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Polycrystalline thin films of chromium doped tungsten disulphide (WS_2) have been deposited onto glass and steel substrates by Aerosol-Assisted Chemical Vapour Deposition (AACVD) using bis(diethyldithiocarbamato)disulfidothioxo tungsten(VI) (WS_3L_2) and tris(diethyldithiocarbamato) chromium(III) [$Cr(S_2CNET_2)_3$] (CrL_3) complexes as precursors in different molar ratios at 450 °C. The deposited films were characterised by p-XRD, SEM, EDX, and Raman spectroscopies. Chromium doping of up to 15 mol% was achieved in WS_2 thin films. The morphology of the doped films changed from lamellar for pure WS_2 to florets in heavily doped material.

Introduction

Layered transition metal dichalcogenides (TMDs) such as tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) have attracted much attention due to several applications in photoelectrochemical (PEC) and photovoltaic (PV) cells, dry electrodes for batteries, gas sensors, and catalytic activity.¹⁻⁸ They are also often used as a dry lubricant in mechanical systems.⁹⁻¹¹ The excellent lubricating behavior is because of the layered crystal structure, in which a central layer atom is formed from tungsten between two layers of sulfur atoms.^{12, 13} Weak non-covalent forces hold the layers together, so shearing of the crystal is easy in the lateral dimension. A number of deposition techniques have been used to grow tungsten disulfide (WS_2) films which include atomic layer deposition (ALD), ion beam deposition, sputtering deposition and pulsed laser deposition and chemical vapour deposition.¹⁴⁻¹⁷ We have used aerosol assisted chemical vapour deposition (AACVD)^{18, 19} for the growth of MoS_2 films onto glass substrates from single source precursors.²⁰ The stoichiometry of metal and ligand composition is easy to control using single source precursors. It is also easy to choose the decomposition temperature by informed precursor design and

minimizes the use of toxic gases.²¹ Yongfeng et al. have reported the deposition of tungsten disulfide films by atomic layer deposition (ALD) technique using $W(CO)_6$ and H_2S as precursors.²² Zhu et al. deposited WS_2 films on AISI 1045 steel by magnetron sputtering followed by ion sulfuration and was performed at low temperature to obtain a WS_2 composite film which showed a superior hardness, elastic modulus and tribological properties compared to other samples prepared by the same method.²³ Zafer et al. reported the deposition of a WS_2 film by an e-beam deposition method. They deposited the W film onto SiO_2 substrate then annealed and finally sulfurization of W film was performed to get the WS_2 film. They studied the etching behavior of the WS_2 film into a series of triangular shaped pits while heating in the air. The triangular pits increase with the increase in the number of layers of tungsten disulfide film.²⁴

It has been demonstrated in previous studies that the doping of metallic elements such as Cr, Cu, Ag, Ti into WS_2 films may improve the hardness, adhesion and wear resistance of the films.²⁵⁻²⁹ The doping of non-metallic elements such as C or N also helps to improve wear resistance properties, hardness, and adhesion of the film.³⁰⁻³³ Jhonattan et al. deposited titanium doped tungsten disulfide film onto AISI 304 stainless-steel substrates using the magnetron co-sputtering DC technique.³⁴ Petr et al. reported W-S-N coating deposited by d.c. reactive magnetron sputtering. They studied the effect of deposition conditions on chemical composition, morphology, tribological and mechanical properties. The hardness of the film deposited with a discharge pressure of 1.2 Pa increased with N content up to 7 GPa and the coatings deposited at lower pressure show hardness around 9 GPa.³⁵ Fredrik et al.

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deposited W-S-C-Cr and W-S-C-Ti coatings by magnetron sputtering they examined both systems and indicated significant amounts of oxides in the form of a layer just underneath the crystalline WS₂ top layer. These coatings contained 40–50 at% C but there was no carbon present in the tribofilms. They also observed that the WS₂ basal plane is surrounded by Fe particles which show the chemical bonding between iron/steel and WS₂.³⁶

Herein we report the deposition of Cr-doped tungsten disulfide (WS₂) thin films onto glass and steel substrates by AACVD from the bis(diethyldithiocarbamato)disulfido, thioxo, tungsten(VI) and tris(diethyldithiocarbamato)chromium (III) complexes as a single source precursor. Such films have not been deposited before by AACVD and this work is the first example of CVD of a series of heavily doped WS₂ films on glass and ferrous substrates.

