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Atmospheric pressure chemical vapour deposition of WO_3 thin films from a volatile fluorinated tungsten oxo-alkoxide precursor, $W(O)(OCH_2CF_3)_4$

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The monomeric tungsten oxo-fluoroalkoxide $W(O)(CH_2CF_3)_4$ (1) was synthesized from $W(O)Cl_4$ and CF_3CH_2OH in the presence of ammonia. It was used in atmospheric pressure chemical vapour deposition experiments to deposit non-stoichiometric $WO_{2.9}$ when used as a single-source precursor or stoichiometric WO_3 when O_2 was used as co-reagent. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: atmospheric pressure CVD; thin film; tungsten oxide; fluoroalkoxide; single-source precursor

Introduction

Tungsten oxide is an important inorganic material with a diverse range of applications.[1] As a transparent conducting oxide (TCO) it is seen as a potential 'smart window', capable of controlling its absorbance of solar radiation as a function of intensity and thus controlling interior lighting and temperature levels. It has potential as a photocatalytic coating which harvests more visible radiation than the widely studied titania,[2–4] while its conductivity also makes it applicable as a gas sensor, for example for NO_2, H_2S and O_3.[5]

The properties of tungsten oxide thin films are strongly dependent on the deposition technique and choice of precursor. Sol–gel,[6] sputtering[7] and spray pyrolysis[8] methods have been reported, but chemical vapour deposition (CVD) offers the greatest potential for large-scale coatings. Precursors for CVD include various classes of organometallics, e.g. $W(CO)_6$,[9] $W(CO)_4(PR_3)_2$ ($R = OEt$) or $W(\eta^3\text{-}C_3H_4)_4$,[10] but compounds with a direct W–O bond have advantages as they may act as single-sources (SSP), delivering both elements of the final film in one go. Although the use of polytungstates in an aerosol-assisted delivery route has recently been reported by Parkin,[11] more emphasis has been placed on the use of tungsten alkoxides $W(OR)_6$ ($R = C_6H_5$, C_6H_4F-4, $C_6H_3F_2$-3,4)[12] and oxo-alkoxides $[W(O)(OR)_4$, $R = Et, Pr^i, Bu^t, CH_2Bu^t]$[13,14] in this regard. However, to our knowledge the only example of such precursors which can be used at atmospheric pressure (AP), a significant advantage for large scale industrial coatings, has been using $W(OEt)_x$ ($x = 5, 6$).[15] Here, the problem of pre-reaction with added O_2 was encountered and overcome using a concentric pipe for the separate delivery of the reactive gases to the reactor. The films were deposited at low temperatures (<350 °C) and were all amorphous. Attempts to deposit films at higher temperatures led to powdery blue deposits on the substrate, which were assumed to be non-stoichiometric tungsten oxide.

Our interest was to identify a more suitable precursor for atmospheric pressure CVD (APCVD) of tungsten oxide, preferably as an SSP. There are two possible approaches to increasing the volatility of tungsten(VI) oxo-tetraalkoxides, either by using bidentate reagents to break up the inherently dimeric nature of these compounds, or using a fluoroalkoxide ligand where the Lewis basicity, and hence bridging capacity, is diminished by the electron-withdrawing nature of the halogen. We and others have reported on the first of these approaches, using either chelating aminoalcohols[16] or β-diketonates[13] as ancillary ligands (L) in precursors of general formula $W(O)(OR)_3(L)$. In this paper we report the synthesis of $W(O)(OCH_2CF_3)_4$, a tungsten oxo-alkoxide with sufficient volatility to generate WO_3 films by atmospheric pressure CVD.

