Photocatalytic deposition of Ag nanoparticles on TiO₂: Metal precursor effect on the structural and photoactivity properties

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Abstract A series of 1 wt.% Ag–TiO₂ photocatalysts were obtained by photodeposition using different organic (acetylacetonate, Ag-A) and inorganic (nitrate, Ag-N, and perchlorate, Ag-C) silver precursors in order to determine the influence of the silver precursor on final properties of the photocatalysts. The resulting photocatalytic materials were characterized by different techniques (UV–Vis DRS, TEM/HRTEM and XPS) and their photocatalytic activity was evaluated in the degradation of rhodamine B (used as model pollutant) in aqueous solution under simulated solar light. The photocatalytic reduction of Ag species to Ag⁰ on TiO₂ was higher with silver nitrate as precursor compared to acetylacetonate or perchlorate. All the Ag-modified TiO₂ photocatalysts exhibited a surface plasmon resonance effect in the visible region (400–530 nm) indicating different metal particle sizes depending on the Ag precursor used in their synthesis. A higher photocatalytic activity was obtained with all the Ag/TiO₂ samples compared with non-modified TiO₂. The descending order of photocatalytic activity was as follows: Ag-A/TiO₂ > Ag-N/TiO₂ > Ag-C/TiO₂ > TiO₂-P25. The enhanced photoactivity was attributed to the presence of different amounts Ag⁰ nanoparticles homogeneously distributed on Ag₂O and TiO₂, trapping the photogenerated electrons and avoiding charge recombination.

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1. Introduction

In recent years, noble metal nanoparticles (e.g., Ag, Au, Cu) have received much attention for new applications in biotechnology, catalysis, electronics, environmental and optics [1–9]. For instance, silver nanoparticles have been investigated in fields such as high-density information storage, photoluminescence and electroluminescence devices, surface-enhanced Raman scattering, heterogeneous catalysis, photocatalysis and disinfection [10–14]. In heterogeneous catalysis, supported silver catalysts have been successfully used at industrial scale for the oxidation of methanol to formaldehyde and ethylene to ethylene oxide [15].

Lately, Ag-doped semiconductor nanoparticles have had much interest in photocatalysis (i.e. degradation of organic pollutants, hydrogen production, CO₂ photoreduction, disinfection), in order to improve the photoconversion yield and allow the extension of the light absorption of wide band gap semiconductors to the visible light [4,11,16–19]. As it is well-known, Ag nanoparticles can trap the excited electrons from titanium dioxide and leave the holes for the degradation reaction of organic pollutants, improving the charge carrier separation [20]. On the other hand, silver nanoparticles can absorb visible light due to localized surface plasmon resonance [21], extending their wavelength response toward the visible region, leading to new applications such as antibacterial textiles, engineering materials, medical devices, food preparation surfaces, air conditioning filters and coated sanitary wares [22].

Concerning the photoactivity of Ag₀/Ag₂O deposited on TiO₂, it has been proposed that the photoexcitation of Ag₂O rather than Ag₀ acts as active sites responsible for the enhanced photocatalytic activity, whereas Ag₀ might contribute to the stability [23]. Also worth mentioning is that the p-Ag₂O/n-TiO₂ nanoheterojunction has shown a significant improved photocatalytic activity under UV–Vis irradiation explained in terms of a better charge separation [24]. Recently, it has been shown that a heterostructure type Ag–Ag₂O/TiO₂, synthesized by a simple electrochemical method, resulted in a high active and stable photocatalyst under visible light, following a Z-scheme charge transfer mechanism [25].

The investigation of the relationship between the synthesis process parameters on the size and morphology of the nanoparticles, which is connected to its optical and electronic properties, has led to a large number of preparation methods [10,11]. In a recent review concerning the synthesis and applications of silver nanoparticles, it has been reported that most synthesis processes produce spherical Ag nanoparticles with less than 20 nm of diameter; they are often synthesized via reduction of AgNO₃ dissolved in water and using reducing agents such as NaBH₄, among other compounds [26].

