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Photocatalytic degradation of phenol on TiO_2 and TiO_2/Pt sensitized with metallophthalocyanines

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Abstract

TiO_2 sensitized with Zn(II) and Co(II) tetracarboxyphthalocyanine (TcPcM) showed relevant photocatalytic activity on the degradation of phenol in the visible spectral region. The photonic efficiencies (η) of phenol degradation were 0.043 on TcPcCo/TiO_2 and 0.033 on TcPcZn/TiO_2. Photodeposition of platinum on TcPcM/TiO_2 enhanced reaction photoefficiency up to $\eta \cong 0.1$. The amount of CO_2 produced with TcPcZn/TiO_2/Pt was 1.95 mol CO_2/mol of initial phenol, which corresponds to about 33% of "initial phenolic index" and with TcPcCo/TiO_2/Pt was 3.5 mol CO_2/mol of initial phenol, about 65% of "initial phenolic index".

Keywords: Phenol; Photodegradation; Sensitized TiO_2; Platinization; Metallophthalocyanines

1. Introduction

Photocatalytic oxidation of organic pollutants with molecular oxygen and solar light is a promising procedure for wastewater treatment [1]. In aqueous medium under UV illumination, TiO_2 is capable to generate highly reactive oxygen species such as $O_2^{\bullet -}$, $HO_2^{\bullet}$, $HO^{\bullet}$, leading to the oxidation of a wide variety of aliphatic and aromatic hydrocarbons [2,3]. In order to extend TiO_2 absorption to the visible region of the spectrum, since only a few percents of the solar light are in the UV range [4], different systems have been studied such as modification of the TiO_2 surface with other semiconductors [5], doping with transition metals [6,7] and photosensitization by impregnating with anchoring dyes [8,9].

When TiO_2 is sensitized with a dye, the sensitizer absorbs photons and pumps electrons into the semiconductor conduction band (CB) [10,11]. Several sensitizers have been employed like: Ru–polypyridine complexes [12–14], metallophthalocyanines [15,16], $[Fe^{II}(CN)_6]^4$ [17], hemicyanine derivatives [18,19], etc.

Phthalocyanines (Pc) are interesting sensitizers since they have visible absorption bands around 670 nm and have a high chemical and thermal stability [20]. Bard and coworkers [21] have used thin films of various metal phthalocyanines (Mg, Zn, Co, Al, Fe and Ti) on the TiO_2 surface to produce photocurrents in aqueous solutions. Charge transfer is favored due to the close position of the TiO_2 CB energy levels with respect to the LUMO orbital energy of the Pc (Fig. 1). When a dye molecule absorbs visible light, it is excited to a higher energy state, the excited dye then injects electrons into the conduction band of TiO_2. The injected electrons are then scavenged by the surface-adsorbed oxygen to yield activated species such as $O_2^{\bullet -}$, $HO^{\bullet}$, etc. [22].

Charge transference from the sensitizer induces an oxidized $^{\bullet}Pc^{+}$. The sensitizer may be regenerated through either one of the following processes: (i) oxidation of dissolved molecules of phenol (Ph) according to reaction (1) [20]:

$$^{\bullet}Pc^{+} + Ph \rightarrow Pc + {}^{\bullet}Ph^{+} \quad (1)$$

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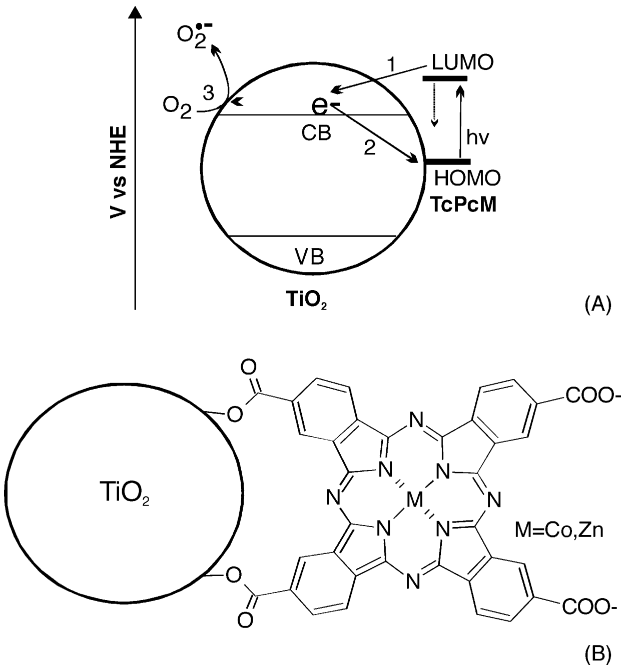

