO$_2$, respectively, as shown in Table 2 and Figure 4.

![Figure 4](image-url). Absorbance and Reflectance spectra pure and Ag-doped SnO$_2$.

![Figure 5](image-url). Estimated energy bandgap plot for undoped and Ag-doped SnO$_2$ NPs.
3.4. **FTIR analysis.**

The functional group of the synthesized samples was verified using FTIR analysis. The FTIR spectra obtained from the synthesized SnO$_2$ and Ag/SnO$_2$ were as shown in Figure 6. The IR spectrum of undoped SnO$_2$ nanoparticles is located at bands 3438, 1628, 973, and 642 cm$^{-1}$. The FTIR band at 3438 cm$^{-1}$ was ascribed to O–H stretching vibration, showing a hydroxyl group. The occurrence of a predominant peak at the 642 cm$^{-1}$ FTIR band was related to metal-oxygen (M-O) bonds which corroborate with the report of Kumar et al., 2015 [42]. The band at 1623 cm$^{-1}$ can be associated with the stretching vibration of surface and interlayer hydroxyl groups (O-H bond) [43].

![FTIR spectrum of SnO$_2$ and Ag/SnO$_2$ nanoparticles.](image)

3.5. **Raman spectroscopy.**

The Raman analysis of the pure SnO$_2$ and Ag/SnO$_2$ nanoparticles was investigated using a Raman system to determine the variety of phonons and synthesized samples' crystallography. The data obtained were in the wavenumber range of 200 - 850 cm$^{-1}$, as shown in Figure 7. The Raman spectrum analysis reveals three peaks in-line with the report for SnO$_2$ crystals.

Peaks at around 633 (cm$^{-1}$) could be assigned to A$_{1g}$, which is symmetric Sn–O stretching, and peaks at around 775 (cm$^{-1}$) could be assigned to B$_{2g}$, which is asymmetric Sn–O stretching, respectively, which correspond to the tetragonal structure of SnO$_2$ [28]. It is clearly observed that Raman peaks increase as the doping concentration increase while peaks of 0.75% Ag/ SnO$_2$ decrease. Remarkably, the band at around 553 (cm$^{-1}$) may be attributed to the vibration mode associated with the vacant site and local order disorder. The addition of dopant introduced a peak around 234 (cm$^{-1}$), which increases as the doping concentration increases. Generally, peaks of A$_{1g}$ and B$_{2g}$ are virtual to the contraction and expansion vibrational modes of Sn–O bonds [28], and the existence of these Raman characteristics measures the tetragonal structure of SnO$_2$. The change in the symmetric and asymmetric Sn-O stretching of the Ag-doped SnO$_2$ nanoparticle may enhance its photocatalytic performance.
3.6. Photocatalytic activity.

The photocatalytic activities of SnO$_2$ and Ag/SnO$_2$ were recorded by the degradation of MB dye under solar light irradiation. Figure 8 (a-e) shows the absorption spectra of an aqueous solution of 25ml MB with 15mg of the different photocatalysts under solar light irradiation for various time intervals. It can be observed that the absorption peaks decrease rapidly with an increase in the exposure time, indicating the degradation of MB. The UV-Vis absorbance spectrum was recorded in the range of 190 to 800 nm, and absorbance maxima were observed at 664 nm. The absorption of MB at 664 nm continuously decreases, and the peak is almost disappeared within 120 min.

It was observed in Figure 9 that the photodegradation efficiency of SnO$_2$ got enhanced with Ag doping; the 1% Ag/SnO$_2$ photocatalyst showed a maximum efficiency of 97.63% among the doped samples. The photocatalytic degradation efficiency of undoped and Ag-doped SnO$_2$ over MB are in the range of 86.89, 94.21, 96.68, 96.30 and 97.63% for undoped SnO$_2$, 0.25% Ag/SnO$_2$, 0.5% Ag/SnO$_2$, 0.75% Ag/SnO$_2$ and 1% Ag/SnO$_2$, respectively as calculated using Beer-Lambert equation. The amount of Ag-doped SnO$_2$ surface is an essential factor optimized to achieve enhanced photocatalytic performance. The effective charge transferability, visible light-harvesting ability, provision of catalytic sites for OH formation also injection of electrons into the SnO$_2$ surface by Ag ions could be accountable for the improved photocatalytic performance of the doped samples [44]. Moreover, the rate constant (k) was calculated by applying a first-order kinetic reaction. And figure 10 compares the photocatalyst's behavior under dark conditions and when it is exposed to visible light.