In particular, the photochemical and photocatalytic reductions have been studied extensively since the decade of the 80s, and they are considered as efficient ways to synthesize nanoparticles directly on semiconductor supports [27]. The photocatalytic deposition is carried out in the presence of metal ions, semiconductor support and hole scavengers. After irradiation, the photogenerated electrons reduce the surface-adsorbed metal ions forming metal clusters, and then, Ag nanoparticles via a repeated reduction process [27]. We recently synthesized Ag/TiO₂ composites by photocatalytic deposition that exhibit strong absorption centered at 420 nm with Ag nanoparticles (around 6–20 nm) uniformly deposited on the semiconductor [10]. As mentioned above, AgNO₃ dissolved in water is the most common salt precursor used in the synthesis of Ag/TiO₂ composites, even in the photochemical routes. Therefore, the present research was focused to the synthesis of Ag/TiO₂ composites by photocatalytic deposition employing different organic (acetylacetone) and inorganic (nitrate and perchlorate) silver precursors. The effect of silver precursor on structural characteristics and photoactivity under simulated solar light was mainly studied.

2. Experimental section

Silver nitrate (Ag-N Fermont 99%), silver perchlorate (Ag-C, Sigma–Aldrich 97%) and silver acetylacetonate (Ag-A, Sigma Aldrich, 98%) were used as silver precursors. Ethanol (absolute, Fermont) was used as solvent and commercial TiO₂ (TiO₂-P25, Evonik) was used as support. The supported Ag nanoparticles were obtained using the photocatalytic route as follows: an ethanolic solution of Ag precursor (0.5 mM) was mixed with TiO₂-P25 in a 100 mL batch reactor and it was dispersed with ultrasonic irradiation. Then a nitrogen flow of 50 mL min⁻¹ was bubbled through the slurry to purge dissolved oxygen and to achieve an inert reaction atmosphere. The batch reactor was irradiated for 4 h using a LuzChem photoreactor (model LZC-4) equipped with 14 low pressure mercury lamps (8 W, λₘₐₓ = 360 nm). After the irradiation time, the obtained material was washed with ethanol, separated by centrifugation and it was dried at 50°C in a convection oven.

The characterization was carried out by UV–Vis diffuse reflectance (GBC Cintra 20), X-ray photoelectron spectroscopy (XPS, ThermoScientific K-Alpha) and structural characterization was achieved from conventional TEM and HRTEM by means of a JEOL FEG 2010 FasTem electron microscope with 1.9 Å of resolution (point to point). For TEM and HRTEM studies, the samples were suspended in ethanol in order to disperse the powders then a drop of the sample was deposited on a lacey carbon copper grid as a TEM support.

The composites were tested in a model reaction such as Rhodamine B (Rhb) degradation in aqueous solutions. Typically, powdered photocatalyst in the amount of 0.1 g L⁻¹ was suspended in aqueous solution of 9.6 ppm of Rhb. The suspension was magnetically stirred in the dark during 30 min to achieve a complete adsorption/desorption equilibrium and then it was irradiated for 60 min with a solar light simulator (Newport model 67005) equipped with a 150 W Xen lamp and a power source which allows to change the light intensity of the lamp. The light intensity was measured using a digital light meter (A.W. Sperry SLM-110) and the measured light intensity was 1.5 mW cm⁻² (I₀) at 20 cm from the source. The reaction temperature was kept constant at 25 °C during all the experiments and aliquots of the reaction medium were periodically sampled and filtered using a PTFE membrane filter (Millipore, 0.45 μm) prior to analysis. The Rhb concentration was measured employing a spectrophotometric method by using a GBC Cintra 20 spectrophotometer and following the decrease in the absorbance of Rhb at 550 nm.
3. Results and discussion