Experimental

Chemicals

All reagents were purchased from Sigma-Aldrich and used without further purification, ammonium tetrathiotungstate [(NH₄)₂WS₄] (99.9%), sodium diethyldithiocarbamate trihydrate NaS₂CN(C₂H₅)₂·3H₂O (≥ 95%) and chromium trichloride hexahydrate (CrCl₃·6H₂O) (≥ 98%). Solvents were purchased from Sigma-Aldrich or Fisher acetone (99.0%) dichloromethane (≥ 99.8%), methanol (99.5%), Hydrochloric acid (HCl) (37%).

Instrumentation

Elemental analysis and thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under nitrogen from 30 °C to 600 °C of the precursors were performed by the University of Manchester, School of Chemistry micro-analytical laboratory. Powder X-ray diffraction (p-XRD) was performed using Bruker D8 Advance diffractometer. All the samples were scanned between 10° to 80° using CuKα radiation (wavelength 1.5406 Å) an increment of 0.02° and the dwell time was 3 seconds for every sample. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm⁻¹, resolution 4 cm⁻¹). Scanning Electron Microscopy (SEM) was carried out using a Philips XL-30 FEG microscope. Energy-dispersive X-ray (EDX) spectroscopy was performed with a Philips EDAX DX4 X-ray micro-analyser SEM.

XPS measurements were carried out using a custom built SpecsTM X-ray photoelectron spectrometer, equipped with a microfocused monochromated Al Kα X-ray source (hν=1486.6 eV) and 150 mm Phoibos hemispherical analyser. The base pressure in the analysis chamber was around 1 × 10⁻⁹ mbar during the measurements. WS₂ films were presented on glass and steel substrates. Spectra are aligned on the binding energy scale relative to the adventitious hydrocarbon C

1s signal at 284.8 eV.³⁷ Peak fitting was performed using the CASA XPS software using a linear background subtraction and a 70:30 Gaussian:Lorentzian mixed peak shape.

Synthesis of bis(diethyldithiocarbamato)disulfido, thioxo, tungsten(VI) [WS₃(S₂CNEt₂)₂] (WS₃L₂)

WS₃L₂ was synthesised as previously reported:³⁸ briefly, an aqueous solution (300 mL) of ammonium tetrathiotungstate (2.91 g, 8.3 mmol) and sodium diethyldithiocarbamate trihydrate (7.6 g, 33.8 mmol) was vigorously stirred with dropwise addition of 2 M HCl solution until a pH of 2 was obtained. Initially, yellow colored precipitates were produced which finally turns dark green with continued HCl addition. The mixture was stirred for 30 minutes. The precipitates were filtered by vacuum and washed with water (3 × 100 mL) and dried in a vacuum oven at room temperature for an hour. The crude product was dissolved in acetone (250 mL), filtered and the precipitates washed with acetone (3 × 40 mL) to give a dark green solution and an orange-brown powder. The green solution was stripped of its solvent by evaporation before drying in a vacuum oven to give WS₃L₂ as a dark green powder (2.53 g, 52.5 %). In addition, the orange-brown powder was dried in a high vacuum to give pure W₄S₄L₂ (0.99 g, 1.25 mmol, 20.9 %). The unit cell of WS₂ and chemical structures of the precursors are shown in Fig. 1. FT-IR (solid), ν_{max}/cm⁻¹: 1511 (C-N), 997 (C=S). Anal. calcd for C₁₀H₂₀N₂S₇W: C, 20.86; H, 3.50; N, 4.86; S, 38.86 %. Found: C, 21.00; H, 3.63; N, 4.78; S, 38.06.

Fig. 1 (a) chemical structures of the precursors used in this study: [WS₃(S₂CNEt₂)₂] (1), and [Cr(S₂CNEt₂)₃] (2). (b) structure of WS₂ with the hexagonal unit cell marked ($a = b = 3.1532 \text{ \AA}$, $c = 12.232 \text{ \AA}$ with $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$), after Schutte.³⁹ Gray atoms represent W and yellow atoms are S.

