Effect of Copper Precursor on the Stabilization of Titania Phases, and the Optical Properties of Cu/TiO_2 Prepared with the Sol−Gel Technique

X. Bokhimi,* A. Morales, and O. Novaro†

Institute of Physics, The National University of Mexico (UNAM), A. P. 20-364,
01000 México D. F., Mexico

T. López, O. Chimal, M. Asomoza, and R. Gómez

Facultad de Química, Universidad Autónoma Metropolitana Iztapalapa, A. P. 54-534,
09340 México D. F., Mexico

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In the sol−gel Cu/TiO_2 system, nanocrystalline brookite, which was stable even after annealing the sample at 400 °C, was generated in high concentrations. This was achieved with copper chloride as copper precursor. The respective samples had a light absorption band at 562 nm that corresponded to an energy bandgap of 2.30 eV, which is smaller than the values reported for titania. When copper sulfate was the precursor, brookite was absent, but nanocrystalline anatase, the main phase, was stabilized even at 800 °C by sulfate ions. After annealing the samples at low temperatures, copper was well dispersed for 1 wt % copper, but part of it segregated forming copper compounds when the copper concentration was 10 wt %. By annealing the samples at 800 °C, copper oxidized to CuO; except in the 10 wt %-copper sample prepared with copper sulfate, where it formed antlerite.

Introduction

When titania is prepared with the sol−gel technique, the concentration and stabilization of the different titania phases—brookite, anatase and rutile—in the sample depend on the hydrolysis catalyst.[1] For a given hydrolysis catalyst, the concentration and stabilization of titania phases change dramatically when during preparation a transition-metal compound is added to the sol. For example, when titania is prepared with hydrochloric acid as hydrolysis catalyst, the main phase in the fresh sample is anatase,[1] but if platinum acetylacetonate is added to the sol, the main phase is rutile.[2] Similar results are reported when a tin compound is added.[3]

Following the above results, we analyzed the effect of CuCl and $CuSO_4$ in the formation and stabilization of the phases in titania prepared with the sol−gel technique. This generated the Cu/TiO_2 system, which is also of interest in catalysis,[4−9] in photoelectrochemistry,[10] and in solar cells.[11]

Cu/TiO_2 catalyst is used in the selective oxidation of unconverted ammonia from power combustion stations[4] and in the reduction of nitric oxide from exhaust emissions.[9]

In this catalyst, the copper dispersion depends on titania phase. For example, in anatase calcined at 720 °C, the dispersed product is copper oxide, but no copper oxide is detected on rutile calcined at 400 °C.[12] When the sample is a mixture of 80 wt % anatase and 20 wt % rutile, a copper oxide film homogeneously covers each titania crystal. This film, by annealing in hydrogen at 300 °C, reduces to metallic copper and is transformed into many isolated small copper crystals, with sizes that decrease with the crescendo of reducing temperature.[9] The copper dispersion on brookite, however, has not been reported.

In Cu/TiO_2 catalyst, copper dispersion depends on the strong interaction of copper with titanium and oxygen atoms.[13,14] It also depends on copper concentration: for low concentrations, copper disperses; but for large concentrations, it agglomerates and forms copper oxide clusters.[12,15] The strong interaction between copper and titania, which causes the high dispersion of copper, is like the interaction between transition metals of group VIII and titania[16] and depends on titania properties.[17]

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† Member of El Colegio Nacional, Mexico.

* To whom correspondence should be addressed. E-mail: bokhimi@fenix.ifisicacu.unam.mx. Telephone: (525)622-5079.

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Pure titania has an interesting future in the industry of solar cells.[11,18] Cells made of nanocrystalline anatase have conversion efficiencies of 10%[18] and cost less than those based on silicon. The presence of rutile in the titania row material used in the cells decreases the conversion efficiency,[18] but the influence of brookite in this conversion is unknown.

Distortion of the local titanium environment influences the optical properties of titania.[19] The local environment of titanium in titania phases is made of distorted oxygen octahedra joined by their edges: three in brookite, four in anatase, and one in rutile.[20] Therefore, a good interpretation of the optical data of any titania sample requires knowledge of the concentration of the phases.