Fig. 1. (A) Representation of the photosensitization of TiO_2: (1) electron injection from the sensitizer to CB, (2) back electro transfer to sensitizer and (3) electron migration and interfacial electron transfer to an O_2. (B) TcPcM anchored to the TiO_2 surface.

and (ii) water may act as an electron donor to regenerate the oxidized sensitizer according to reaction (2) [12]:

$$2^{\bullet}PC^{+} + H_2O \rightarrow 2Pc + 2H^{+} + \tfrac{1}{2}O_2 \qquad (2)$$

In this case, the reduction potential of the $^{\bullet}TcPcM^{+}/TcPcM$ couple (E_p = 1.1–1.2 V versus NHE) [23] is more positive than the O_2/H_2O potential (E_p = 1.05 V versus NHE at pH 3). Degradation of phenol on Pc/TiO_2 may proceeds using water as an electron donor to regenerate the oxidized sensitizer so the process continues indefinitely. Since water is in large excess reaction (2) may be favored.

Iliev has studied the photocatalytic activity of H_2Pc/TiO_2 on phenol oxidation in basic medium [24], the produced oxidation was attributed to the superoxide radical formed on the TiO_2 CB, and detecting a mixture of CO_2, fumaric, maleic and formic acids as final products. However, electron back transfer to the HOMO orbital of the sensitizer competes with the superoxide formation decreasing photoactivity, see path 2 (Fig. 1) [25,26].

Deposits of noble metals on semiconductors are effective traps for the CB electrons, due to the formation of a Schottky barrier at the metal–semiconductor junction, increasing the excited electron life time [27–29]. When Pt is deposited on the sensitized TiO_2, electron transfer from the CB to electron acceptors could be enhanced. The main enhancing effect of platinization seems to be a higher rate of production of oxidizing species. Bae and Choi [25] reported an increase in the degradation rate of perchlorinated compounds (20 times), when sensitized TiO_2 with ruthenium complexes was modified with noble metal deposits.

In this work, we have investigated the photodegradation of phenol under visible light irradiation with TiO_2 sensitized with Zn(II) and Co(II) tetracarboxyphthalocyanine (TcPcM), linked through ester bond. A significant increase in the phtotocatalytic degradation of the phenol was observed when $TcPcM/TiO_2$ was modified with platinum deposits.

2. Experimental

2.1. Reagents and equipment

TiO_2 P25 was purchased from Degussa. Phenol (99% purity), urea and NaOH were acquired from Merck. Trimellitic anhydride, ammonium molibdate, 4-aminoantipyrine, potassium ferrocyanide and potassium hexachloroplatinate were obtained from Aldrich. Ammonium chloride, nitrobenzene and methanol were purchased from J.T. Baker. Zn(II) and Co(II) sulfate and $Ba(OH)_2$ were obtained from Carlo Erba. HCl 37% and H_2SO_4 98% were acquired from EM Science. All reagents were analytical grade and used without further purification.

BET surface areas were measured by nitrogen adsorption at 77 K, using a Micromeritics FlowSorb II 2300 device. Electronic spectra were measured on a HP8453 spectrophotometer. Diffuse reflectance spectra were measured with a Lamda 4 Perkin-Elmer instruments spectrophotometer, using an integrating sphere. FT-IR spectra were recorded with a Brucker spectrophotometer and Raman spectra were measured with a Perkin-Elmer GX NIR-FT. Reaction products were identify using a HP6890 GC equipped with a HP-5 column (100 m, 0.32 mm, 0.25 μm) coupled to a HP5973 MS detector.

2.2. Catalysts preparation

Phthalocyanines were synthesized according to the method described by Achar et al. [30]: Zn(II) or Co(II) sulfate (0.048 mol), trimellitic anhydride (0.176 mol) and urea (1 mol) were mixed with ammonium chloride (0.085 mol) and ammonium molibdate (0.004 mol), the mixture was pulverized and dissolved in 10 mL of previously heated nitrobenzene and then refluxed at 185 °C during 4 h. The dark blue solid obtained was crystallized in a 0.1N NaOH and 1N HCl solution.