Experimental

Materials, reagents and instrumentation

Elemental analyses were performed using a Carlo-Erba Strumentazione E. A. model 1106 microanalyser operating at 500 °C; results were calibrated against an acetanilide $[PhNHC(O)CH_3]$ standard. ^1H and ^{13}C NMR spectra were recorded using either Jeol JNM-GX-270FT (270 MHz) or Jeol EX-400 (400 MHz) Fourier transform spectrometers, while ^{183}W NMR spectra were recorded on a Jeol EX400 (400 MHz) machine. Chemical shifts are in ppm with respect to either Me_4Si (^1H, ^{13}C) or 1 mol dm^{-3} solution of Na_2WO_4/D_2O (^{183}W); coupling constants are in Hz. SEM was carried out on a Jeol JSM-6310 microscope equipped with an Oxford Instruments ISIS EDXS attachment. XRD was performed using a Philips PW1130 generator operating at 45 kV and 40 mA to power a copper fine-focus X-ray tube, in conjunction with a PW 1820 goniometer fitted

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with thin-film optics and a proportional X-ray detector. The transmission and reflectance spectra of the coated samples (*ca* 2 cm square) were measured between wavelengths 240 and 260 nm inclusive using a Hitachi u-4000 spectrometer calibrated with a rhodium mirror.

All manipulations during this synthesis were carried out under a nitrogen or argon atmosphere using standard Schlenk techniques or in a dry box fitted with a recirculation system. Tetrahydrofuran, toluene and hexane were dried over and distilled from sodium-benzophenone immediately prior to use; 2,2,2-trifluoroethanol was purchased from Aldrich and dried over molecular sieves once opened.

Synthesis

*Synthesis of W(O)(OCH_2CF_3)$_4$ (**1**)*

Tungsten oxychloride (5.00 g, 14.6 mmol) was dissolved in tetrahydrofuran (*ca* 120 ml) to give an orange solution. To this solution was added 2,2,2-trifluoroethanol (8.79 g, 87.8 mmol) with stirring. Ammonia was then bubbled through the solution for 25 min, giving a white precipitate. The white precipitate (NH_4Cl) was filtered off and the solvent removed *in vacuo* to give a brown solid. After extraction into toluene and evaporation of the solvent, the solid residue was washed with hexane and pumped dry to give an off-white powder (5.38 g, 62%). Sublimation of the off-white powder at approximately 180–190 °C gave a white compound which had the appearance of cotton wool. Yield [based on $W(O)Cl_4$] was 1.35 g (16%). Analysis found (calculated for $C_8H_8F_{12}O_5W$): C, 14.8 (16.1); H, 1.23 (1.35)%. NMR [δ (ppm), CD_3CN soln]. ^1H: 4.89 (q, CH_2, $^3J_{HF} = 8.9$); ^{13}C : 71.8 (q, CH_2, $^2J_{CF} = 35$ Hz), 125.7 (q, CF_3, $^1J_{CF} = 277$); ^{19}F : −76.9 (t, CF_3, $^3J_{FH} = 8.7$); ^{183}W : −249. IR data (NaCl plates, nujol mull, cm^{-1}): 1402, 1277, 1194, 1163, 1109, 956, 839, 783, 711, 667, 623. Electron Impact (EI) mass spectrum, *m/z*: 497 [$W(O)(OCH_2CF_3)_3$, 89%], 439 [$WF_3(OCH_2CF_3)_2$, 4%], 417 [$W(O)F(OCH_2CF_3)_2$, 53%], 359 [$WF_4(OCH_2CF_3)$, 13%], 337 [$W(O)F_2(OCH_2CF_3)$, 30%], 257 [$W(O)F_3$, 34%].

CVD experiments

Since the synthesis of **1** was problematic and low yielding, the pre-sublimed, crude, off-white powder was used in the bubbler during CVD experiments. This presented no difficulties as sublimation experiments had demonstrated that **1** was the only volatile species present. The bubbler was loaded with the precursor in a dry-box fitted with a recirculation system and, once removed from the dry-box, the bubbler was immediately connected to the CVD apparatus and flushed with nitrogen gas.

APCVD experiments were carried out both in the absence of, and in the presence of, an additional oxygen gas flow. The films were deposited on a 4 mm glass substrate coated with a thin film of SiCO, which acts as a blocking layer to prevent sodium diffusion into the deposited film. Details of our APCVD apparatus are given elsewhere,[17,18] while deposition conditions are displayed in Table 1. Once deposited, the films were analysed by glancing angle X-ray diffraction to determine their composition and by SEM to give an indication of the surface morphology of the film. The transmission/reflection spectra of the films were also recorded to determine if any selectivity to solar radiation was evident.

