Large-Scale Production of Large-Size Atomically Thin Semiconducting Molybdenum Dichalcogenide Sheets in Water and Its Application for Supercapacitor

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To progress from laboratory research to commercial applications, it is necessary to develop an effective method to prepare large quantities and high-quality of the large-size atomically thin molybdenum dichalcogenides (MoS2). Aqueous-phase processes provide a viable method for producing thin MoS2 sheets using organolithium-assisted exfoliation; unfortunately, this method is hindered by changing pristine semiconducting 2H phase to distorted metallic 1T phase. Recovery of the intrinsic 2H phase typically involves heating of the 1T MoS2 sheets on solid substrates at high temperature. This has restricted and hindered the utilization of 2H phase MoS2 sheets suspensions. Here, we demonstrate that the synergistic effect of the rigid planar structure and charged nature of organic salt such as imidazole (ImH) can be successfully used to produce atomically thin 2H-MoS2 sheets suspension in water. Moreover, lateral size and area of the exfoliated sheet can be up to 50 μm and 1000 μm², respectively. According to the XPS measurements, nearly 100% of the 2H-MoS2 sheets was successfully prepared. A composite paper supercapacitor using the exfoliated 2H-MoS2 and carbon nanotubes delivered a superior volumetric capacitance of ~410 F/cm³. Therefore, the organic salts-assisted liquid-phase exfoliation has great potential for large-scale production of 2H-MoS2 suspensions for supercapacitor application.

Layered two-dimensional (2D) materials have drawn tremendous attention after Geim and Novosolov demonstrated that adhesive tape could be utilized to mechanically exfoliate graphite into one-atom-thick layers that can be used in atomically thin electronic devices1. Graphene is the most well-known 2D nano-material owing to its superior physical, chemical and mechanical properties, though it has a zero bandgap which restricts its application in energy storage and low-power electronics2. Structurally similar to graphene, the lamellar structure of transition metal dichalcogenides (TMDs) includes planes where the atoms of the transition metal and sulfur are covalently bonded and the nearby planes stack upon each other via a weak coupling interaction3. Due to their promising electronic and chemical properties, TMDs have attracted considerable attention in research as 2D layered materials. Recently, there has been a focus on atomically thin TMD preparations, most notably molybdenum dichalcogenides (MoS2), because they are expected to show superior capacitive properties, which allows for potential applications in electronic devices4,5. However, the lack of an effective exfoliation method for the large-scale production of high-concentration atomically thin 2H-MoS2 sheets has been one of the obstacles to studying their chemical and physical properties and to using them for novel and practical applications.

Owing to high production prices and limited scalability, mechanical exfoliation limits the use of 2H-MoS2 materials to fundamental research and special applications6. Similarly, the chemical vapor deposition method may be an alternative route for the scalable production of 2H-MoS2 materials. However, it is not only hard to precisely control the stoichiometry ratio, but this method also involves high prices and rather low yields5. In contrast,
the liquid phase exfoliation method is characterized by high scalability and relatively low production costs, and it does not require transfer techniques, thus making it suitable for producing 2H-MoS2 materials in bulk quantities. Recently, liquid-phase routes have been demonstrated by sonication MoS2 powder in properly chosen solvents such as a mixture of ethanol and water or dimethylformamide and N-methylpyrrolidone, which can directly exfoliate MoS2 powder and disperse the exfoliated MoS2 sheets owing to their compatible surface energies. Coleman et al. have demonstrated that liquid-phase exfoliation of MoS2 powder in N-methylpyrrolidone with ultrasonication is a practical route to achieving the preparation of MoS2 sheets. However, this method yields multi-layered sheets of MoS2, and thin sheets are very rarely observed. Recently, large amounts of multi-layered MoS2 suspension were successfully prepared after more than 100 hours of sonication or several hours of grinding. This, however, provided exfoliated MoS2 nanosheets less than 100 nm in size and affected its unique and original properties. Moreover, N-methylpyrrolidone is expensive and requires special attention while handling. Unfortunately, one of the most ideal dispersion media, water, has a non-compatible surface energy that is too high to have an effect on its own for MoS2 exfoliation. The best-known group of exfoliants involves electron donors, for example, organolithium compounds. Bulk MoS2 can be exfoliated with lithium (Li) under rigorous conditions for more than 72 hours to obtain reduced LiMoS2 with an expanded structure; this can be further exfoliated by a sonication-assisted process. However, Li-assisted exfoliation leads to a structural change in MoS2 from the thermodynamically stable semiconducting 2H phase to the metastable metallic 1T phase. Moreover, 1T-MoS2 turns into nanometer-sized flakes after exfoliation along with the occurrence of metal nanoparticle formation and Li,S agglomeration. This has dramatically hindered the development of atomically thin MoS2 sheets in most applications that require a pristine structure and large sheets with high concentrations. Recently, an electrochemical method was successfully established to produce MoS2 sheets. Nevertheless, mass production through this process is limited because Mo5+ and Mo6+ are generated. Exploration has recently been further extended to produce exfoliated MoS2 sheets by the use of exfoliants in water or polymers in tetrahydrofuran. Polymer-assisted exfoliation methods in an aqueous solution with high-power probe sonication were reported, but the final concentration of less than 0.5 mg/mL and resulting small sheets were still far from the demands of practical applications requiring large quantities. Inspired by the liquid phase exfoliation of graphene, a method with similar exfoliation principles may be an approach to boost the production of atomically thin 2H-MoS2 sheets.