Synthesis of *tris*(diethyldithiocarbamato)chromium (III) [$\text{Cr}(\text{S}_2\text{CNET}_2)_3$] (CrL_3)

The complex was synthesized by the literature method.⁸ Briefly, chromium trichloride hexahydrate (4.0 g, 18 mmol) was dissolved in water (250 mL). Concentrated hydrochloric acid was added to adjust the pH to 5. The acidic green solution of chromium trichloride hexahydrate was added dropwise to the aqueous solution of monosodium salt of diethyl dithiocarbamate (12.0 g, 54 mmol). The colour of the reaction mixture was changed to blue. These blue precipitates were removed by filtration and dried at room temperature in a vacuum oven. Column chromatography was used to purify the chromium complex. The bright blue band at the solvent front was collected. The solvent (dichloromethane) was removed under vacuum to obtain the pure product (1.2 g, 13%); mp, 260–261 °C. FT-IR (solid) $\nu_{\text{max}}/\text{cm}^{-1}$: 2975 (w), 2930 (w), 1491 (m), 1460 (m), 1450 (m), 1433 (m), 1376 (m), 1356 (m), 1269 (m), 1208 (m), 1144 (m), 1098 (m), 1074 (m), 995 (m). Anal. Calc for $\text{C}_{15}\text{H}_{30}\text{N}_3\text{S}_6\text{Cr}$: C, 36.27; H, 6.09; N, 8.46%. Found: C, 37.10; H, 6.03; N, 8.30 %.

Aerosol-Assisted Chemical Vapor Deposition (AACVD)

The glass and X65 steel substrates were thoroughly washed with acetone to remove any contamination and used for the deposition of thin films. In a typical deposition, 0.2 g (0.35 mmol) of total precursors (WS_3L_2 and CrL_3) was dissolved in 25 ml of tetrahydrofuran (THF) in a two-necked 100 ml round-bottomed flask with a gas inlet. The solution was held over a piezoelectric humidifier and the aerosol thus created was carried by a stream of argon ($180\text{--}200\text{ cm}^3\text{ min}^{-1}$) into a quartz tube containing glass and steel substrates. The argon flow rate was controlled by a Platon flow gauge. The reactor tube was placed in a Carbolite furnace set at 450 °C. The deposition of metal chalcogenides onto glass and steel substrates was continued for 90–100 min in all experiments.

Results and discussion

Thermogravimetric Analysis

Thermogravimetric analyses (TGA) of the precursor CrL_3 shows single step decomposition while WS_3L_2 shows four step decomposition (Fig. 2), at 133.50, 197.08, 319.71 and 394.13 °C which correspond to weight

loss of 10.7%, 16.7%, 7.79% and 7.84% respectively with a total weight loss of 43.0%. The theoretically calculated weight loss for the formation of pure WS_2 is 57.0%. Marks et al. have proposed that the small difference between calculated and theoretical weight loss is due to residue in the TGA analysis of transition metal dithiocarbamate complexes.⁴⁰ The stepwise decomposition of dithiocarbamate complexes have been previously observed, with EtSH, EtNCS, CS_2 , and H_2S expected as the volatile by-products.^{40–43} TGA of WS_3L_2 shows rapid, initial decomposition which possibly forms $\text{WS}_2(\text{S}_2\text{CNET}_2)$ and the remaining dithiocarbamate slow down the further growth of WS_2 by terminating the reactive edge sites of WS_2 where growth occurs most rapidly.^{44, 45}

Deposition of Cr-doped WS_2 thin films by AACVD

The temperature chosen for deposition of materials by AACVD was 450 °C as both precursors are completely decomposed to the metal chalcogenide products by inspection of the TGA trace (Fig. 2). Deposition of tungsten disulfide (WS_2) and Cr-doped WS_2 films was performed by AACVD. The molar ratio of precursor

Fig. 2 TGA of $[\text{WS}_3(\text{S}_2\text{CNET}_2)_2]$ (WS_3L_2) and $[\text{Cr}(\text{S}_2\text{CNET}_2)_3]$ (CrL_3) complexes

WS_3L_2 and CrL_3 was changed to give 5%, 10% and 15% at% feeds. The deposited films were characterised by powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM) and Raman and energy dispersive X-ray (EDX) spectroscopies.