Platinization of TiO_2 was performed by photodeposition [25]: 200 mL of an aqueous suspension of TiO_2 (0.1 g), containing 8.1 mL (0.2 mol) of methanol and 0.012 g (0.02 mol) of potassium chloroplatinate, was irradiated with a 200 W medium pressure mercury lamp (Osram) during 30 min under constant stirring. After irradiation, the sample was washed twice with bidistilled water, centrifuged and dried at 70 °C. The Pt loading on TiO_2 was 0.2 wt%.

Anchorage of TcPcM on TiO_2 and on TiO_2/Pt surfaces was done by adding 0.05 g of TiO_2 to 50 mL of dye solution (0.07–0.3 mM), adjusting pH to 3.0 with 0.1N H_2SO_4 magnetically stirred during 30 min [25]. The solid was filtered, washed with distilled water and dried at room temperature during 24 h. The amount of linked sensitizer on the support was determined by desorption of the TcPcM with concentrated H_2SO_4 and the supernatant solution was analyzed by UV/vis spectroscopy.

2.3. Photodegradation reactions

Photocatalytic degradation of phenol was performed using a batch reactor with an immersion lamp (100 W halogen lamp, Osram). The light was passed through a potassium dichromate solution (1 M) in order to remove UV light and to improve the homogeneity of light intensity distribution [17]. Air was bubbled into the reaction medium from the bottom with an air pressure pump. The photon flow per unit volume was determined by actinometrical measurements using 200 mL of potassium ferrioxalate solution (0.15 M): $[K_3Fe(C_2O_4)_3 \cdot 3H_2O]$ [31].

In a typical experiment, 20 mg (0.21 mmol) of phenol and 200 mg (0.08–0.28 mmol Pc) of catalyst were mixed in 200 mL H_2O. The suspensions were stirred in the dark during 1 h (to assure adsorption/desorption equilibrium of phenol). The degradation of phenol was determined by UV–vis spectrophotometry using the 4-aminoantipyrine method [32]. This method determines the ‘‘phenolic index’’: $C_F = \Sigma_i f_i C_i$, where C_F represents the sum of the concentration of phenol and its derivatives (C_i) such as dihidroxy-, trihydroxybenzenes and other polyphenols. The contribution of the individual compounds (f_i) to the phenolic index is different, for pure phenol the contribution is 1 ($f_{phenol} = 1$) [33]. In this study, the ‘‘phenolic index’’ was used to compare the catalytic activity of different photocatalysts. CO_2 was measured as $BaCO_3$ precipitate by bubbling an air stream from the reactor into a $Ba(OH)_2$ solution [24,34].

3. Results and discussion

3.1. Catalysts characterization

Tables 1 and 2 show TcPcM’s FT-IR [25] and Raman [35] characteristic absorption bands. Raman peaks at 1548 cm^{-1} (ν: TcPcCo) and 1516 cm^{-1} (ν: TcPcZn) exhibited a shift due to the influence of the metallic center on the benzopyrrol ring frequencies [36].

Fig. 2 shows TiO_2andTcPcM/TiO_2’s FTIR spectra. Formation of O═C–O–Ti is evidenced by the band at 1210 cm^{-1} (Fig. 2A) [37–40]. In Fig. 2B and C, Raman spectra of free TcPcM and TcPcM/TiO_2 show a weak band near 1380 cm^{-1} due to the presence of carboxylic acid groups [37,41].