Table 1. Summary of deposition conditions used during APCVD experiments

Film ID	R1	R2
Quantity of precursor used (g)	4.44	1.53
Reactor temperature (°C)	600	600
Bubbler temperature (°C)	190	190
Run time (min)	20	20
Carrier gas (N_2) flow rate (l/min)	1–0.1	1.0
Diluent gas (N_2) flow rate (l/min)	3.0	3.0
Oxygen gas flow rate (l/min)	0	0.6

Results and Discussion

Synthesis and spectroscopy

The fluorinated oxo-alkoxide (**1**) was prepared by the route previously reported for other $W(O)(OR)_4$ (R = Me, Et, Pr^i, *cyclo*-C_6H_{11}) species.[19]

$$W(O)Cl_4 + 4CF_3CH_2OH + 4NH_3 \xrightarrow{THF} W(O)(OCH_2CF_3)_4 + 4NH_4Cl \quad (1)$$

The initial impure, off-white powder was sublimed at atmospheric pressure to give a white compound with the appearance of cotton wool; the yield of **1** was low (16%). Compound **1** was sensitive in the atmosphere, as demonstrated by a colour change from white to pale blue on standing for several minutes in air.

The NMR spectra of **1** are consistent with the presence of a single fluoroethoxide environment. The ^1H NMR showed a quartet centred at 4.85 ppm due to the CH_2 group with a $^3J_{HF}$ coupling (8.9 Hz) consistent with literature data (cf. $^3J_{HF}$ 8 Hz).[20] An unresolved multiplet at 3.8 ppm, some 20 times smaller in intensity than the above quartet, could indicate traces of free ligand due to decomposition during sublimation. **1** does not appear to be fluxional based on the sharp peaks present. The ^{13}C NMR showed two quartets centred at 125.7 and 71.8 ppm due to the CF_3 and CH_2 groups, with ^1J (277 Hz) and ^2J (35 Hz), respectively, consistent with literature values. The ^{19}F NMR showed a triplet at −76.9 ppm due to coupling with the protons present on the CH_2 group. The ^{183}W NMR spectrum consisted of a single peak at −249.7 ppm (referenced to 1 mol dm^{-3} Na_2WO_4/D_2O) with a linewidth of 6 Hz. Dimeric $W(O)(OR)_4$ (R = Me, Et, *c*-C_6H_{11}) containing six-coordinate tungsten had shifts in the range 62.9–140.3 ppm, while monomeric analogues which include bulkier R groups (Bu^t, $C_6H_3Pr^i{}_2$-2,6) have a lower coordination number (five) and significantly more upfield chemical shifts (−386.9, −493.6 ppm, respectively).[19] The ^{183}W NMR chemical shift for **1** (−249.7 ppm) could place it in either category. However, ^1H NMR spectra recorded for **1** have shown no evidence of alkoxide bridges so the ^{183}W NMR chemical shift value recorded is likely to be that for a five-coordinate monomeric compound, $W(O)(OCH_2CF_3)_4$. The ^{183}W NMR also rules out the presence of a homoleptic, six-coordinate $W(OCH_2CF_3)_6$ as such species also exhibit very upfield ^{183}W chemical shift e.g. $W(OPh)_6$ −474.8 ppm.[12]

The EI mass spectrum of **1** showed no parent molecular ion. The most intense tungsten-containing fragment was centred at *m/z* 497 and corresponds to $[W(O)(OCH_2CF_3)_3]^+$. The tungsten-containing fragments then decrease in units of 80 *m/z*, consistent with the loss of $C_2H_2F_2O$, e.g. β-F transfer to tungsten and elimination of the aldehyde $HF_2CC(H)O$. The loss of 80 *m/z* units continues until the last recorded tungsten fragment at 257 *m/z*, which corresponds to $[W(O)F_3]^+$. A similar decomposition has been seen to occur in $Zr[OCMe_2(CF_3)]_4$, which showed loss of units of *m/z* 108 corresponding to the empirical formula $C_4H_6F_2O$, 3,3-difluorobutan-2-one.[21] There are no fragments containing two metals which might suggest that **1** is dimeric; weak fragments at 679 [<0.5%, $W(OCH_2CF_3)_5$], 599 [3%, $WF(OCH_2CF_3)_4$] and 519 [6%, $WF_2(OCH_2CF_3)_3$] could plausibly origninate from traces of $W(OCH_2CF_3)_6$ present, but in the absence of any evidence in the ^{183}W NMR that this is the case, it it likely they are artefacts of the EI methodology.

