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CO_2 Adsorption by *para*-Nitroaniline Sulfuric Acid-Derived Porous Carbon Foam

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Abstract: The expansion product from the sulfuric acid dehydration of *para*-nitroaniline has been characterized and studied for CO_2 adsorption. The X-ray photoelectron spectroscopy (XPS) characterization of the foam indicates that both N and S contents (15 and 9 wt%, respectively) are comparable to those separately reported for nitrogen- or sulfur-containing porous carbon materials. The analysis of the XPS signals of C1s, O1s, N1s, and S2p reveals the presence of a large number of functional groups and chemical species. The CO_2 adsorption capacity of the foam is 7.9 wt% (1.79 mmol/g) at 24.5 °C and 1 atm in 30 min, while the integral molar heat of adsorption is 113.6 kJ/mol, indicative of the fact that chemical reactions characteristic of amine sorbents are observed for this type of carbon foam. The kinetics of adsorption is of pseudo-first-order with an extrapolated activation energy of 18.3 kJ/mol comparable to that of amine-modified nanocarbons. The richness in functionalities of H_2SO_4-expanded foams represents a valuable and further pursuable approach to porous carbons alternative to KOH-derived activated carbons.

Keywords: porous carbon; nitrogen; sulfur; CO_2; nitroaniline; sulfuric acid

1. Introduction

There are two general classes of material employed for CO_2 separation: physical and chemical sorbents. All materials in various degrees are adsorbents, since CO_2 is always captured on the surface both physically or chemically depending on whether chemical reactions are involved in the adsorption process. Reactive functional groups can be present or intentionally added to the surface, making the material a chemical adsorbent. When reactive groups are also present underneath the surface and the bulk is accessible through diffusion, the material is a chemical absorbent, and capture of CO_2 is not limited to the surface alone. Chemical sorbents are also referred as to reactive sorbents given the essential role played by chemical reactions in the sorption process. Chemical sorbents usually include amines, also introduced in task-specific ionic liquids [1,2]; another class of reactive sorbents is the alkali-metal-based oxides [3]. Many commonly used ionic liquids, suitable for high-pressure capture, are expensive and toxic [4], while alkali-metal oxides suffer from deactivation and limited durability [3,5]. Although these materials show high selectivity, their other drawbacks have meant that research has focused on the study of porous carbons (PCs) [6,7], metal-organic frameworks (MOFs) [8,9], microporous zeolites [10], high surface area silica-based amine-modified sorbents [11,12], and crosslinked amine sorbents [13–15]. Chemically activated PC adsorbents have large surface areas and pore volumes associated with micro- and mesoporous structure, and as a result show significantly improved CO_2-capturing capacity as compared to traditional carbonaceous materials [16].

Contrary to some recent claims [17], it has been shown in multiple studies that the presence of nitrogen- or sulfur-doping in PC materials does not enhance the uptake of CO_2 or the selectivity [18–20]. Instead, the presence of N, S, and O are more to do with the generation of the optimum pore size and distribution [16]. The reason the residual N or S does not contribute to any chemical reactivity of CO_2 (as would be expected with amine functionality) is that the optimum nitrogen-doped porous carbon (NPC) and sulfur-doped porous carbon (SPC) are prepared using KOH oxidative activation at high temperatures. Amine functional groups can act as a chemical reagent with CO_2 to form various species including carbamates and/or bicarbonates [21–23], with the latter usually considered in the presence of water, although recent studies support the formation of hydronium carbamates [24,25]. However, this amine functionality is progressively removed during the high temperatures required to generate the porosity in the presence of KOH [26]. Thus, it is of interest to determine whether a lower temperature route to a NPC or SPC would provide residual functionality for chemical adsorption.

A well-known approach to the formation of carbon-based foams is the acid-promoted dehydration/oxidation of *para*-nitroaniline ($H_2NC_6H_4NO_2$) that is the basis of pyrotechnic snakes [27]. Heating *para*-nitroaniline in the presence of sulfuric acid at a mole ratio of about 0.5–2.0 and at temperatures above 200 °C results in the eruption of a carbon-based foam with an increase in volume of over 100 times. Subsequent studies have focused on determining the reactivity of different nitroaniline isomers and derivatives, and the elucidation of the species formed during the reaction and characterization of the products [28]. Most importantly, it has been observed that significant N- and S-based functionality is present. We are therefore interested in whether such a low-temperature N- and S-doped PC material (NSPC) could offer chemical adsorption of CO_2 on porous carbon substrates.