In the present paper, the effect of copper precursor (1 and 10 wt % copper) in the formation of the different titania phases was studied. Samples were analyzed with X-ray powder diffraction and UV−vis spectroscopy. The crystalline structure of titania phases and tenorite were refined with the Rietveld method, which also provided the phase concentrations and their average crystallite size.

Experimental Section

Sample Preparation. *$CuSO_4$ Precursor.* A water solution of copper sulfate (Baker 99%) was prepared, stirred, and refluxed. Sulfuric acid (Baker 98%) was added to it until obtaining pH 3. Titanium ethoxide (Alfa Products 99%) was dropwise added to this solution, with stirring and refluxing until gel formation. Gels were dried in air at 70 °C for 12 h. For the analysis, samples were annealed in air for 12 h at 400 and 800 °C.

$CuCl_2$ Precursor. Samples were prepared like those with copper sulfate and sulfuric acid, but with copper chloride (Baker 99%) and hydrochloric acid.

Copper concentrations were 1 and 10 wt %.

Characterization. *X-ray Diffraction.* The crystalline structure of the phases in the samples was characterized with X-ray powder diffraction and refined with the Rietveld method. The diffraction patterns of the specimens, prepared by packing sample powder into a glass holder, were measured at room temperature with a Siemens D-5000 diffractometer that had Cu Kα radiation and a monochromator in the secondary beam. Intensity was measured in the step scanning mode for 2 θ angles between 20° and 110°, with a step of 0.02° and a measuring time of 2 s/point. Crystalline structures were refined by using the DBWS-9411[21] and WYRET[22] programs. Peak profiles, modeled with a pseudo-Voigt function, had average crystallite size as one of the profile-breadth fitting parameters.[23] The standard deviations, showing the variation of the last figures of the corresponding number, are given in parentheses. When the numbers corresponded to parameters obtained from the Rietveld refinement, the estimated standard deviations are not estimates of the analysis as a whole but only of the minimum possible probable errors based on their normal distribution.[24]

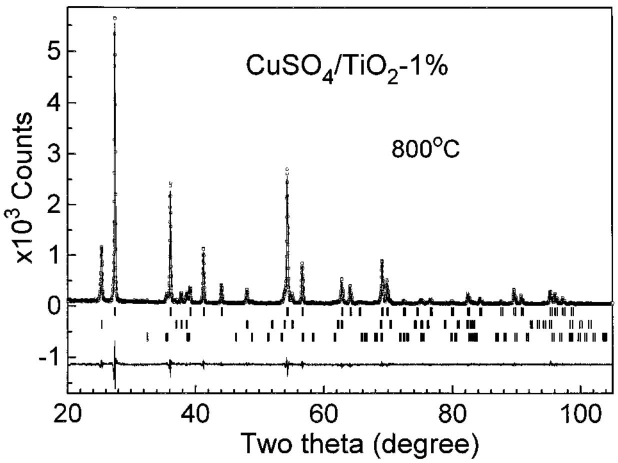

Figure 1. Rietveld refinement plot of Cu/TiO_2, with 1wt % copper, prepared with copper sulfate, and annealed at 800 °C. Upper tick marks correspond to rutile (R_F = 0.024); middle tick marks, to anatase (R_F = 0.056); and lower tick marks, to tenorite (R_F = 0.12).

For each phase, the scale factor, the average crystallite size, the lattice parameters, the isotropic temperature factor, the cation occupancy, and the atom coordinates (when they are variable) were refined.

UV−Vis Spectroscopy. By using the diffuse reflectance technique, UV−vis spectra were measured in a Varian Cary-III spectrophotometer coupled to an integration sphere.

Results and Discussion

Samples had the three titania phases brookite, anatase, and rutile. The crystalline structure was refined by using the atom positions and symmetry reported by Bokhimi et al.[1] Brookite has an orthorhombic unit cell described by space group *Pbca*; anatase, a tetragonal unit cell described by space group $I4_1/amd$; and rutile, a tetragonal unit cell, described by space group $P4_2/mnm$.

Samples also had tenorite. Its crystalline structure was refined with a monoclinic unit cell, having four Cu and four O atoms, with a symmetry described by space group *C*2/*c*. Copper atoms were located at ($^1/_4$, $^1/_4$, 0) and oxygen atoms at (0, u, $^1/_4$), with u values around 0.078.