Fig. 1 shows the UV–Vis diffuse reflectance spectra for Ag/TiO$_2$ composites using silver acetylacetonate (Ag-A/TiO$_2$), silver perchlorate (Ag-C/TiO$_2$) and silver nitrate (Ag-N/TiO$_2$) as Ag precursors and bare TiO$_2$-P25. The absorption edge of all samples was practically located at $\lambda = 380$ nm, which is consistent with the intrinsic band gap absorption of anatase TiO$_2$ (3.2 eV). Note the broad absorption band from 400 to 800 nm for all Ag photocatalysts, highlighting the maxima at 470, 505 and 530 nm for Ag-C/TiO$_2$, Ag-A/TiO$_2$ and Ag-N/TiO$_2$, respectively, attributed to the characteristic surface plasmon resonance (SPR) of metal cluster or Ag nanoparticles deposited on TiO$_2$, depending on the Ag precursor. In fact, colloidal Ag nanoparticles prepared previously by our group showed a narrow absorption peak with a maximum at 400–420 nm, resulting an average Ag particle size distribution of 2–5 nm [10]. Therefore, the results presented in Fig. 1 could indicate that changes of the plasmon maxima location from 400–420 nm to 530 nm, would be related to the size, distribution, and chemical interaction of the Ag NPs deposited on TiO$_2$, induced by the type of Ag precursor used in the synthesis [28]. Indeed, the use of different silver precursors led to different coloration in the final photocatalyst, a pale brown color was observed with AgClO$_4$ and certain shades of purple with AgAc and AgNO$_3$. In general, the red-shifted resonance wavelength is strongly related to the size of the nanoparticle [29], therefore, as we loaded the same nominal amount of silver (1 wt.%), then, the type of Ag precursor had an effect on the size of Ag nanoparticles. A possible explanation of this effect is the observed decrease of the photocatalytic efficiency of TiO$_2$ in the presence of inorganic salts, such as NO$_3^-$, Cl$^-$, SO$_4^{2-}$ [29]. At this point, comparing the area under the curve of Ag composite prepared with AgClO$_4$ in Fig. 1, it seems that Ag cations coming from AgNO$_3$ were easier to reduce than those from AgClO$_4$ and AcAg.

Fig. 2 shows several HRTEM images for Ag-A/TiO$_2$ photocatalyst. In Fig. 2a, the anatase phase was identified by the spacing $d = 0.352$ nm indexed as (101). In the second image, two NPs can be observed, one of them was TiO$_2$ and another was AgO, this confirmed the deposit of Ag on the TiO$_2$ surface. Also, two kinds of silver oxides, AgO and Ag$_2$O were identified. The AgO phase was identified by two plane spacings, $d = 0.241$ nm and $d = 0.263$ nm, indexed as (111) and (100), respectively. The Ag$_2$O was detected by the (002) and (100) reflections corresponding to the spacing $d = 0.246$ nm and $d = 0.260$ nm, respectively. The last high resolution image shows a well-defined hexagonal nanoparticle of Ag$_2$O with a length of 15 nm and width of 12 nm approximately which had a spacing $d = 0.263$ nm indexed as (100). Fig. 2b reveals similar crystallographic planes for AgO with the spacings $d = 0.246$ nm and $d = 0.260$ nm indexed as (002) and (100), respectively. For AgO, the reflection (111) was observed. However, in the two last images of Fig. 2b, metallic silver (Ag$^0$) was detected by the reflection (200) with a spacing of $d = 0.205$ nm. Finally, in Fig. 2c a higher region is presented where it is possible to observe the same crystalline phases, belonging to TiO$_2$, AgO and Ag$^0$, as reported above, which revealed the formation of a composite material.

Fig. 3 shows the TEM and HRTEM images for Ag-C/TiO$_2$ photocatalyst. Fig. 3a displays the TEM micrographs where it can be observed TiO$_2$-P25 nanocrystals with sizes between 20 and 50 nm, also it is observed that the TiO$_2$ nanoparticles are interconnected by channels with diameters of 20 nm. Here, the TiO$_2$ nanoparticles presented a roughness on their surface that makes it difficult to observe the Ag NPs that were identified by HRTEM in the form of Ag$_2$O. Probably, the TiO$_2$ nanocrystals were attacked by the chlorine species provoking the oxidation of the Ag NPs. In Fig. 3b are presented HRTEM images belonging to the anatase phase, which is also identified by the spacing $d = 0.352$ nm and indexed as (101) and the silver oxide Ag$_2$O was identified by the spacing $d = 0.246$ nm and indexed as (002).