Table 1
Assignment of characteristic TcPcM frequencies observed in the FT-IR spectra

Characteristic frequencies (cm^{-1})	Assignment
1700–1714	C═O stretch
1398–1385	O–H inflexion
1328–1346	C–O stretch
1642–1664	C═N stretch
1520	C═C stretch
1147, 1090, 1047, 930, 828, 739	Phthalocyanine skeleton

Table 2
Raman spectra assignments of characteristic TcPcM frequencies

Characteristic frequencies (cm^{-1})		Assignment
TcPcCo	TcPcZn	
1616	1611	C═O stretch
1548	1516	Isoindole stretch
1464	1490	Isoindole stretch
1432	1426	Isoindole stretch
1343	1339	Pyrrole stretch
1276	1282	C–O stretch
1126	1137	Pyrrole breathing
1036	1035	C–H bend
853	847	Macro stretch
690	686	Macro breathing
598	610	Benzene deformation
430	430	Benzene deformation
335	295	M–N stretch

Free and anchored TcPcMs were quantified also by UV–vis spectroscopy in concentrated H_2SO_4. The amounts of TcPcM anchored on TiO_2 and TiO_2/Pt are indicated in Table 3.

Diffuse reflectance spectra (Fig. 3) show Q band of TcPcM/$TiO_2$and TcPcM/TiO_2/Pt. Naked TiO_2 does not show absorption in the visible range; however, platinized TiO_2 becomes darker [27].

As shown in Table 3, three different amounts of MPc (M = Co, Zn) were anchored on TiO_2 and TiO_2/Pt.

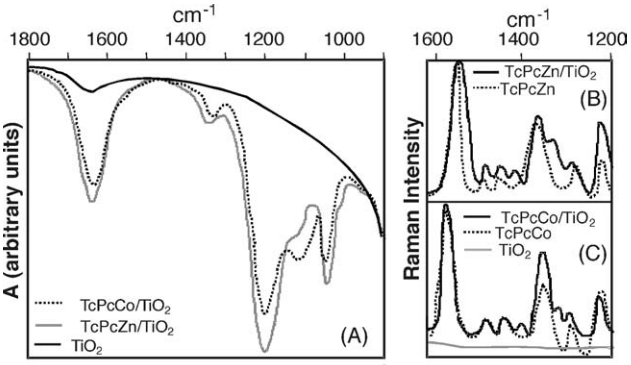

Fig. 2. (A) FT-IR spectra of TiO_2, TcPcM/TiO_2 (M = Co, Zn). (B) Raman spectra of TcPcZn and TcPcZn/TiO_2 systems. (C) Raman spectra of TcPcCo, TiO_2 and TcPcCo/TiO_2.

Table 3
Specific surface area of TiO_2, TiO_2/Pt, TcPcM/ $TiO_2$and TcPcM/TiO_2/Pt

Solid	Area ($m^2\ g^{-1}$)
TiO_2 (Degussa P25)	49.7
TiO_2/Pt	44
0.081 mmol TcPcCo/g TiO_2	23.6
0.16 mmol TcPcCo/g TiO_2	21.7
0.28 mmol TcPcCo/g TiO_2	35.7
0.15 mmol TcPcCo/g TiO_2/Pt	40.4
0.07 mmol TcPcZn/g TiO_2	17.8
0.15 mmol TcPcZn/g TiO_2	44.6
0.28 mmol TcPcZn/g TiO_2	38.4
0.16 mmol TcPcZn/g TiO_2/Pt	40.9

When MPc is anchored on TiO_2, a decrease of BET area is observed. However, when TiO_2/Pt is functionalized, no reduction or increase of specific surface areas was observed.

3.2. Phenol photocatalytic degradation on TcPcM/TiO_2

Fig. 4 shows the photodegradation of phenol by TcPcM/TiO_2. After 1 h of illumination with light of $\lambda > 430$ nm (incident light intensity was 3.52 μEinstein $L^{-1}\ s^{-1}$ in the range 420–560 nm), the change in ‘‘initial phenolic index’’ was 35% ($k = 6.5 \times 10^{-3}\ min^{-1}$, where k is the pseudo-first-order transformation rate constant) with TcPcZn (0.15 mmol)/g TiO_2 and 45% ($k = 8.5 \times 10^{-3}\ min^{-1}$) with TcPcCo (0.16 mmol)/g TiO_2. No transformation of phenol was detected with pure TiO_2 upon illumination with visible light, and TcPcMs/TiO_2 did not display any catalytic activity in the dark.

Fig. 5 shows the photonic efficiency (η) of phenol degradation with TcPcM/TiO_2, where $\eta = kC_0/I_0$, C_0 is the initial phenol concentration and I_0 is the incident photonic flow per unit volume. The results indicate that a sensitization effect is observed and an excess of sensitizer did not increase the photoactivity [42–44].