Figures 1 and 2 are typical Rietveld refinement plots from samples containing anatase, rutile, and tenorite.

Some samples contained crystalline phases different from those of titania and tenorite. The crystallographic data reported in the literature for these phases, however, were insufficient to refine their structures; therefore only titania phases and tenorite were refined (Figures 3 and 4). The presence of these extra phases partially affected the final values of the parameters associated to the refined phases, but they did not change the observed tendency of the parameters associated to titania phases and tenorite. In some cases (Figure 3) the amount of these phases was small, and in some others (Figure 4) the diffraction peaks of titania phases were so broad, and the area under them so large, that the contribution of the new extramicrocrystalline phases, with very narrow peaks, was negligible.

$CuSO_4$ Precursor. The samples prepared with $CuSO_4$ contained anatase and rutile but not brookite (Table 1). For 1 wt % copper, the samples annealed at 70 and 400 °C had anatase mixed with an amorphous

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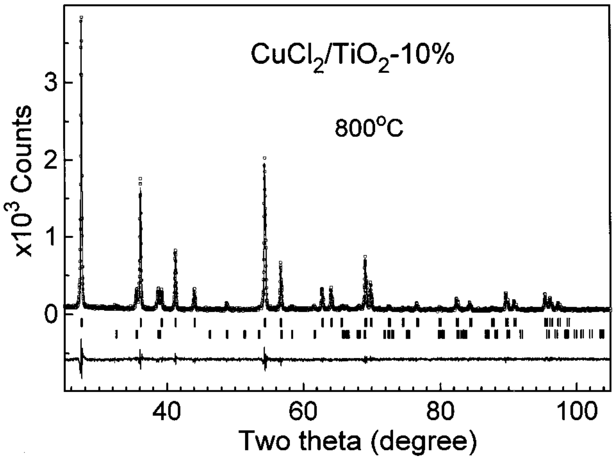

Figure 2. Rietveld refinement plot of Cu/TiO$_2$, with 1 wt % copper, prepared with copper chloride and annealed at 800 °C. Upper tick marks correspond to rutile ($R_F = 0.032$); lower tick marks, to tenorite ($R_F = 0.12$).

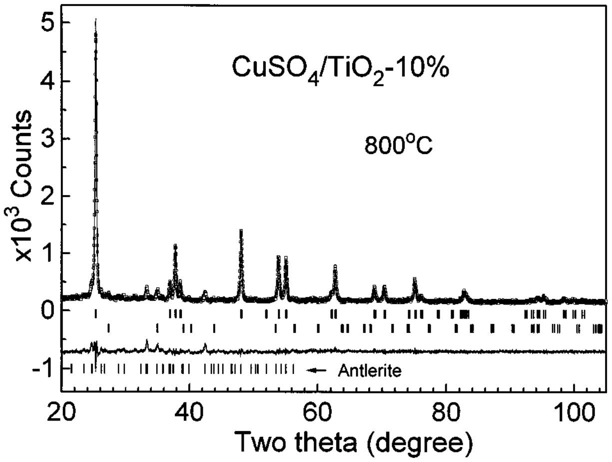

Figure 3. Rietveld refinement plot of Cu/TiO$_2$, with 10 wt % copper, prepared with copper sulfate and annealed at 800 °C. Upper tick marks correspond to anatase ($R_F = 0.038$); lower tick marks to tenorite ($R_F = 0.23$). The reflections associated to antlerite are also indicated.

phase (Figure 5), which was not refined, because the software we used for the refinement does not have this possibility. At these annealing temperatures, no peaks associated with any copper compound were observed, which is in accordance with previously reported results.[12] This means that copper was highly dispersed into anatase or in the amorphous phase. After annealing the sample at 800 °C, the amorphous phase and a part of anatase were transformed into rutile and tenorite (Figure 1).

When copper concentration was increased to 10 wt %, copper segregated as bonattite ($CuSO_4{\cdot}3H_2O$) after annealing the sample at 400 °C or lower temperatures (Figure 6) and as tenorite and antierite ($Cu_3SO4(OH)_4$) after annealing the sample at 800 °C (Figures 3 and 6). In this case, sulfate ions stabilized anatase, the main phase (Table 1). The sulfate ions in anatase and its small crystallite size (Table 2) make the sample attractive to be tested as a catalyst.