Raman Spectroscopy of thin films

Fig. 3 Raman spectrum of of Cr-doped WS_2 films deposited by AACVD onto glass substrates at 450 °C.

Fig. 4 Raman spectrum of of Cr-doped WS_2 films deposited by AACVD onto steel substrates at 450 °C.

Fig. 5 p-XRD patterns of thin films deposited onto glass substrates by AACVD from $[\text{WS}_3(\text{S}_2\text{CNET}_2)_2]$ at 450 °C by AACVD. The standard pattern is tungsten sulfide, WS_2 (ICDD No: 01-084-1398). p-XRD pattern (a) shows WS_2 without Cr-doping (b) 5 at% Cr, (c) 10 at% Cr, (d) 15 at% and (e) 20 at% Cr-doped into WS_2 .

Fig. 6 p-XRD pattern of thin films deposited onto steel substrate from $[\text{WS}_3(\text{S}_2\text{CNET}_2)_2]$ at 450 °C by AACVD. Black and red standard patterns show tungsten sulfide, WS_2 (ICDD No: 01-084-1398) and hexagonal iron sulfide, FeS (ICDD No: 01-089-6272) respectively. p-XRD pattern (a) shows deposition of WS_2 without Cr-doping, (b) 5 at% Cr, (c) 10 at% Cr, (d) 15 at% and (e) 20 at% Cr-doped into WS_2 . The star (*) and hash (#) symbols represent the reflections from FeS and steel substrate respectively.

Raman spectroscopy was used to study $\text{W}_{1-x}\text{Cr}_x\text{S}_2$ films deposited onto glass and steel substrates. The pure WS_2 film had two main bands observed at 418 cm^{-1} and 352 cm^{-1} corresponding to the A_{1g} and E_{2g}^1 modes along with a small shift at 170 cm^{-1} . The Raman spectra for the Cr-doped WS_2 films deposited onto glass are shown in Fig. 3. There was a significant change in Raman spectra observed with the increase of chromium in the films. The intensity of the band observed at 170 cm^{-1} increases with the increase of chromium. There was another shift appeared at 207 cm^{-1} which correspond to first-order longitudinal acoustic (LA) mode, was not present in pure WS_2 film. Upon increasing the amount of chromium in the films deposited on steel substrate, the intensity of the LA(M) longitudinal acoustic mode at 207 cm^{-1} was enhanced.⁴⁶ The Raman spectra for the Cr-doped WS_2

films deposited onto steel are shown in the Fig. 4. The Raman spectra for films deposited on steel substrate are same as films deposited on the glass substrate.

Powder X-ray Diffraction (p-XRD)

The p-XRD pattern of WS_2 films deposited onto glass substrates showed two main reflections at $2\theta = 14.2^\circ$ for (002) plane and $2\theta = 33.5^\circ$ which is assigned to the (101) (Fig. 5). Hence the tungsten disulfide thin films deposited onto the glass substrate by AACVD have preferred orientation in the (002) plane. The p-XRD

patterns of $W_{1-x}Cr_xS_2$ deposited onto glass substrate for the ratios 5, 10, 15 and 20 at% Cr show the reflection at $2\theta = 14.24^\circ$, 14.34° , 14.36° and 14.36° respectively which can be assigned to the (002) and $2\theta = 33.5^\circ$ which is assigned to the (101) plane become more intense with the increase in molar ratio of CrL_3 from 5 to 15 mole %. However, the p-XRD pattern of the thin film with 20 at% Cr shows comparatively weak reflection at $2\theta = 33.5^\circ$ for (101) which indicates the decrease in crystallinity with the increase in dopant. The graphical representations of the change in calculated d-spacing versus the amount of chromium found experimentally in the films show an almost linear dependence (Fig. 7). This suggests that the doping of chromium into the WS_2 structure contracted the structure in the z-direction, pulling the layers of WS_2 together. PXRD patterns of films grown on steel (Fig. 6) are markedly different in appearance compared to those grown on glass. We see the diffraction peaks from WS_2 and steel, but also the pattern of a troilite subphase (FeS). Marks et al have also observed this phenomenon when growing MoS_2 on steel, and it was attributed to an iron sulphide interphase between the steel substrate and the thin film,⁴⁰ which leads to a seamless crystalline interface between thin film and substrate. This can also influence the morphology of the films produced (vide infra).