This study demonstrates that atomically thin MoS2 sheets in the 2H phase can be prepared by organic salts such as imidazole (ImH) or pyridiniumtribromide (PyBr3). The exfoliated 2H-MoS2 sheet dimensions can be as large as to 1000 μm2. In addition, nearly 100% of the composition was of the thermodynamically stable 2H phase structure. These exfoliants are cheap and commercially available, and the method can be performed under ambient conditions. Moreover, the 2H-MoS2 suspension allows for the preparation of high electrical conductive composites for energy storage applications.

Results and Discussion

Figure S1a shows a photograph of the experimental setup for the ultrasonication exfoliation of 2H-MoS2 powder (Fig. S1b). A suspension of the exfoliated 2H-MoS2 sheets was prepared from commercial 2H-MoS2 powder via an ImH or PyBr3 exfoliation process followed by ultrasonication. Figure 1a shows that liter-scale 2H-MoS2 suspensions can be prepared through Im+-assisted exfoliation. These highly-dispersed suspensions of 2H-MoS2 sheets can stand for more than a year, and the suspension remained dark green in color, as shown in Fig. 1b. To unveil the exfoliation mechanism of the layered 2H-MoS2, we performed a photoluminescence (PL) experiment. First, the Im− solution showed PL emission at 388 nm (Fig. 1c; black solid line) under irradiation at 270 nm. Then, the MoS2 powder was added to the Im− solution. After shaking the mixture, the 2H-MoS2/Im− solution was left on the bench for 30 minutes (Fig. 1c; red dotted line). The PL intensity of the 2H-MoS2/Im− solution decreased, indicating that Im− molecules, nearly one atom in thickness, adsorbed to the layered 2H-MoS2. Finally, the MoS2 powder was exfoliated by ultrasonication to generate large quantities of the atomically thin 2H-MoS2 sheets in suspension. Interestingly, the PL intensity of 2H-MoS2/Im− was fully quenched (Fig. 1c; blue line), which demonstrates that nearly all of the Im− molecules adsorbed to the exfoliated 2H-MoS2 surfaces. The zeta
potential of the suspension of the exfoliated 2H-MoS₂ sheets was −22.4 mV (Fig. 1d), which demonstrated its superior aqueous stability with the assistance of Im⁻ molecules. The negative surface charges provide evidence of electrostatic repulsion forces between each of the exfoliated 2H-MoS₂ sheets, resulting in a stable aqueous suspension. In the X-ray diffraction (XRD) patterns, the intensity of the (002) reflection of the exfoliated 2H-MoS₂ is significantly weaker than the bulk MoS₂ powder, which means that a large amount of the exfoliated 2H-MoS₂ thin sheets prepared were highly exfoliated (Fig. S2)²¹,²⁷-²⁹. Just as reported in the literature, the planar structure of the MoS₂ flakes was hydrophobic³⁰,³¹. Meanwhile, the ring of the Im⁻ molecules also possesses a hydrophobic property³². Therefore, the mechanism for the Im⁻-assisted exfoliation of layered 2H-MoS₂ materials is attributed to hydrophobic-hydrophobic interaction. The exfoliated 2H-MoS₂ flakes are stabilized due to the electrostatic repulsive forces generated by the planar charged organic molecules.