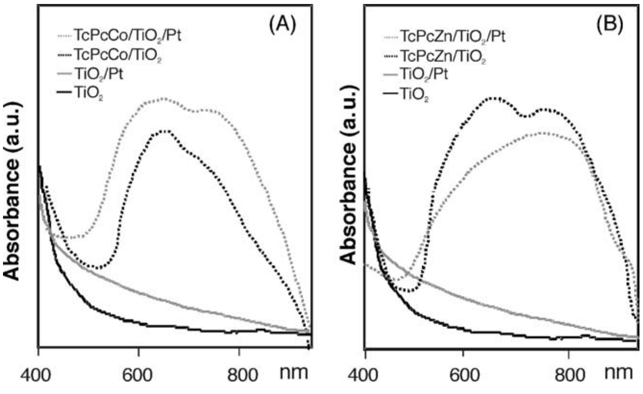

Fig. 3. Comparison of the UV–vis diffuse reflectance spectra of TiO_2, TiO_2/Pt and sensitized TiO_2. (A) TcPcCo/TiO_2 and TcPcCo/TiO_2/Pt. (B) TcPcZn/TiO_2 and TcPcZn/TiO_2/Pt.

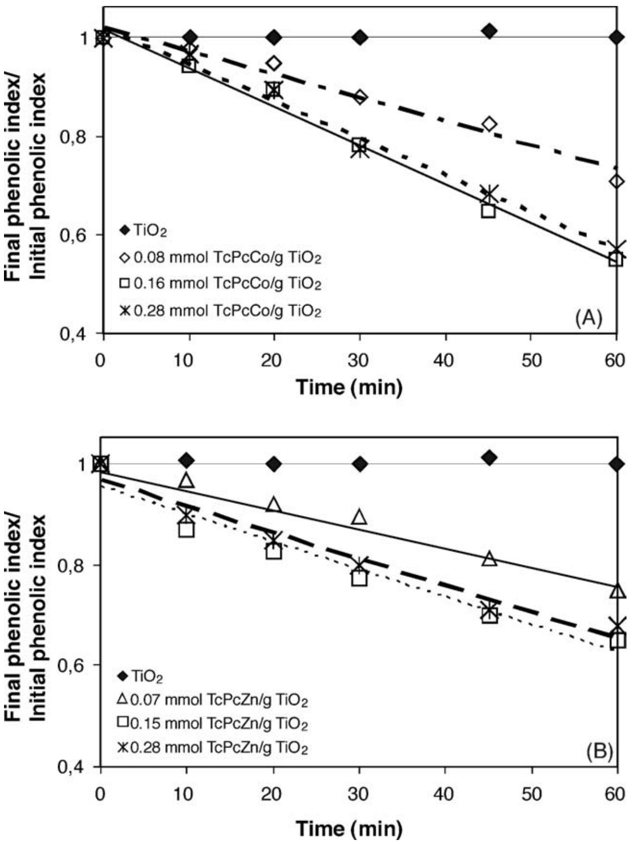

Fig. 4. Time evolution of the phenolic index (C_F) as a function of time, varying the amount of anchored sensitizer. (A) TcPcCo/TiO_2. (B) TcPcZn/TiO_2. *Experimental conditions*: [Phenol] = 100 ppm, reaction volume 200 ml, [TiO_2] = 1 g L^{-1}, $T = 20 \pm 2$ °C.

3.3. Platinization effect on the degradation of phenol

Fig. 6 shows the effect of platinization of TcPcM/TiO_2 on phenol photocatalytic degradation. The TiO_2/Pt without sensitizer did not show activity under visible light [25]. The rate constant for phenol photo-decomposition was increased up to $20 \times 10^{-3}\ min^{-1}$ with TcPcZn (0.15 mmol)/g TiO_2/Pt and up to $21 \times 10^{-3}\ min^{-1}$ with TcPcCo (0.16 mmol)/g TiO_2/Pt (Fig. 6A).

The photonic efficiencies after 60 min of reaction time were 0.10 (TcPcZn/TiO_2/Pt) and 0.11 (TcPcCo/TiO_2/Pt) (Fig. 6B). According to Bae and Choi [25], the highly enhanced degradation on sensitized TiO_2/Pt could be due to platinum electron trapping, which is fast enough to compete with electron back transfer (path 2 in Fig. 1), thereby increasing the probability of interaction with molecular oxygen to form highly reactive species such as $O_2^{\bullet -}$.