Fig. 4a shows TEM and HRTEM micrographs of the Ag-N/TiO$_2$ photocatalysts, in the first TEM image only the titania nanocrystals can be observed. The second HRTEM image shows a population of silver nanoparticles (dark particles) with average size of 1 or 2 nm both on the surface as inserted or embedded into the nanocrystals of TiO$_2$. The Ag NPs deposited had a spheroid shape and a high population density on the TiO$_2$ support. In the same way, as the other samples discussed above, in Fig. 4b the HRTEM micrographs reveal the presence of the anatase phase identified by the spacing $d = 0.352$ nm and indexed as (101). Fig. 4c shows a HRTEM image of two coupled nanoparticles indicating the presence of a composite material formed by Ag$_2$O, identified with the spacing $d = 0.246$ nm and indexed as (002), and another nanoparticle of the anatase phase identified by the spacing $d = 0.352$ nm and indexed as (101); the next HRTEM image only presents two silver oxide species, Ag$_2$O and AgO with the spacing $d = 0.246$ nm and $d = 0.289$ nm and indexed as (002) and (011), respectively.

The peak positions presented by the diffraction patterns were all in good agreement with those given in ASTM data cards PDF#211272 for the anatase phase, PDF#011167 for Ag$^0$, PDF#431038 for AgO and PDF#191155 for Ag$_2$O.

The high resolution XPS spectra of Ag 3d of Ag/TiO$_2$ composites are shown in Fig. 5. As mentioned above, HRTEM results showed the presence of Ag$^0$ and Ag$_2$O, then, a deconvolution analysis of XPS raw spectra allowed us to estimate the presence of three Ag species. It is well-known that the

Figure 1 UV–Vis diffuse reflectance spectra of bare TiO$_2$-P25 and Ag/TiO$_2$ composites prepared by photodeposition using different Ag precursors: A = acetylacetonate, C = perchlorate, N = nitrate.
Ag (3d\textsubscript{5/2}) binding energies of Ag, Ag\textsubscript{2}O and AgO are located at 368.2, 367.8 and 367.4 eV, respectively [30]. Also, high resolution spectra of O 1s and Ti 2p of Ag/TiO\textsubscript{2} composites are shown in Figs. S1 and S2 in the Supporting information, respectively. All the composites presented similar spectra and, in the case of O 1s, it can be observed an asymmetrical peak centered at 529.9 eV which can be attributed to lattice oxygen and surface oxygen [31]. In the Ti 2p spectra it can be observed two symmetrical peaks corresponding to Ti 2p\textsubscript{3/2} (458.9 eV) and Ti 2p\textsubscript{1/2} (464.6 eV) transitions which can be attributed to Ti\textsuperscript{4+} species [31].

Regarding the Ag\textsuperscript{0} surface amount in all samples, it was slightly higher than the surface amount of Ag\textsubscript{2}O and the amount of AgO was negligible. According to the signals in XPS spectra, the ratio Ag\textsuperscript{0}/Ag oxidized species was very similar for Ag-N and Ag-A (~1.3) and for Ag-C was lower (~1.1). These results agreed with other works where silver was also photodeposited, although the formation of Ag\textsubscript{2}O is not discussed [32]. Indeed, it is very difficult to conclude the exact amount of each of the Ag surface species due to the quite close values of their binding energy. However, after being exposed to air environment, our Ag/TiO\textsubscript{2} samples began to change from their original color, slightly brown or purple, to dark purple, which could be characteristic of the formation of silver oxides. Some authors have explained the formation of Ag\textsubscript{2}O deposited on TiO\textsubscript{2}, due to oxygen ions reverse-spill over as the dominant oxidation mechanism of deposited Ag\textsuperscript{0} (Eqs. (1) and (2)) [33]

\[
4\text{Ag}^0 + \text{O}_2 \rightarrow 2\text{Ag}_2\text{O} + e^- \quad (1)
\]
\[
2\text{Ag}^0 + \text{O}^- \rightarrow \text{Ag}_2\text{O} + e^- \quad (2)
\]
Fig. 6 shows the relative concentration \(C/C_0\) versus irradiation time for the photocatalytic degradation of RhB with TiO$_2$-P25 and Ag/TiO$_2$ samples, under simulated solar light. As can be seen, all the samples showed a similar degradation profile reaching between 80% and 95% degradation of RhB after 60 min. The Ag-A/TiO$_2$ composite, prepared using silver acetylacetonate as precursor, showed the highest activity, closely followed by the Ag-N/TiO$_2$ catalyst. The Ag-C/TiO$_2$ sample showed a slightly better activity than TiO$_2$-P25, which was the less active. The degradation profiles of RhB using all materials followed an apparent first order kinetic and the values of the calculated constants are shown in Fig. 7b. As expected, the obtained values followed the decreasing order: Ag-A/TiO$_2$ > Ag-N/TiO$_2$ > Ag-C/TiO$_2$ > TiO$_2$-P25.