2. Results and Discussion

A porous carbon foam was prepared by the sulfuric acid-mediated dehydration/oxidation of *para*-nitroaniline. The product is a black, highly porous foam, which crumbles upon physical handling. From earlier work, it is known that neither texture nor volume of the foam is affected by the mole ratio of reactants, while the expansion of the foam is dependent on the heating schedule [28]. For this reason, particular attention has been given to ensure reproducible and full wetting of the nitroaniline powder with sulfuric acid and heating to form homogeneous reactive mixture before incipient expansion of the foam, as detailed in the Experimental section.

As can be seen from the thermogravimetric analysis (TGA) curves (Figure 1), the CO_2 adsorption capacity of NSPC foam is ca. 7.9 wt% (or as is ordinarily stated, 1.79 mmol CO_2/g adsorbent) at 25 °C and 1 atm. This is comparable to a number of different porous carbon sorbents: commercial activated carbon (BPL 9.2 wt%, G-32 H 11.0 wt%), ammonia-treated activated carbon (C35N400 7.6 wt%), activated graphite fibers (G-900 5.9 wt%), and mesoporous carbon (CMK-3 7.6 wt%) [6]. Although greater CO_2 uptake has been registered for various other carbon materials from 2.0 to about 5.7 mmol/g at 25 °C and 1 bar [5], the capacity of *para*-nitroaniline-derived NSPC is a significant achievement, since no high-temperature KOH activation treatment is used in the present case.

In Figure 1, the CO_2 uptake is shown to decrease as a function of increasing temperature, consistent with surface adsorption where the residence time of gas on the surface of NSPC is shorter as the temperature is increased. This is a commonly observed effect of porous carbons; a significant example is N-doped porous carbons obtained from the pyrolysis of monoliths of resorcinol–formaldehyde polymer gels, whose CO_2 capacity drops from 3.13 to 1.64 mmol/g in going from 25 to 60 °C at 1 atm [29].

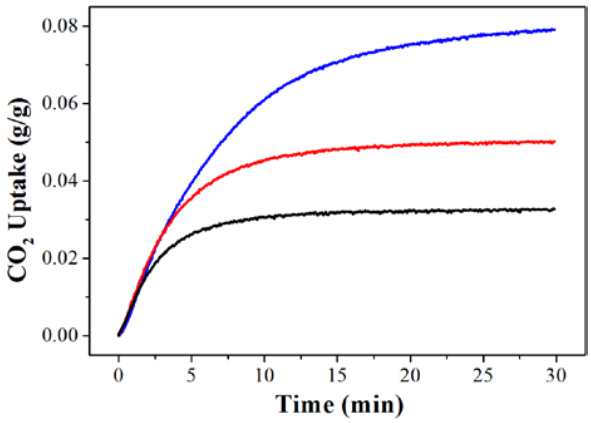

Figure 1. Plot of CO_2 uptake for nitrogen- and sulfur-doped porous carbon (NSPC) as a function of time using pure CO_2 at 1 atm at the temperatures of 24.5, 44.7, and 65.0 °C in blue, red, and black, respectively.

Notably, the recorded values of heat of adsorption for NSPC are greater than those typically observed for physical adsorption of CO_2. The heat flows registered during the CO_2 uptakes are presented in Figure 2. As expected, these are all exothermal, and the amount of heat released per mole of CO_2 is 113.6, 115.9, and 121.3 kJ/mol at 24.5, 44.7, and 65.0 °C, respectively. Integral molar heat of adsorption is a key parameter to distinguish physisorption from chemisorption [30]. Physisorption results from weak interactions, and the heat released upon adsorption is relatively small in the range of 5–45 kJ/mol, whereas chemisorption consists of chemical reactions with the formation of stable species confined on the surface of a solid with the release of larger amounts of heat in the range of 80–400 kJ/mol. The typical heat of absorption of CO_2 in standard amine scrubbing systems is about 80 kJ/mol to form carbamates [31], and it is shown to increase with increasing temperature to up to 110 kJ/mol, as is seen for the values recorded in the present case [32]. This is a strong indication of the presence of intact reactive amine functionality on the NSPC surface, a key result of the present study since the chemical–thermal dehydration/oxidation of *para*-nitroaniline does appear to generate a porous carbon foam, while preserving the nature of part of the functional groups of the starting material. This is entirely different from the KOH activation of N- or S-bearing precursor materials, where the harsher alkaline chemistry and much higher temperature used are the cause for an entire loss of amine or thiol groups to form N- or S-doped graphitic materials.

