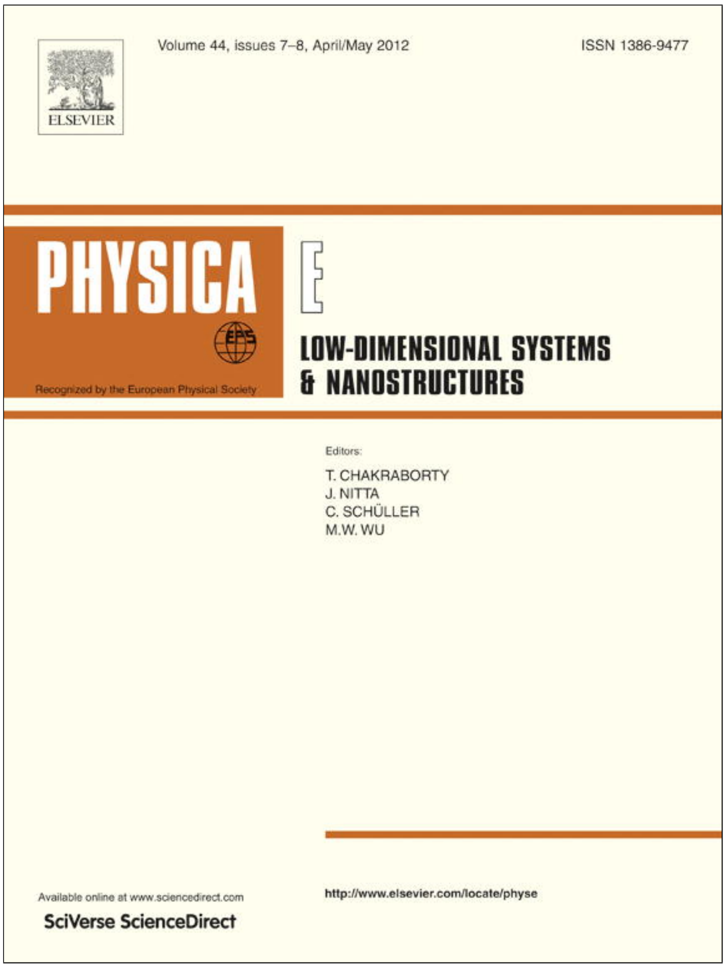

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Monitoring influence of chemical preparation procedure on the structure of graphene nanosheets

Chengbo Shi [a,b], Lei Chen [a,b], Zhiwei Xu [a,b,*], Yanan Jiao [a], Yinglin Li [a,b], Chunhong Wang [a,b], Mingjing Shan [a,b], Zhen Wang [a,b], Qiwei Guo [a]

[a] *Key Laboratory of Advanced Braided Composites, Ministry of Education, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China*
[b] *School of Textiles, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China*

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ABSTRACT

A comparison concerned about the three approaches (Hummers' method, improved method and Marcano–Tour's method, which all have been published and widely quoted in the field of producing graphene oxide) for the preparation of graphene oxide is discussed. The monitoring effect of preparation procedure is determined by investigating the influences of chemical reagents and reaction conditions on the structure of graphene nanosheets. The structure of graphene oxide and chemically reduced graphene is characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. The exact mechanisms concerned about the effects of chemical reagents on the product structures are briefly described. The incorporation of H_3PO_4 and the addition of excessive H_2SO_4 and $KMnO_4$ are proved to make a higher oxidation degree compared with the traditional methods. Ice in Marcano–Tour's method is also seen to be beneficial to the increase of the graphite oxide interlayer spacing. Surprisingly, the graphene, which is prepared by reducing the product of Marcano–Tour's method, shows less defects than the other two ones. In addition, the graphene oxide produced by improved method is found to confront with few difficulties during the reduction process.

1. Introduction

Graphene, a two-dimensional sheet composed of sp^2-hybridized carbon, with single-atom thickness, is one of the most exciting materials being investigated today, not only out of academic curiosity but also with potential applications in mind [1–3]. A few- and single-layer transferable graphene nanosheets are firstly obtained by mechanical exfoliation of bulk graphite [4] and by epitaxial chemical vapor deposition [5–7]. In the electronic and optical fields, graphene prepared by these two methods shows great prospects due to the preserved structures in the preparation process [8] To date, however, the most popular method to prepare graphene is by exfoliation and then reduction of graphite oxide (GO) for low performance applications [8–15].