These samples had a constant light absorption between 800 and 360 nm and an absorption band in the ultraviolet region (Figure 7), which began rising at 400 nm and held almost constant at 332 nm. In the samples annealed at 400 °C the band rising began at 386 nm, and shifted to 365 nm when they were annealed at 800 °C. The band rising was like that observed in semiconductors with direct band transitions, which occur between the maximum of valence band and the minimum of conduction band.[25] Energy bandgaps were almost independent of copper concentration and annealing

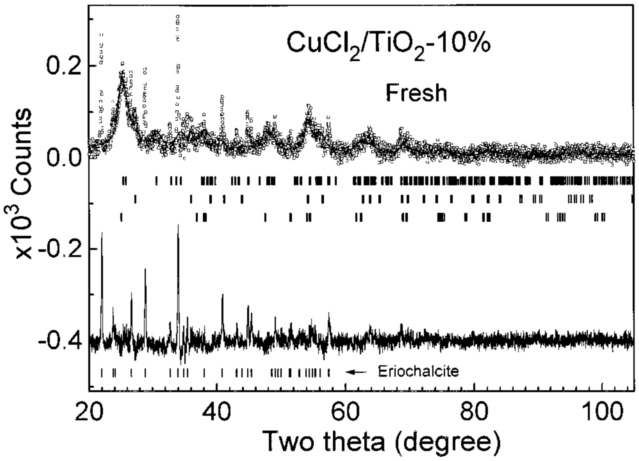

Figure 4. Rietveld refinement plot of a fresh Cu/TiO$_2$ sample with 10 wt % copper, and prepared with copper chloride. Upper tick marks correspond to brookite ($R_F = 0.054$); middle tick marks, to rutile ($R_F = 0.084$); and lower tick marks, to tenorite ($R_F = 0.055$). The reflections associated to Eriochalcite are also indicated.

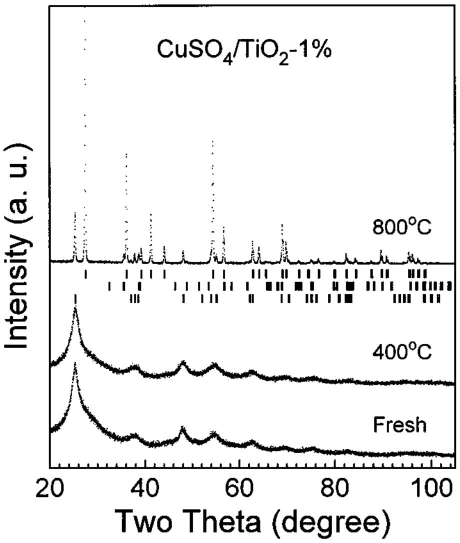

Figure 5. Temperature dependence of X-ray powder diffraction patterns of Cu/TiO$_2$ with 1 wt % copper and prepared with copper sulfate. Upper tick marks correspond to rutile; middle tick marks, to tenorite; and lower tick marks, to anatase.

Table 1. Concentration of Titania Phases as a Function of Temperature

sample	*T* (°C)	brookite (wt %)	anatase (wt %)	rutile (wt %)
CuSO$_4$/TiO$_2$−1%	70		100	
	400		100	
	800		16.2	83.8
CuSO$_4$/TiO$_2$−10%	70		100	
	400		100	
	800		98.1	1.9
CuCl$_2$/TiO$_2$−1%	70	45.3	52.7	2.0
	400	46.7	6.5	46.8
	800			100
CuCl$_2$/TiO$_2$−10%	70	63.5	22.0	14.5
	400	37.8	27.9	34.3
	800			100