Figures 2a,c show transmission electron microscopy (TEM) images of a thin 2H-MoS₂ sheet. Figure S3 shows large flakes of the exfoliated 2H-MoS₂. The exfoliated 2H-MoS₂ sheets are characterized through the edge of the sheets which shows that large-area 2H-MoS₂ flakes are mostly all monolayer via the high resolution TEM (HRTEM) images as shown in the inset of Fig. S3. The exfoliated 2H-MoS₂ sheets had a maximum lateral size of over 50 μm, which is nearly two orders of magnitude larger than using exfoliant-assisted methods¹⁶,¹⁷ or the solvent exfoliated method¹¹,¹². Intriguingly, the production of thin 2H-MoS₂ sheets with an unprecedented sheet size of up to 1000 μm² was achievable (Fig. 2a). The HRTEM images in Fig. 2b,d show that the lattice structure of the edge of the exfoliated 2H-MoS₂ sheet was not damaged during the ultrasonic exfoliation process. In addition, the diffraction patterns of the insets in Fig. 2b,d show lattice spacing of 0.2764 and 0.2797 nm, respectively; both match the (100) plane of typical 2H-MoS₂ sheets³³. On the basis of the above results, the synergistic effect of the charged nature and the planar structure of the Im⁻ and Py⁺ enabled both the exfoliation of 2H-MoS₂ and
The exfoliant of Im−-assisted 2H-MoS2 sheets exhibited two Raman characteristic peaks at around 387 and 409 cm−1. Therefore, we studied the phase exfoliation of single-layer 2H-MoS2 sheets, demonstrating the successful preparation of single-layer 2H-MoS2 sheets. The peak FWHM values and the integrated intensity ratios were similar to those reported after mechanical exfoliation of 2H-MoS2 sheets. According to previous studies, the thermodynamically stable 2H phase of MoS2 is the trigonal prismatic phase where every molybdenum atom is coordinated by six neighboring sulfur atoms. However, the MoS2 structure could form a metastable phase where the coordination of Mo atoms becomes octahedral (1T-MoS2) upon organolithium-assisted exfoliation. Therefore, we studied the phase exfoliation of single-layer 2H-MoS2 sheets, demonstrating the successful preparation of single-layer 2H-MoS2 sheets.

The average thickness of 743 measured sheets from the substrate to the sheet was found to be ~0.9 nm, as shown in Fig. S4a. This statistical thickness is in good agreement with the reported 2H-MoS2 monolayer thickness of 0.9 ~ 1.2 nm. Figure S4b indicates that the flake size of most of the exfoliated 2H-MoS2 sheets ranged from a few square micrometers to one thousand square micrometers. Based on the results of the PL, zeta potential, XRD, TEM and AFM measurements, a proposed schematic illustration of 2H-MoS2 exfoliation is shown in Fig. S5.

Further structural characterization of the already-prepared concentration of the exfoliated 2H-MoS2 sheets (1 mL) was diluted with about 400 mL of water and used to evaluate the absorption spectrum of the 2H-MoS2 sample, as shown in Fig. 3a. The peaks centered at 400, 451, 612 and 673 nm were the representative absorption bands of the exfoliated 2H-MoS2 sheets. The peaks at 400 and 451 nm could be ascribed to the direct transition from the valence band to the conduction band. The excitonic peaks at 612 and 673 nm, responsible for the K point of the Brillouin zone, were also clearly observed. These two characteristic peaks demonstrate the existence of high-quality atomically thin 2H-MoS2 sheets. By utilizing Beer’s law and the extinction coefficient centered at 672 nm, we can estimate the concentration of the exfoliated MoS2 sheets was ~2 mg/mL in our supernatant. However, the extinction coefficient may change with the solvent, so the value of 2 mg/mL should be considered a rough estimate. To obtain a more accurate concentration, we filtered the already-prepared 2H-MoS2 suspension. Then, it was dried at 200 °C for 2 h to remove the physiosorbed exfoliant of Im−. The concentration of the exfoliated 2H-MoS2 sheets was ~4 mg/mL. The Im−-assisted exfoliated 2H-MoS2 sheets exhibited two Raman characteristic peaks at around 387 and 409 cm−1 with full-width-half-maximum (FWHM) values of 3.6 and 6.8 cm−1, corresponding to the E1g and A1g modes, respectively, as shown in Fig. 3b. Note that the Raman frequency difference between E1g and A1g is consistent with that of chemically exfoliated single-layer MoS2. The ratio (E1g/A1g) of the integrated intensity of the Im−-assisted exfoliated 2H-MoS2 sheets was 0.59. Moreover, Fig. S6 shows that the Py−-assisted exfoliated 2H-MoS2 also showed two Raman characteristic peaks with FWHM values of 6.2 and 4.4 cm−1, corresponding to A1g and E1g modes, respectively. The ratio (E1g/A1g) of the integrated intensity of the Py−-assisted exfoliated MoS2 sheets was 0.47. The peak FWHM values and the integrated intensity ratios were similar to those reported after mechanical exfoliation of single-layer 2H-MoS2 sheets, demonstrating the successful preparation of single-layer 2H-MoS2 sheets.