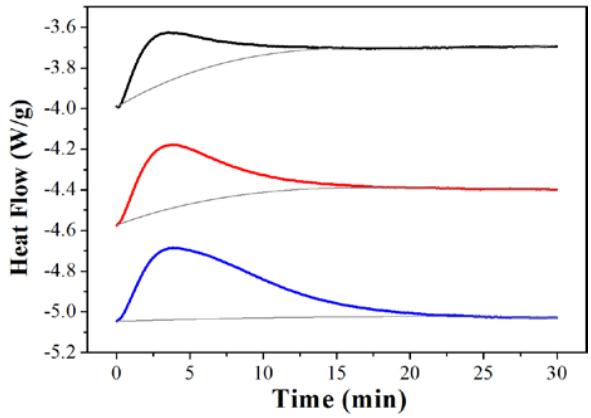

Figure 2. Plot of heat of flow for the adsorption of CO_2 on NSPC as a function of time using pure CO_2 at 1 atm at the temperatures of 24.5, 44.7, and 65.0 °C in blue, red, and black, respectively. The baselines in gray were used to integrate the curves and calculate the corresponding integrate molar heat of adsorption at each temperature. The corresponding CO_2 uptake curves are given in Figure 1.

Chemisorption is the dominant mechanism of CO_2 capture based on the integrated values of molar heat of adsorption, thus there should be significant suitable functional groups present on the NSPC foam. X-ray photoelectron spectroscopy (XPS) analysis of NSPC foam confirms the presence of significant nitrogen (15 wt%) and sulfur (9 wt%) as well as oxygen (23 wt%), as shown in Figure 3. Based upon our prior work [16], it would be expected that the carbon content (50 wt%) should result in a PC with low CO_2 uptake, since maximum CO_2 uptake is achieved for pyrolyzed PC having a surface area $\geq$2800 m^2/g, a pore volume $\geq$1.35 cm^3/g, and a C content between 80 and 95 wt% [16]. However, the NSPC foams compare favorably to NPCs prepared from the pyrolysis of polypyrrole (PPy) at 500–800 °C using a KOH:PPy weight ratio of 2. In fact, the CO_2 uptake of such pyrolyzed NPCs is in the range of 1.5–2.5 mmol/g at 24 °C and 1 bar single component CO_2 [16], comparable to the 1.79 mmol/g of the present NSPC. This is further evidence of the different mechanisms of adsorption between KOH-activated NPC or SPC porous carbons and H_2SO_4-expanded NSPCs, hence the high CO_2 uptake of the latter despite the limited amount of carbon present in the sorbent.

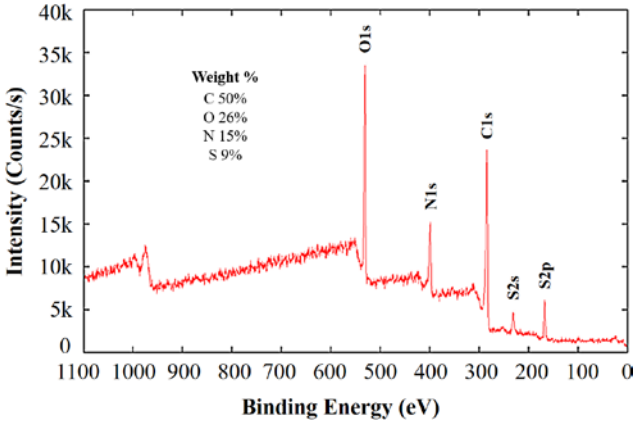

Figure 3. X-ray photoelectron spectroscopy (XPS) survey spectrum of NSPC foam.