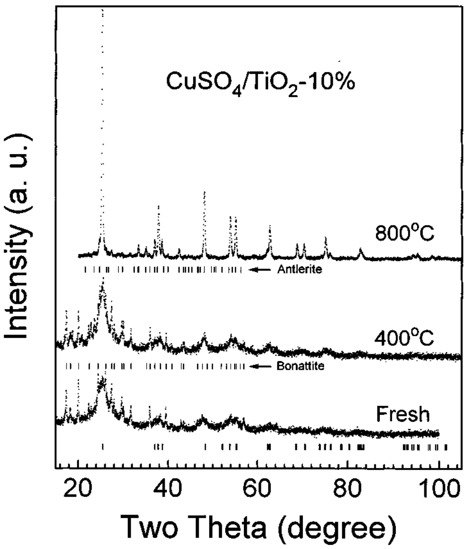

Figure 6. Temperature dependence of X-ray powder diffraction patterns of Cu/TiO$_2$ with 10 wt % copper and prepared with copper sulfate. The reflections associated to antlerite and to bonattite are indicated. The tick marks below the diffractogram of the fresh sample correspond to anatase.

Table 2. Average Crystallite Size of Titania Phases as a Function of Temperature

sample	T (°C)	brookite (nm)	anatase (nm)	rutile (nm)
CuSO$_4$/TiO$_2$−1%	70		3.5 (1)	
	400		3.5 (1)	
	800		87 (5)	128 (3)
CuSO$_4$/TiO$_2$−10%	70		2.6 (1)	
	400		3.8 (2)	
	800		48 (2)	47 (5)
CuCl$_2$/TiO$_2$−1%	70	4.4 (2)	4.6 (3)	12 (2)
	400	5.2 (3)	5.9 (4)	12 (2)
	800			56 (2)
CuCl$_2$/TiO$_2$−10%	70	5.2 (1)	8.3 (9)	14 (3)
	400	14 (5)	15 (3)	8.3 (8)
	800			109 (3)

Table 3. Energy Bandgap as a Function of Temperature

	E_g (eV)		
sample	70 °C	400 °C	800 °C
CuSO$_4$/TiO$_2$−1%	3.23	3.37	3.43
CuSO$_4$/TiO$_2$−10%	2.95	3.32	3.44
CuCl$_2$/TiO$_2$−1%	2.30	3.07	3.08
CuCl$_2$/TiO$_2$−10%	2.30	3.07	3.08

temperature (Table 3).

CuCl$_2$ Precursor. The samples prepared with CuCl$_2$ had a high concentration of nanocrystalline brookite (Table 1), with an average crystallite size of only a few nanometers (Table 2).

Brookite was stable even after annealing the sample at 400 °C (Table 1 and Figures 9 and 10). For 1 wt % copper, in the X-ray diffraction pattern no copper compound was observed (Figure 9); therefore, copper must be well dispersed. For 10 wt % copper (Figure 10), in the fresh sample, however, most copper segregated as eriochalcite ($CuCl_2{\cdot}2H_2O$), which was transformed into paratacamite ($Cu_2Cl(OH)_3$) when the sample was annealed at 400 °C (Figure 10). After the sample was annealed at 800 °C, the eriochalcite eventually was transformed into tenorite, while anatase and brookite were transformed into rutile (Figure 10).

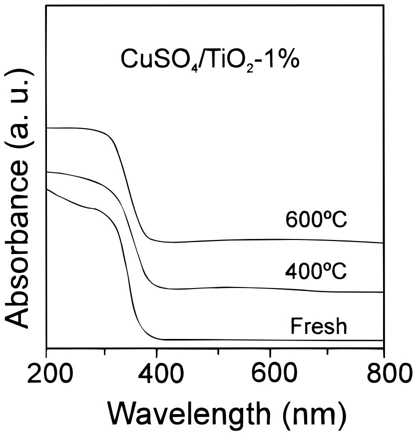

Figure 7. Temperature dependence of UV−vis spectrum of Cu/TiO$_2$ with 1 wt % copper and prepared with copper sulfate.

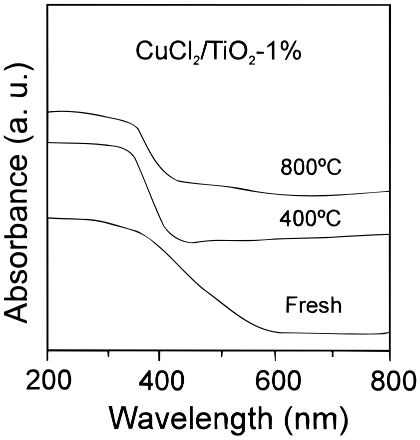

Figure 8. Temperature dependence of UV−vis spectra of Cu/TiO$_2$ with 1 wt % copper and prepared with copper chloride.