The amount of CO_2 produced in phenol photodegradation with TcPcZn/TiO_2/Pt was 1.95 mol CO_2/mol of initial phenol, corresponds to about 33% of degraded phenol and with TcPcCo/TiO_2/Pt was 3.5 mol CO_2/mol of initial phenol, corresponds to about 65% of degraded phenol. Effort to identify other products by GC–MS technique was failed.

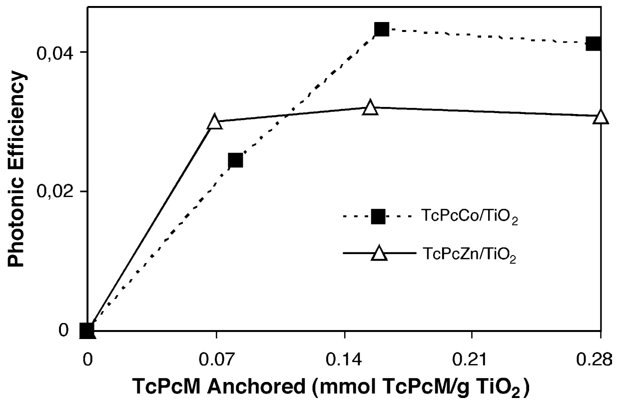

Fig. 5. Photonic efficiency of the degradation of phenol as a function of the amount of anchored TcPcM on TiO_2.

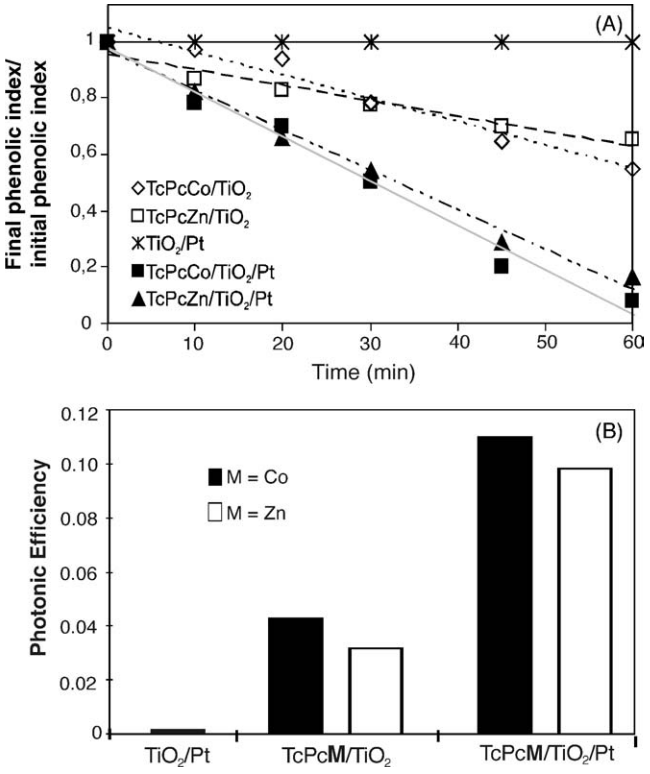

Fig. 6. Effect of the platinization of $TcPcM/TiO_2$ (0.16 mmol Pc/g TiO_2) on the time evolution of the "phenolic index" upon visible light irradiation. (A) Comparison of the photodegradation rate of $TcPcM/TiO_2$, TiO_2/Pt and $TcPcM/TiO_2$/Pt as a function of the time. (B) Photonic efficiency increase of the platinized systems.

4. Conclusions

Enhancement of the photocatalytic activity of TiO_2 sensitized with Zn(II) and Co(II) tetracarboxyphthalocyanine, under irradiation with visible light, has been achieved. This could be explained by charge transfer from the excited sensitizer to the TiO_2 CB. Platinum deposits on the TiO_2surface increased the activity, perhaps due to the formation of a Schottky barrier at the metal semiconductor contact, thereby increasing electron lifetime in the TiO_2 CB and possibly increasing superoxide radical formation that would lead to a higher phenol photodegradation.

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