The C1s signal (Figure 4a) is consistent with the presence of both aliphatic and aromatic carbon species, in addition to a range of O- and N-functionalized species (Table 1). Aliphatic sp^3 carbon is likely due to adventitious carbon commonly encountered on surfaces exposed to airborne organic matter. Aromatic sp^2 carbon is related to the products of expansion, where residual or reacted benzene moieties maintain their aromaticity. Benzene moieties are also in agreement with the signal of $\pi \rightarrow \pi^*$ transition of the aromatic ring detected at 291.5 eV [26]. Remarkably, a significant amount of carbon is found at unusually low binding energy, 283.5 eV, and given the chemistry involved in the expansion process it is reasonable to associate this peak to conjugated sp^2 carbon that is known to appear at low binding energy in its oxidized form, as reported in the case of polycarbazole [33]. The peaks at higher binding energy are associated with the presence of carbon atoms bearing a number of different functionalities including alcohol, amine, nitrile, carbonyl, amide, and carboxylic groups. The exact identification of all or a part of these groups is beyond the scope of this study, however it is important to note that 26.6 atom % of the surface carbon atoms bear intact functional groups. In agreement with an overall nitrogen content of 15 wt% (Figure 3), it is likely that a significant part of these are amine groups also supported by the heat of adsorption (Figure 2), typical of the reaction of amine with CO_2.

The N1s signal (Figure 4b) shows the rich and diverse number of nitrogen functionalities present on the surface of the NSPC foam. Starting from the lower binding energy peaks (Table 1), the peak at 398.0 eV is assigned to the presence of azole/triazole moieties [34], while that at 399.1 eV is commonly associated to primary amines, nitrogen included in aromatic rings, and nitrile functionality. It is interesting to note that the largest peak (about 35 atom %) of the nitrogen signal belongs to the latter group. Amide, amino acid, carbazole [33], and uracil [35] are also possible chemical moieties formed upon expansion. Ammonium is also formed together with amino benzenesulfonic acid; both species,

including the extensive formation of sulfonic acid groups, have previously been reported in the literature [28]. The nitrogen of polyaniline is normally found at 403.0 eV, which might indicate that a smaller amount of nitrogen (1.9 atom %) is present with conjugated aniline units, although N-oxide functions are also in the same binding energy range. Finally, some of the nitro groups remain in the foam unreacted and some are converted to nitroso groups, as also proposed in earlier literature [28]. It is evident that the surface chemistry of NSPC foam is fairly complex, and this richness of functionality is a distinguishing feature of H_2SO_4-expanded porous carbons compared to KOH-activated ones where N and S are mainly integrated in the graphitic structure of the materials.

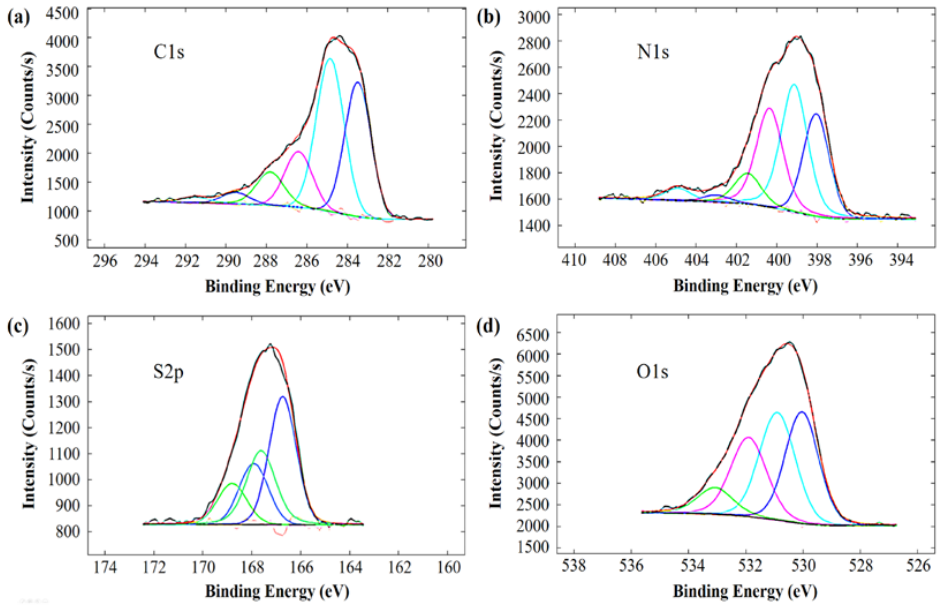

Figure 4. High resolution XPS spectra and corresponding deconvolution peaks for (**a**) C1s; (**b**) N1s; (**c**) S2p; and (**d**) O1s of NSPC foam. Deconvolution peaks are showed in color underneath experimental signals in black.