Also, Table 3 compares the existing literature with the present work, where it is noticed that this present study is very promising in the degradation of organic pollutants.

| Synthesis method       | Photocatalyst (mol/wt%) | Dye                | Degradation (%) | Time (min) | References |
|------------------------|-------------------------|--------------------|-----------------|------------|------------|
| Hydrothermal           | Ag/SnO$_2$·g-$\text{C}_3\text{N}_4$ | RhB                | 94              | 240        | [45]       |
| Hydrothermal           | Ag/SnO$_2$              | Nitrogen Oxide     | 70              | 30         | [34]       |
| Soft Chemical route    | Ag/SnO$_2$ (0, 5, 10, 15%) | MO                | 93.44           | 180        | [46]       |
Figure 8. Absorbance spectra of MB solution under solar irradiation for (a) Pure SnO$_2$, (b) 0.25%, (c) 0.50%, (d) 0.75%, (e) 1% Ag/SnO$_2$ nanoparticle.
Figure 9. Percentage degradation plot of Undoped SnO$_2$, 0.25% Ag/ SnO$_2$, 0.50% Ag/ SnO$_2$, 0.75% Ag/ SnO$_2$, and 1.0% Ag/ SnO$_2$.

Figure 10. Rate of concentration degradation of MB dye against time.

3.7. Mechanism of photocatalysis.

The mechanism of photocatalysis of undoped SnO$_2$ and Ag-doped SnO$_2$ photocatalyst with MB under solar light is shown in Figure 11. Generally, the production electron and hole (e$^-$/h$^+$) pair are the origin of the photocatalytic degradation method.

During the photocatalytic process, electrons (e$^-$) in the valance band (VB) can be transferred to the conduction band (CB), holes (h$^+$) of the same amount are generated in the VB. These photogenerated (e$^-$/h$^+$) pairs can aid the chemical reactions with organic pollutants. In the process of chemical reaction, the holes in the VB react with hydroxide ions or H$_2$O adsorbed at the surface of the photocatalyst to generate hydroxyl radicals (OH). However, electrons in the CB can reduce O$_2$ to make superoxide radicals (*O$_2^-$) and subsequently other reactive oxygen species (i.e., H$_2$O$_2$ and OH$^-$). Consequently, holes and OH as an oxidation agent are immensely reactive toward organic pollutants and positively influence dye degradation [35,46].

Ag/SnO$_2$ showed enhanced photocatalytic performance than undoped SnO$_2$. The enhanced photocatalytic performance was shown by Ag/SnO$_2$ over the undoped SnO$_2$, which can be attributed to the acceptance of impurity by Ag in doping of SnO$_2$, and it acts as an electron trap
that prevents recombination of \((e^-/h^+)\), which is a vital influence in determining the photocatalytic performance. Furthermore, the synergy interaction of enhanced visible light absorption, the presence of electron traps in \(\text{Ag/SnO}_2\), and visible light-assisted plasmon resonance play a helpful role in enhancing photocatalytic activity [31]. Moreover, \(\text{Ag/SnO}_2\) has a higher electron reaction with adsorbed \(\text{O}_2\) than undoped \(\text{SnO}_2\). Also, the narrow bandgap is another important factor to enhance the photocatalytic activity of \(\text{SnO}_2\). These results show an efficient photocatalytic activity of the \(\text{Ag/SnO}_2\).

![Figure 11. Mechanism of photocatalysis of Ag/SnO2 nanoparticles.](image)

### 4. Conclusions

In summary, the coprecipitation method has successfully prepared undoped and \(\text{Ag/SnO}_2\) NPs at a lower doping concentration of silver below 1%. The incorporation of \(\text{Ag}\) into \(\text{SnO}_2\) has been successfully revealed in the XRD pattern. Also, the optical properties showed the effect of \(\text{Ag}\) doping into \(\text{SnO}_2\), thereby narrowing the bandgap of \(\text{SnO}_2\). The Raman spectroscopy also showed the successful incorporation of \(\text{Ag}\) into the \(\text{SnO}_2\) lattice. A notable photocatalytic performance towards \(\text{MB}\) dye solutions were recorded to be 86.89, 94.21, 96.68, 96.30 and 97.63 for undoped, 0.25, 0.5, 0.75 and 1% \(\text{Ag/SnO}_2\) NPs respectively. It was revealed in the photocatalytic results that a lower doping concentration of \(\text{Ag}\) into \(\text{SnO}_2\) has an enhanced photocatalytic performance when compared with existing literature. The improved photocatalytic performance could be attributed to the narrower bandgap of \(\text{Ag/SnO}_2\). Therefore, a lower doping concentration of \(\text{Ag}\) has proved effective in the degradation of \(\text{MB}\) dye under solar light irradiation.

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Conflicts of Interest

The authors declared no conflict of interest.

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