SEM and Energy dispersive X-ray (EDX) Spectroscopy

Energy dispersive X-ray (EDX) spectroscopy of the $W_{1-x}Cr_xS_2$ thin films deposited by AACVD at $450^\circ C$ using mixtures of WS_3L_2 and CrL_3 showed a linear relationship between the mol% of chromium in the feed solution and the mol% of chromium found in the alloyed thin films (Fig. 8). The target composition and elemental composition found by EDX spectroscopy is given in the table 1. W and S were found in films generated from the decomposition of WS_3L_2 alone, with ca. 33.38 at. % W found in the film, close to the theoretical value of 33 at. % W in WS_2 . Other peaks observed include Si and O from glass substrates and Fe on

steel substrates.

Table 1 Results summary for the composition of $W_{1-x}Cr_xS_2$ thin films as-measured by EDX spectroscopy.

Target Composition	Precursors Ratio (mmole)	EDX results (atomic %)	Alloy film Stoichiometry
WS_2	W: 0.350 Cr: 0.000	W: 33 S: 66	$W_{1.001}S_{1.999}$

Fig. 8 Plot of mol% Cr found by EDX spectroscopy in $W_{1-x}Cr_xS_2$ thin films deposited by AACVD at $450^\circ C$ as a function of varying Mol% of Cr in the AACVD feed.

$W_{0.95}Cr_{0.05}S_2$	W: 0.333 Cr: 0.017	W: 31 S: 67 Cr: 0.6	$W_{0.916}Cr_{0.049}S_{2.035}$
$W_{0.90}Cr_{0.10}S_2$	W: 0.315 Cr: 0.035	W: 33 S: 64 Cr: 3.2	$W_{0.988}Cr_{0.097}S_{1.915}$
$W_{0.85}Cr_{0.15}S_2$	W: 0.298 Cr: 0.052	W: 29 S: 67 Cr: 4.6	$W_{0.861}Cr_{0.139}S_2$

Fig. 7 Changes in d-spacing for the (002) plane in WS_2 vs chromium dopant found experimentally using EDX spectroscopy for the deposition of $W_{1-x}Cr_xS_2$ thin films onto glass substrates by AACVD at $450^\circ C$.

The morphologies of WS_2 and Cr-doped WS_2 thin films were imaged using secondary electron scanning electron microscopy (SE SEM). SE SEM images of the films deposited onto glass and steel substrate at $450^\circ C$ are shown in Fig. 9 and Fig. 10 respectively. The SE SEM images of the pure WS_2 film deposited on glass substrate showed floret morphology while the film deposited with 5% Cr-doped showed orbicular shaped crystallites. The SEM images of WS_2 thin films with 10 at% Cr-doped show triangular shape crystallites. Whereas the crystallites of the WS_2 thin film with 15 at% Cr-doping show floret morphology. The crystallites of pure WS_2 deposited onto steel substrate at $450^\circ C$ show lamellar morphology. The SEM images of WS_2 films deposited with 5 at%, 10 at% and 15 at% Cr-doping show predominant growth of dense sheet-like crystallites. It is suspected that the major differences in morphology between films grown on

Fig. 9 SEM images (10 kV) of Cr-doped WS_2 thin films (a) shows 0 at% Cr-doped (b) 5 at% Cr (c) 10 at% Cr and (d) shows 15 at% Cr-doped into WS_2 films deposited onto glass substrate at 450 °C by AACVD.

Fig. 10 SEM images (10 kV) of Cr-doped WS_2 thin films (a) shows 0% Cr-doped (b) 5 at% Cr (c) 10 at% Cr and (d) shows 15 at% Cr-doped into WS_2 films deposited onto steel substrate at 450 °C by AACVD.

Fig. 11 EDX spectrum maps (20 kV) of W $L\alpha$, Cr $K\alpha$ and S $K\alpha$ emission in (a) 15 at% Cr-doped WS_2 thin films deposited onto glass substrate and (b) onto steel substrate at 450 °C respectively.

steel and films grown on glass are due to the substrate influencing the growth of the crystalline inorganic thin film and this is presumably caused by growth of the WS_2 phase over the FeS phase, as-observed in pXRD (vide supra).