Table 1. Summary of chemical analysis of NSPC foam as determined by XPS.

Signal	Peak (eV)	atom %	Assignment
C1s	283.5	32.4	oxidized conjugated C
	284.9	39.3	aromatic C
	286.4	14.3	C–OH, C–NR_2, –C≡N
	287.8	9.2	C=O, C(O)NH
	289.5	3.1	C(O)OH
	291.5	1.7	$\pi \rightarrow \pi^*$ transition of the aromatic ring
N1s	398.0	24.5	azole/triazole N
	399.1	34.8	–NH_2, aromatic N, –C≡N
	400.4	27.0	C(O)NH, amino acid, carbazole, uracil
	401.4	8.4	ammonium, amino benzenesulfonic acid
	403.0	1.9	polyaniline, N-oxide
	404.9	3.4	–NO_2, –N=O
S2p	166.75 and 167.93	59.6	sulfite
	167.62 and 168.80	40.4	sulfate, sulfonic, sulfonate
O1s	530.0	32.2	sulfinyl (organic)
	530.9	33.3	amino acid CO_2H
	531.9	25.4	methacrylate, terephthalate, sulfone
	533.1	9.1	H_2O, CO_2H

The other two XPS signals are the S2p and O1s (Figure 4c,d, respectively), the deconvolution of these confirms some of the species identified in the C1s and N1s. The two sulfur doublets (1.18 eV separation, 2:1 area ratio) are associated to sulfite (166.75 and 167.62 eV) formed upon the reduction of sulfuric acid known to act as an oxidant of nitroaniline [28], and to residual sulfate and sulfonic acid/sulfonate groups (167.62 and 168.80 eV) formed upon thermal decomposition of nitroaniline [28]. The deconvolution of the O1s supports the presence of carboxylic groups individual or within amino acid moieties, while methacrylate and terephthalate groups could also be present. Finally, the oxygen of sulfinyl and sulfone could be formed from the further reduction of sulfonic groups during incipient expansion of the foam.

The kinetics of adsorption of CO_2 of the NSPC foam has been analyzed in detail following the approach presented in our previous work [36]. Briefly, the fitting of the experimental data presented in Figure 1 have been performed using six different kinetic models: Elovich, pseudo-first-order, pseudo-second-order, pseudo-*n*th-order, modified Avrami, and extended model. The results of the fittings are provided in Table S1 of the Supplementary Material. The model that best describes the adsorption behavior of the NSPC foam is the pseudo-first-order with R^2 of 0.9986, 0.9987, and 0.9973 at 24.5, 44.7, and 65.0 °C, respectively. While an improvement of the quality of the fittings (better R^2) is obtained with the other models, except for Elovich and pseudo-second-order, it is important to note that the results obtained for the pseudo-*n*th-order, modified Avrami, and extended model are essentially corrections to a pseudo-first-order behavior. In fact, the values of the additional parameters of these three models (n for the pseudo-*n*th-order, m for the modified Avrami, and n and m for the extended model) are all close to 1, the value for which all these models correspond to the pseudo-first-order model. For this reason, the activation energy (E_a) of CO_2 adsorption for the NSPC foam has been extrapolated from the slope of the Arrhenius plot of $\ln(k_1)$ versus $1/T$ (Table S1) to find that E_a = 18.3 kJ/mol. This value is comparable to those previously found for polyethylenimine (PEI)-functionalized single-walled carbon nanotubes (PEI-SWNT, E_a = 13.3 kJ/mol [36]) and graphite oxide (PEI-GO, E_a = 22.6 kJ/mol [36]). This significant finding further supports the amine-CO_2 surface chemistry of NSPC foams, and the unique feature of H_2SO_4-expanded nitroaniline foams to produce amine-functionalized porous carbons without the need for further amine impregnation or functionalization.