Collectively, the spectroscopic data for **1** suggest a monomeric $W(O)(OCH_2CF_3)_4$ rather than an alkoxide-bridged dimer. Since the fluoro-alkoxide ligand used is not bulky, the driving force for the formation of the monomer must be on electronic grounds. Thus, the electron-withdrawing effect of the fluorine atoms on the oxygen lowers its basicity to mitigate against bridging. The volatile nature of **1** in comparison with known non-fluorinated oxo-tetraalkoxides, indicated by its sublimation at atmospheric pressure, is also consistent with a monomeric structure.

CVD

APCVD experiments have been carried at 600 °C using **1** as precursor, without (R1) and with (R2) oxygen added. Both deposited films covered the full length of the glass substrate and were well adhered with no powdery surface layer evident. However, R1 was very different in visual appearance from the film deposited when pre-mixing oxygen in the reactive gas flow (R2). Film R1 was very thick (estimated from SEM analysis 303 ± 12 nm) and there was a grey surface layer to the film which could be carbon or just due to the thickness of the film. Approximately 18 months after deposition, the film appears yellow in transmission, although the grey surface layer remains. Despite the haziness and dark colour of the film, coloured interference fringes could be seen if the film was held up to the light. Film R2 displayed no coloured interference fringes consistent with a thinner film (estimated from SEM analysis 86 ± 9 nm) and appeared quite hazy. It was yellow in colour when removed from the reactor, indicating stoichiometric WO_3.

Both films gave X-ray diffraction patterns (Fig. 1) indicating their crystalline nature, in contrast to the only other APCVD films from a tungsten alkoxide [$W(OEt)_x$, $x = 5, 6$ at $T < 350$ °C] which were amorphous.[15] The broad hump occurring between 15 and 32° in the diffraction pattern of R2 is due to the glass substrate, consistent with the thin nature of the film.

Peak match software suggested the presence of both stoichiometric orthorhombic WO_3 (PDF 20–1324) and non-stoichiometric tetragonal $WO_{2.9}$ (PDF 18–1417) in film R1. The main line in the diffraction pattern corresponds to (001) from the standard WO_3 pattern at 23.102°, and the enhanced intensity of this peak could indicate some preferred orientation in this direction. However, the presence of some non-stoichiometric $WO_{2.9}$ cannot be ruled out as the enhanced intensity of peak seen in the pattern at *ca* 24°, to the right of the main peak, could correspond to a contribution from the (110) line in the $WO_{2.9}$ standard sample at 23.791°. The presence of some non-stoichiometric $WO_{2.9}$ in this film would not be unexpected as the film was deposited with no additional oxygen added to the reactive gas flow, and so could easily be oxygen deficient.