According to XPS analyses and TEM/HRTEM results, Ag$_0$ and Ag$_2$O were detected in all the Ag/TiO$_2$ catalyst, which could explain the improved photo activity of these materials compared to that shown by TiO$_2$-P25 [34,35]. As it is well-known, metal nanoparticles deposited on TiO$_2$ act as electron reservoirs, enhancing the electron-hole separation and, therefore, enhancing the photocatalytic performance [30,36]. Although all Ag/TiO$_2$ materials contained a similar amount of Ag$_0$ NPs, the observed differences between Ag-A/TiO$_2$ or Ag-N/TiO$_2$ catalysts and Ag-C/TiO$_2$ sample could be attributed to other factors, such as morphology and size of the Ag nanoparticles [37], the presence of surface plasmon resonance (SPR) [32] or metal-support interactions [38–40].

The influence of SPR on the photocatalytic performance, under visible light illumination, has been explained mainly by two mechanisms [32]: charge transfer and local electric field enhancement. In the charge transfer mechanism, the SPR excites the electrons in the Ag nanoparticles, which are transferred to the conduction band of TiO$_2$, leaving a “plasmonic hole” [32] in the metal nanoparticle. According to this mechanism, it is not necessary to excite the TiO$_2$ to produce charge carriers, which are produced in the metal nanoparticle under illumination with light corresponding to the SPR excitation wavelength and it has been found that these plasmonic charge carriers can participate in several redox reactions [32,41–43]. In the second mechanism, it is proposed that irradiation of metal nanoparticles with wavelengths near their SPR frequency can generate intense local electric fields near the metal–TiO$_2$ interface. In these regions the generation rate of the charge carriers can be 1000 times higher than that generated in the bulk TiO$_2$ and this enhanced generation rate is responsible for the improvement in the observed photoactivity [44–46].

Accordingly, our photoactivity results can be coarsely correlated with the ratio of surface species Ag$_0$/Ag$_2$O which...
were slightly higher with Ag-N/TiO₂ and Ag-A/TiO₂ catalysts. At this point, we can speculate during the reaction at being excited the photocatalyst, the photogenerated electrons can reduce Ag₂O (E⁰ Ag⁺/Ag = +0.80 V) more efficiently than the oxygen reduction reaction (E⁰ O₂/O₂⁻ = −0.33 V) [47], which, could explain an improved photocatalytic activity compared with bare TiO₂ due to in situ formation of Ag nanoparticles. Additionally, silver oxide nanoparticles and the oxygen reduction reaction (E⁰ O₂/O₂⁻ = −0.33 V) [47], which, could explain an improved photocatalytic activity compared with bare TiO₂ due to in situ formation of Ag nanoparticles. Additionally, silver oxide nanoparticles and
TiO$_2$ act as Vis and UV light harvesters, respectively, which can transfer electrons from their conduction band mainly to surface silver nanoparticles, avoiding charge recombination.

In order to verify the influence of some reaction variables, a second set of experiments was carried out. Hereafter, the Ag-N/TiO$_2$ photocatalyst was employed and the tested variables were RhB initial concentration, photocatalyst loading and light intensity. In Fig. 7a, the relative RhB concentration profiles versus time, in function of the initial concentration of RhB, are shown. As can be noted, the conversion after Figure 5  High resolution Ag 3d XPS spectra of Ag/TiO$_2$ composites prepared by photodeposition using different Ag precursors: (a) Ag-A/TiO$_2$, (b) Ag-N/TiO$_2$, (c) Ag-C/TiO$_2$. A = acetylacetonate, C = perchlorate, N = nitrate.