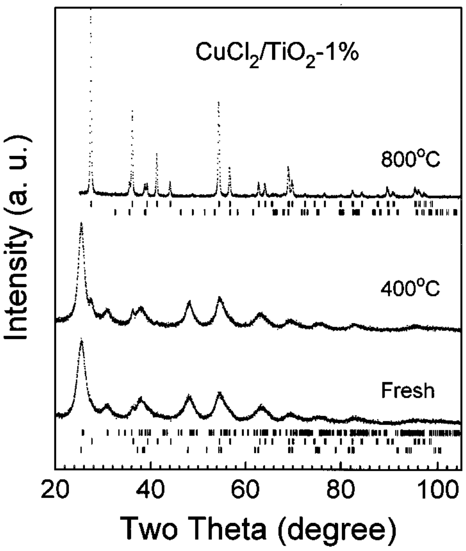

Figure 9. Temperature dependence of X-ray powder diffraction patterns of Cu/TiO$_2$ with 1 wt % copper and prepared with copper chloride. Below the diffractogram of the sample annealed at 800 °C, the upper tick marks correspond to rutile; the lower tick marks, to tenorite. Below the diffractogram of the fresh sample, the upper tick marks correspond to brookite; the middle tick marks, to rutile; and the lower tick marks, to anatase.

Fresh samples had an absorption band in the ultraviolet region that began at 562 nm and held constant at 368 nm (Figure 8). The corresponding energy band-

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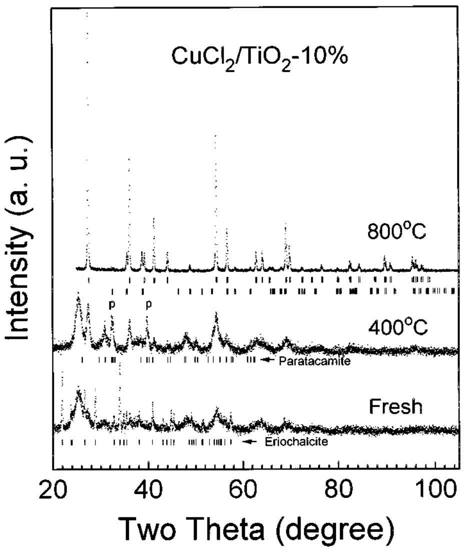

Figure 10. Temperature dependence of X-ray powder diffraction patterns of Cu/TiO_2 with 10 wt % copper and prepared with copper chloride. The reflections of Eriochalcite and paratacamite are indicated. The two stronger reflections of paratacamite are indicated with the letter p. Below the diffraction pattern of the sample annealed at 800 °C, the upper tick marks correspond to anatase; the lower tick marks, to rutile.

gap was only 2.30 eV, which is smaller than the typical values reported for titania. This small-energy bandgap could be produced by a transition from the valence band of the nanocrystalline CuO to the conduction band of nanocrystalline TiO_2, whose grains are in good contact as a consequence of the interdispersion of the two phases produced by the sol–gel method, like in the Cu/ZnO system.[26] The energy bandgaps of the annealed samples were larger than those obtained in the fresh samples (Table 3).

Conclusions

The generated titania phase concentrations depended on copper precursor. When copper sulfate was the precursor, the initial phase was nanocrystalline anatase, which, for 1 wt % copper partially, transformed into rutile, but for 10 wt % copper, it was stabilized by sulfate ions. This precursor did not generate brookite, which was in high concentrations when $CuCl_2$ was the precursor.

The samples with brookite had a small-energy bandgap, produced by a good contact between CuO and titania nanocrystals. This result is of great interest for titania-based solar cells and for titania-based photocatalyts and electrodes.

At low annealing temperatures, for the copper precursors used in the present study, copper was well dispersed for 1 wt % copper, but it segregated for 10 wt % copper. After the samples were annealed at 800 °C, for both copper concentrations, copper segregated forming tenorite when the precursor was $CuCl_2$, but it produced antlerite when the precursor was $CuSO_4$ and the copper concentration 10 wt %.

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