EDX mapping of 15 at% chromium doped $\text{W}_{1-x}\text{Cr}_x\text{S}_2$ films deposited onto glass and steel substrate by AACVD at 450 °C (Fig. 11) demonstrated that in both cases W, Cr and S are distributed uniformly throughout the film.

X-Ray Photoelectron Spectroscopy (XPS)

The survey spectra (Fig. 12) show the presence of W and S peaks for both films. Both samples show evidence of C and O contamination, most likely arising from adsorbed hydrocarbon contamination and adsorbed water/hydroxyl species. The glass mounted sample shows a significant

amount of sodium contamination. The coated steel sample shows evidence of Cu. Neither sample has Cr peaks in the topmost 10 nm of the surface, suggesting tungsten oxide is formed at the surface, burying the Cr below.

Detailed scans of the W 4d and S 2p are shown in Fig.13 & 14. The Cu 2p spectrum indicates two Cu species with

Fig. 12 The XPS surveys spectra of Cr-doped WS₂ thin films deposited onto glass and steel substrate at 450 °C by AACVD.

Cu 2p_{3/2} peaks at binding energies of 932.6 and 935.0 eV. The strong and complex satellite centred around a binding energy

Fig. 13 Deconvoluted W 4d spectrum of thin films deposited onto glass and steel substrate by AACVD

of 942.6 eV indicates that these Cu species are in the Cu(II) oxidation state. The Cu 2p_{3/2} peak at the higher binding energy (B.E.) is consistent with Cu(II) hydroxide species⁴⁷, and is consistent with the presence of the O 1s peak observed in the survey spectrum. The lower energy peak has a binding energy, which could be due to CuO or CuS species.

Fig.14 Deconvoluted S 2p spectrum of thin films deposited onto glass and steel substrate by AACVD

The W 4d spectra show (Fig. 13) two sets of spin orbit doublets for the two films. The binding energies of the W 4d_{5/2} of 243.7 eV and 247.4 eV are consistent with WS₂ and WO₃ species respectively [refs], suggesting significant oxidation of the films in the topmost surface region and supporting the suggestion that the Cr remains buried in the film.

S 2p spectra (Fig. 14) can be fitted with three sets of spin orbit doublets in agreement with earlier work on WS₂ and MoS₂. These are consistent with the presence of sulfate (S 2p_{3/2} B.E. = 168.3 eV)⁴⁸, and terminal S²⁻ and/or S₂²⁻ (S 2p_{3/2} B.E. = 162.0 eV) and bridging S₂²⁻ and/or apical S²⁻ (S 2p_{3/2} B.E.= 163.4 eV) in the WS₂^{49,50}.

Conclusions

WS₂ and Cr-doped W_{1-x}Cr_xS₂ thin films were deposited onto glass and steel substrates by AACVD using bis(diethyldithiocarbamato)disulfido, thioxo, tungsten(VI) [WS₃(S₂CNEt₂)₂] and tris(diethyldithiocarbamato)chromium (III) [Cr(S₂CNEt₂)₃] complexes as precursors. Scanning electron microscopy (SEM) indicated that the morphology and the microstructure of the deposited thin films significantly changes with the addition of chromium as a dopant. The EDX spectroscopy confirmed the presence and composition of the dopant.

The powder x-ray diffraction patterns confirmed the films grown onto the glass substrate were highly crystalline and

gave monophasic hexagonal WS₂ whereas the films deposited onto the steel substrate produced a mixture of hexagonal tungsten sulfide (WS₂) and hexagonal Iron sulfide which is due to strong adhesion or a chemical bonding between iron/steel and WS₂. The Raman spectroscopy also confirmed the presence of the chromium in W_{1-x}Cr_xS₂ films.

In summary, this method affords excellent control over dopant concentration by using dual pre-cursors in the feed. The work reported herein is a very simple and inexpensive route for the deposition of Cr-doped tungsten disulfide thin films which has the potential for scalability.

Conflicts of interest

There are no conflicts to declare.

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