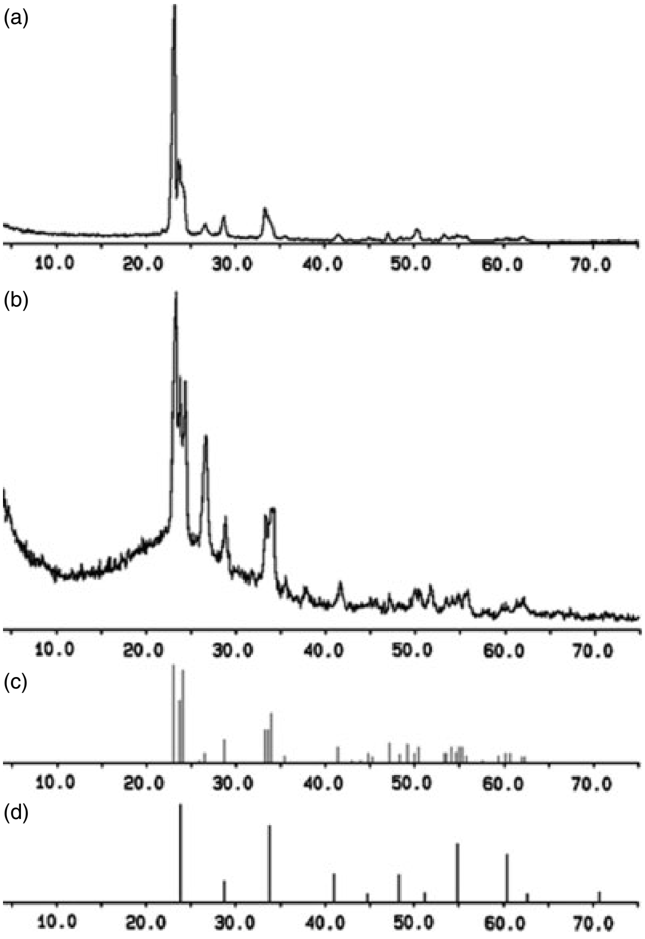

Figure 1. XRD of the films deposited from **1** (a) R1 and (b) R2. Literature data are also shown for (c) randomly oriented WO_3 (PDF 20–1324) and (d) randomly oriented $WO_{2.9}$ (PDF 18–1417).

Peak match software for R2, deposited in the presence of O_2, suggested the presence of only stoichiometric WO_3, consistent with its yellow colour. The three peaks seen at 23.102, 23.727 and 24.118° in the randomly orientated WO_3 standard are clearly seen in the diffraction pattern collected for R2, in contrast to the pattern collected for R1. Additionally, the peak at 26.609° is relatively intense when compared with other peaks, which could indicate a degree of preferred orientation in the (120) direction within this film.

SEM of the film R1 are shown in Fig. 2. In both pictures the glass substrate, the undercoat and the deposited film are easily seen and a film thickness of *ca* 303 nm estimated. The surface roughness of the film appears high and the film seems to have been deposited in an almost random fashion with crystallites appearing to have grown in all directions. The surface roughness and random nature of the crystallites could well account for the generally poor transmission of the film (see below). Figure 3 shows the film deposited with additional oxygen added to the reactive gas flow (R2). The surface roughness of the film again looks quite high; however, the film appears to have grown in a more uniform fashion than R1. A film thickness of 86 nm is consistent with the sampling of the underlying glass substrate in the X-ray diffraction analysis [Fig. 1(b)].

The transmission-reflectance spectra have been recorded on both films, where:

$$\text{Absorption} = 100\% - (\text{transmission} + \text{reflectance})$$

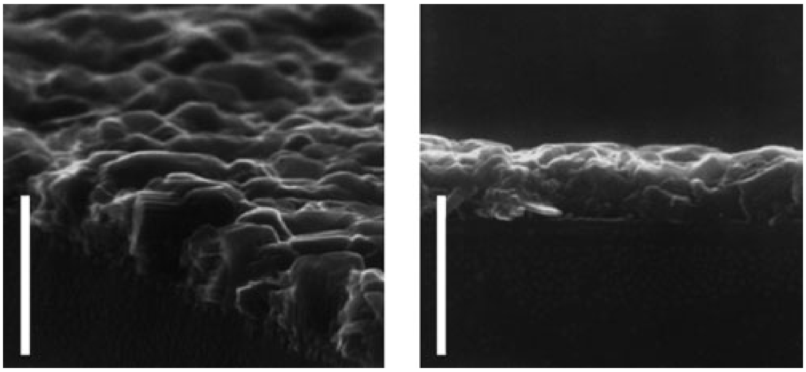

Figure 2. SEM of the film R1; bar = 600 nm.

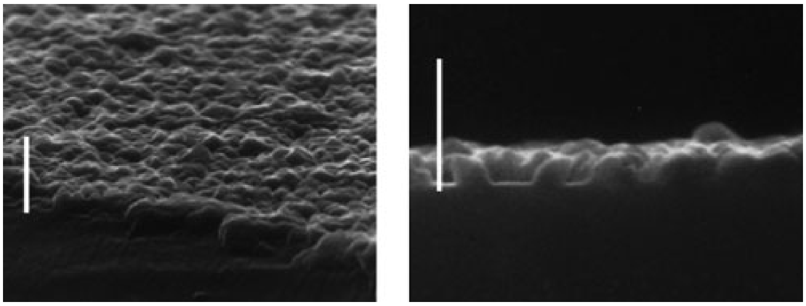

Figure 3. SEM of the film R2; bar = 300 nm.