We employed thermogravimetric analysis (TGA) to explore the thermal stability of the exfoliated 2H-MoS2 sheets. Figure 4a shows the TGA profile of the Im−-assisted exfoliated 2H-MoS2 sheets. The TGA curve of the exfoliated 2H-MoS2 sheets shows one weight loss stage around 160 °C. The weight loss region with about 12% loss of the original weight which occurred around 110–190 °C was due to the decomposition of the adsorbed imidazolium molecules. After 200 °C, no further weight loss occurred. The differential TGA curve showed the Im−-assisted exfoliated MoS2 sheets had one major peak at 167 °C, which is consistent with the decomposition temperature of pure imidazole (Fig. S7). The TGA result demonstrates that there was no detectable oxidization in the exfoliated 2H-MoS2 sheets. This confirmed that the production process did not result in the formation of S–O derivatives on the exfoliated 2H-MoS2 sheets. According to previous studies, the thermodynamically stable 2H phase of MoS2 is the trigonal prismatic phase where every molybdenum atom is coordinated by six neighboring sulfur atoms. However, the MoS2 structure could form a metastable phase where the coordination of Mo atoms becomes octahedral (1T-MoS2) upon organolithium-assisted exfoliation. Therefore, we studied the phase composition of the exfoliated MoS2 sheets with X-ray photoelectron spectroscopy (XPS). The Mo 3d of the XPS spectrum is shown in Fig. 4b. The Mo 3d spectrum shows peaks centered at 229.1 and 232.3 eV, corresponding to the Mo4+ 3d3/2 and Mo4+ 3d5/2 components of 2H-MoS2, respectively. In addition, the spectrum shows two unobservable peaks at 228.3 and 231.4 eV, corresponding to the Mo4+ 3d5/2 and Mo4+ 3d3/2 components of
1T-MoS2, respectively. Similarly, in the S 2p core level spectrum, Fig. 4c shows that two peaks were observed at 162.0 and 163.3 eV, corresponding to the S 2p3/2 and S 2p1/2 components of 2H-MoS2, respectively. Additionally, the spectrum shows two weak peaks at 161.1 and 162.4 eV, corresponding to the S 2p3/2 and S 2p1/2 components of 1T-MoS2, respectively. Moreover, no signals were detected in the range of 166 to 170 eV, indicating that sulfur elements also persisted in non-oxidized form. These results are in agreement with reported studies on MoS2 single crystals, showing that the exfoliated MoS2 sheets are predominantly in the 2H phase44. The exfoliated MoS2 sheets contain over 95% of the 2H phase after exfoliant-assisted exfoliation. The remaining less than 5% of the non-2H phase was nearly fully converted to the 2H phase after annealing at 200 °C (Fig. S8). This exfoliation method demonstrates that exfoliated 2H-MoS2 sheets preserve their thermodynamically stable semiconducting properties. This is in contrast to Li exfoliated MoS2 in which the semiconducting properties of the sheets are perturbed due to their phase structural changes from the 2H to 1T phase. In addition, it is worth mentioning that the peak at 236 eV did not show a significant signal, attributed to Mo6+ 3d5/2, indicating that the oxidized form of Mo6+ is difficult to detect. This result is superior to that of electrochemically exfoliated MoS2 sheets that oxidize the pristine charge of Mo4+ to Mo5+ and Mo6+21.