3. Experimental

3.1. Materials and Characterization

Sulfuric acid (Sigma-Aldrich, ACS Reagent, 95.0%–98.0%, Saint Louis, MO, USA) and *para*-nitroaniline (Sigma-Aldrich, ≥99.0%) were used as received. All water was ultrapure (UP), obtained from a Millipore Milli-Q UV water filtration system (EDM Millipore, Billerica, MA, USA). Samples were characterized by X-ray photoelectron spectroscopy. Measurements carried out in a PHI Quantera scanning XPS microprobe (Physical Electronics, Chanhassen, MN, USA). The wt% of chemical elements was determined by XPS survey scans with pass energy of 140 eV. For detailed elemental analysis, high-resolution multi-cycle elemental scans with pass energy 26 eV was performed. Each spectrum was then deconvoluted by appropriate basis functions. Before spectral fitting, each spectrum was corrected for reference binding energy for C1s to 284.8 eV.

3.2. Synthesis of N/S-Doped Porous Carbon Foam (NSPC)

para-Nitroaniline (0.2–0.5 g) was placed in a ceramic crucible and wet with sulfuric acid while mixing with a stir glass rod, and the drop-by-drop addition of acid was continued until all powder was uniformly wet. An extra 2–3 drops were added before heating up the mixture by placing a propane flame under the crucible. While heating, the mixture turned to a yellow-brownish melt first and then to a black liquid, and this was kept hot by removing the flame at times until visible vapors stop evolving and a homogenous liquid phase was obtained after a few minutes. The flame was then placed back to

bring the mixture to boil and eventually to incipient expansion of a light black foam. Plenty of fumes were also released during expansion. The foam was characterized and used as prepared without further treatment.

3.3. CO_2 Adsorption

CO_2 adsorption experiments were carried out with a TA Instruments Q600 TGA/DSC (TA Instruments, New Castle, DE, USA) using atmospheric pressure CO_2 (High purity research grade, 99.99%, Matheson Trigas, Basking Ridge, NJ, USA). The general procedure for the adsorption experiments is described as follows. NSPC foam (1–2 mg) was loaded into an alumina pan and placed on the balance arm of the TGA. The chamber was closed and purged with a steady flow of Ar (70 mL/min). The temperature of the system was ramped from room temperature to 110 °C at a rate of 10 °C/min in order to degas and dehydrate the sample. After the desorption was completed, the sample was brought and kept to the desired temperature value until a constant weight was achieved. The gas in the system was then changed to CO_2 (20 mL/min). Upon changing gases, an immediate increase in weight was observed indicating that the NSPCs were adsorbing the CO_2. The CO_2 flow was continued until constant weight was attained. For the kinetics studies, the regression analysis of the CO_2 adsorption curves (weight versus time) was performed with OriginPro 9.0 software (OriginLab Corporation, Northampton, MA, USA) using the Levenberg–Marquardt iteration algorithm for nonlinear curve fitting, as previously reported in reference [36].

4. Conclusions

In summary, we have shown that the thermally induced sulfuric acid-initiated dehydration of *para*-nitroaniline appears to be a promising alternative method to prepare N- and S-doped porous carbon (NSPC) foams with good CO_2 chemical adsorption properties. The maximum CO_2 adsorption capacity of NSPC foams is comparable to that of a number of commercial activated carbon sorbents. Most importantly, the demonstrated presence of intact amino groups among a large number of other functionalities in the NSPC foams reveals that H_2SO_4-initiated incipient expansion of nitroanilines have the unique advantage of preserving chemical functionalities that otherwise are lost in the widely employed thermal KOH activation of synthetic and natural organic precursors. Accordingly, other chemical compounds should be considered and tested to verify whether this long established—but still poorly understood and rarely applied—approach could work beyond nitroanilines, potentially opening up new avenues to chemically functionalized porous carbon sorbents.

Supplementary Materials: Supplementary materials can be found at http://www.mdpi.com/2311-5629/2/4/25/s1.

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Author Contributions: Enrico Andreoli prepared the porous carbon samples, performed XPS analysis, CO_2 uptake measurements, and kinetics studies. Both authors created the Figures and contributed to the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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