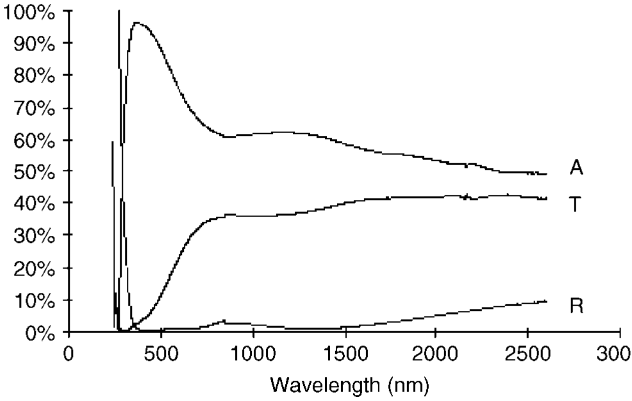

Figure 4. Transmission-reflectance-absorption spectra recorded for R1.

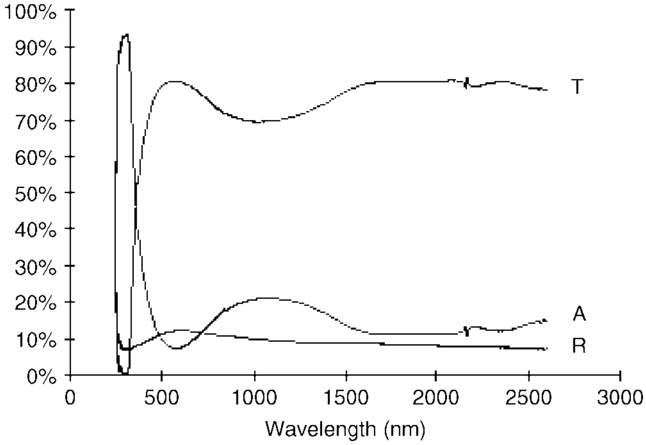

Figure 5. Transmission-reflectance-absorption spectra recorded for R2.

For solar control applications good transmission is required in the solar spectrum (350–780 nm) and either absorb or reflect at longer wavelengths (780–2000 nm).[22] For R1 (Fig. 4), the transmission of visible radiation is very poor with a maximum transmission in the visible of approximately 35% at 700 nm. While the thickness of the film could, in part, be responsible, SEM analysis also suggests that the poor transmission from this film could also be a result of surface roughness. The calculated absorption curve shows that the film is absorbing around 60% of the visible radiation at 700 nm. However, in the infrared portion of the solar spectrum a small hump in the absorption curve can be seen (800–1400 nm), which suggests that the film may have some selectivity to the solar spectrum.

Figure 5 displays the transmission/reflectance/absorption spectra for R2. This film was deposited while pre-mixing oxygen with the reactive gas flow and has been characterised by glancing angle X-ray diffraction as crystalline stoichiometric WO_3. The visible transmission of this film is quite high, over 80% at 550 nm, although the thinness of the film as determined by glancing angle X-ray diffraction and SEM analysis may be influencing the result. In the infrared region of the solar spectrum (780–2000 nm) the film transmission drops to a minimum of about 70% at 1000 nm, mirrored by an increase in the absorption curve over the same region. However, the film is displaying good selectivity to the solar spectrum in the right region for solar control applications despite the thinness of the film. This result contrasts with an earlier report which has observed superior optical properties for amorphous WO_3 films (usually deposited at $T < ca$ 300 °C to avoid crystallization) in comparison with polycrystalline films.[14]

Summary

In summary, we have synthesized a monomeric five-coordinate tungsten(VI) oxotetraalkoxide $W(O)(OCH_2CF_3)_4$ by mitigating the tendancy to form alkoxy-bridged dimers by use of a fluorinated alcohol as ligand. This monomeric compound is sufficiently volatile to allow APCVD experiments to be conducted from which crystalline tungsten oxide thin films (either non-stoichiometric, or stoichiometric if formed in conjunction with the use of oxygen gas) were deposited in a single step with no post-deposition annealing. This is only the second example of the APCVD of tungsten oxide from a tungsten alkoxide and the first to deposit crystalline films. The films deposited have been characterized by glancing angle X-ray diffraction, SEM and have shown some selectivity to the solar spectrum in the infrared region.

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