The versatility of the exfoliation method allowed us to fabricate composite papers by directly adding dispersed carbon nanotubes (CNTs) to the 2H-MoS2 suspension. Free-standing 2H-MoS2/CNTs papers were peeled off from the filtered membrane, as shown in Fig. 5a. Scanning electron micrographs (SEM) of the 2H-MoS2/CNTs paper at low (Fig. 5b) and high (Fig. 5c) magnification clearly showed that the 2H-MoS2 sheets were wrapped in CNTs. To clearly understand the distribution of the 2H-MoS2 sheets in the 2H-MoS2/CNTs paper, Fig. 5d shows the mapping image from Raman spectroscopy of the composite paper by extracting the frequency of the characteristic peak of E2g. The information in the Raman mapping spectrum shows similar Raman intensity of E2g, which indicates a uniform dispersion of the 2H-MoS2 in the composite paper. To compare the electrical conductivity of the composite papers, we compared a pure MoS2 crystal with the composite papers. The addition of CNTs increased the electrical conductivity, σ, from ~10−6 S/cm for the 2H-MoS2 only film to ~6 × 10−6 S/cm for the 2H-MoS2/CNTs composite paper. The electrical conductivity of the 2H-MoS2/CNTs hybrid paper compares superiorly with some of the other 2D materials’ electrodes for supercapacitors38. The capacitance of the 2H-MoS2/CNTs hybrid paper was obtained using cyclic voltammery (CV). The resulting CVs for potential ranged from 0 to 0.8 V versus NHE, as shown in Fig. S9a. The galvanostatic charging/discharging curves for the 2H-MoS2/CNTs paper were recorded at different current densities as depicted in Fig. S9b. Figure S9c shows the volumetric capacitances at various current densities of supercapacitors based on 2H-MoS2/CNT composite papers. The volumetric capacitance of the 2H-MoS2/CNT hybridized supercapacitor was ~410 F/cm3 at a current density of 2 A/cm2. This value is superior to that of a film-based supercapacitor consisting of ZnO/graphene film (0.36 F/cm3)39 MoS2/CNTs (0.7 F/cm3)40, MoS2/reduced graphene oxide/CNTs (5.2 F/cm3)40, and reduced graphene oxide/MoS2 (30 F/cm3)41. Moreover, it is higher than the value of the best micro-supercapacitor based on carbide-derived carbon film42. The improved performance of the 2H-MoS2/CNTs paper electrodes could be possibly attributed to three reasons. First, the Mo atoms of the exfoliated 2H-MoS2 sheets possess many oxidation states from +2 to +6, promising a representative pseudo-capacitance behavior with high specific capacitance for 2H-MoS2/CNTs hybrid paper43. Second, the interconnected high conducting CNTs network provides electric double-layer capacitance and also serves as a conductive material for charge transport and transfer42,43. Finally, the dispersed CNTs of the 2H-MoS2/CNTs composite paper serve as spacers to mitigate restacking between the exfoliated 2H-MoS2 sheets44,45. The cyclic stability of the 2H-MoS2/CNTs hybrid paper electrodes in a 0.5 M K2SO4 electrolyte was tested over 2,300 cycles (Fig. S9d) and maintained a capacitance in excess of 95% after 2,300 cycles.

**Conclusion**

We have demonstrated a universal route to the large-scale production of a high-concentration of large, atomically thin 2H-MoS2 sheets that can be made by adding an organic salt. The lateral size and area of the exfoliated 2H-MoS2 can reach 50 μm and 1000 μm2, respectively, which is nearly two orders of magnitude greater than that of mechanically, Li-assisted chemically exfoliated MoS2 sheets. The spectral analysis, which incorporated TEM, AFM, XRD, UV-vis, PL, Raman, XPS and TGA measurements, confirmed that the exfoliated MoS2 sheets
predominately exhibited the 2H phase. We anticipate that fast progress in areas like hybrid paper processing and electronic device fabrication involving large-scale production of high-concentration, large, atomically thin 2H-MoS₂ sheets will develop from these results.