Figure 6  (a) Relative RhB concentration profiles versus time for the different Ag/TiO$_2$ composites under visible light irradiation. (b) Calculated pseudo-first order constants. A = acetylacetonate, C = perchlorate, N = nitrate.
60 min of irradiation time was inversely proportional to the RhB initial concentration. Also, it can be observed a slight change in the concentration profile above ~29 ppm. This change can be observed better in Fig. 7b, where the calculated pseudo-first order constants were plotted against the initial concentration of RhB. As it is well-known, the photocatalytic

![Figure 7](image1.png)

**Figure 7**  (a) Relative RhB concentration profiles versus time in function of RhB initial concentration. (b) Calculated pseudo-first order constants. The photocatalyst used was Ag-N/TiO$_2$ (N = nitrate).

![Figure 8](image2.png)

**Figure 8**  (a) Relative RhB concentration profiles versus time in function of photocatalyst loading. (b) Calculated pseudo-first constants. The photocatalyst used was Ag-N/TiO$_2$ (N = nitrate).

![Figure 9](image3.png)

**Figure 9**  (a) Relative RhB concentration profiles versus time in function of the relative light intensity. (b) Calculated pseudo-first order constants. The photocatalyst used was Ag-N/TiO$_2$ (N = nitrate).
reactions can be described by the Langmuir–Hinshelwood (LH) model, which states that at lower concentrations of substrate a pseudo-first order kinetics is observed, and at higher concentrations, a pseudo-zero order kinetics is observed [48]. The change in the slope observed in Fig. 7b can be related to the change in the reaction order, suggesting that the photocatalytic degradation of RhB can be fitted to the LH model.

The influence of photocatalyst concentration in the degradation of RhB is shown in Fig. 8. It can be observed that the presence of the semiconductor was important because the photolysis of RhB was negligible under simulated solar light (see Fig. 8a). As the catalyst concentration was increased to 0.04 g L\(^{-1}\), the conversion after 60 min was increased to 70%, reaching a maximum of 85% at 0.3 g L\(^{-1}\) and above. It is to be noted that a linear relationship between the calculated pseudo-first order constant and the catalyst concentration was observed in the range of 0.04–0.1 g L\(^{-1}\) (see Fig. 8b). Above this value, the calculated constant was non-dependent of the catalyst concentration, due to the screening effect produced by an excess of suspended particles which resulted in an inefficient absorption of light by the photocatalyst, as observed in other photocatalytic systems [49].

Finally, the influence of the light intensity over the photocatalytic degradation of RhB is presented in Fig. 9. The conversion at 35 min was proportional to the relative light intensity ranging from 50% to 95% with the higher light intensity (Fig. 9a). A linear relationship between the pseudo-first order constants and the relative light intensity was clearly observed (Fig. 9b). This behavior was previously observed in other photochemical systems [48,50] where the reaction rates can be linear at low light intensities, square root dependent at intermediate light intensities and at high light intensities it remains constant.

4. Conclusions

It was studied the effect of the silver precursor on the structural and photocatalytic properties of Ag/TiO\(_2\) composites by using a photodeposition method. The photocatalytic reduction of Ag\(^+\) to Ag\(^0\) on TiO\(_2\) was higher with AgNO\(_3\) as a precursor than AgClO\(_4\) or silver acetylacetonate. In all composites, a surface plasmon resonance was clearly observed in the range of \(\lambda = 400–530\) nm, with a coloration slightly brown to purple, denoting metal particle sizes from 2 to 20 nm. Bulk and surface analysis confirmed the presence of Ag and Ag\(_2\)O and traces of AgO. Ag oxidized species were probably formed by the reaction of Ag\(^0\) with oxygen species after being exposed to the environment. Ag\(^0\) dispersion on TiO\(_2\) was in the order: Ag-N/TiO\(_2\) > Ag-C/TiO\(_2\) > Ag-A/TiO\(_2\), however the ratio of Ag\(^0\)/AgO was \(~1.3\) for Ag-N/TiO\(_2\) and Ag-A/TiO\(_2\) and for Ag-C/TiO\(_2\) was lower (\(~1.1\)). Upon modifying TiO\(_2\)-P25 with Ag\(^0\)/Ag-O, the rate constant of Rh-B degradation under simulated solar light was higher than pure TiO\(_2\). It seemed that the higher photocatalytic activity, obtained with silver acetylacetonate as the precursor, was due to the higher amount of Ag surface species than to Ag particle size or metal dispersion.

Declaration of interest

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jscs.2015.05.009.

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