Methods

Materials. Molybdenum (IV) sulfide (99% metals basis; ~325 mesh powder) were purchased from Alfa Aesar. Imidazole (99%, ACROS) and pyridinium tribromide (TCI) were used without further purification as the exfoliant. Considering large-scale production of the 2H-MoS₂ suspension and the high cost, ImH is preferred. Single-walled carbon nanotubes powder (CG300-L16) were produced by SouthWest NanoTechnologies Inc. Multi-walled carbon nanotubes powder and Triton X-100 utilized in this study were produced by Golden Innovation Business Co. Ltd.

Exfoliation of MoS₂ powder. To exfoliate MoS₂ powder to form 2H-MoS₂ suspension, a high concentration of exfoliated 2H-MoS₂ sheets was prepared by using a Chromtech model UP-500 ultrasonic homogenizer with a ½-inch ultrasonic tip. 10 g of the MoS₂ powder, 20 g of imidazole and 1000 mL of deionized water (Elga Ltd., HighWycombe, Bucks, UK) was added to a 1000 mL beaker and sonicated with tip sonication (100 ~ 500 W) in continuous mode for 2 h. The exfoliation process was performed under an N₂ environment at controlled temperature of 15°C (CC-1010, Panchun Sci. Corp.).

Preparation of 2H-MoS₂/CNT composite papers. The 108 mg CNT was sonicated in a water bath with the assistance of aqueous Triton X-100 dispersant for 1 h to achieve the CNT suspension of 1L. Then was poured CNT dispersion of 250 mL and the Im⁻-assisted exfoliated as-exfoliated 2H-MoS₂ nanosheets suspension of 50 mL into the beaker. The mixture was sonicated with tip sonication (100 ~ 500 W) for 30 minutes to enhance materials mixing. The mixture was filtrated via a filtration membrane with a pore size of 0.2 μm (cellulose acetate, Advantec) under positive pressure. Randomly dispersed 2H-MoS₂/CNT composite papers with a thickness of ~10 μm were washed thoroughly with distilled water to remove the dispersant and the exfoliant. All 2H-MoS₂/CNT composite papers were dried at 200°C under vacuum for 1h to evaporate the moisture, residual dispersant and the exfoliant, producing a final 2H-MoS₂/CNT composite papers with a electrical conductivity of ~600 S/cm.
**Characterization.** The exfoliated 2H-MoS₂ sheets were deposited by dip coating onto a freshly mica or Si substrate for Raman, PL, AFM and XPS studies. Raman spectra were recorded using a multipurpose spectrometer (JHR550, Horiba Jobin Yvon) with a 532 nm excitation laser source in air under ambient conditions, the power of the laser was set below 100 mW, the spot-size of the laser was approximately 5 μm, and the peak of Si at 520.7 cm⁻¹ was used for calibration. The PL spectrum was measured using a PL spectrophotometer (Hitachi F-4500, Japan). The ultraviolet-visible (UV-vis) absorbance spectra were recorded on a Unicam UV-300 UV-vis spectrophotometer using quartz cuvettes. The XPS measurements were carried out by using a Thermo K-Alpha (VGs) with Al Kα X-ray (1486.6 eV) as radiation source. The binding energies were calibrated with Au 4f7/2 at 84.0 eV. The morphology and structure of the exfoliated 2H-MoS₂ sheets were investigated using TEM (JEOL JEM-2100) and HRTEM (Hitachi H-7100) with the exfoliated 2H-MoS₂ sheets directly transferred onto a formvar-coated or CA) was used to characterize the thickness of the exfoliated 2H-MoS₂ sheets. The analyses of sample weight loss the laser was set below 100 mW, the spot-size of the laser was approximately 5 μm and a distance of 1.6 mm between two adjacent probes. Measurements were carried out using a KeithLink probe station in order to provide current between −5 mA to 5 mA. Each sheet of 2H-MoS₂/CNT paper was cut into 5 cm × 5 cm squares for the electrical measurements.

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**Author Contributions**

I.-W.P.C. designed the exfoliation experiments. Y.X.C. and C.W.W. performed the dispersion experiments. I.-W.P.C. wrote the paper and took the photograph of the Fig. S1. All the authors discussed the data and commented on the manuscript. All authors reviewed the manuscript.

**Additional Information**

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