In 1958, a faster and safer route to prepare graphite oxide was reported by Hummers and Offeman [10]. Graphite intercalation compounds obtained by the intercalation of sulfuric acid between the graphite layers are commonly used in chemical and electrochemical industrial applications, under the name of Expandable Graphite [13,16,17]. Marcano et al. supplied an improved method for producing GO, which yields a higher fraction of well-oxidized hydrophilic carbon material and produces no toxic gas [18]. Unilamellar colloids of GO were successfully produced from graphite in Mallouk's work [19]. Kotov and Dekany et al. had prepared ultrathin films with self-assembled GO platelets and polyelectrolytes [20]. Furthermore, it is often essential that GO can be transformed back into a conductive graphitic material, and indeed, either in thin films or in bulk, partial restoration of the graphitic structure can be accomplished by chemical reduction, to chemically converted graphene (CCG) [21–25]. Ruoff and co-workers prepared single-layer graphene by exfoliation of graphite oxide via ultrasonic treatment, followed by chemical reduction with hydrazine hydrate [25]. W. Gao et al. devised a complete reduction process through chemical conversion by sodium borohydride and sulfuric acid treatment, followed by thermal annealing [26]. Very recently, Li et al. fabricated ultra-smooth graphene nanoribbons by combining thermal exfoliation of Expandable Graphite with chemomechanical breaking of the resulting graphene sheets by sonication [27]. During the reduction process, the graphitic structure is not fully restored using these conditions. Significant defects are introduced due to the transformation of sp^2 carbon into sp^3 configuration [28].

Generally speaking, a lot of efforts have been committed in the preparation of graphene nanosheets. However, the way the various

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[*] Corresponding author at: Key Laboratory of Advanced Braided Composites, Ministry of Education, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China. Tel./fax: +86 22 83955231.
E-mail address: xuzhiwei@tjpu.edu.cn (Z. Xu).

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reagents and the alternation procedure affect the structure of graphene nanosheet is not fully understood. This is necessary to be investigated to monitor the structure of graphene nanosheets. To assure the effect mechanisms of various reagents and preparation processes on the structure of GO and reduced GO, in this study, we cited three methods (Hummers method [10], improved method and Marcano–Tour's method [18] which all have been widely used in the field of GO production) to prepare GO. These three kinds of GO were then reduced. X-ray diffraction (XRD), Raman spectra and X-ray photoelectron spectroscopy (XPS) were introduced to characterize the structure of GO and reduced GO.

2. Experimental

2.1. Preparation of GO

Graphite oxides are prepared using three different procedures: Hummers' method, improved method and Marcano–Tour's method.

For Hummers' method [10], concentrated H_2SO_4 (69 mL) is added to a mixture of graphite flakes (3.0 g, 1 wt. equiv.; Table 1) and $NaNO_3$ (1.5 g, 0.5 wt. equiv.), and the mixture is cooled to 0 °C. Then $KMnO_4$ (9.0 g, 3 wt. equiv.) is added slowly in portions to keep the reaction temperature below 20 °C. The mixture is warmed to 35 °C and stirred for 30 min, at which time water (138 mL) is added slowly, producing a large exotherm to 98 °C. External heating is introduced to maintain the reaction temperature at 98 °C for 15 min, then the heat is removed and the mixture is cooled using a water bath for 10 min. Additional water (400 mL) and 30% H_2O_2 (3 mL) are added, producing another exotherm. For workup, the mixture is sifted and then filtered at 4000 rpm for 4 h to decant the supernatant away. The solid obtained on the filter is vacuum-dried overnight at room temperature to get HGO eventually.

For the improved method [18], a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) is added to a mixture of graphite flakes (3.0 g, 1 wt. equiv.) and $KMnO_4$ (18.0 g, 6 wt. equiv.), and the mixture is cooled to 0 °C for 2 h. In the reaction, it produces a slight exotherm to 35 °C for 0.5 h. The mixture is heated to 50 °C and stirred for 12 h and then poured into water (400 mL) with 30% H_2O_2 (3 mL). The mixture is purified as described above (sifting, filtration, multiple washings, centrifugations and decanting, vacuum drying) to give IGO I.

Compared with the improved method, the difference in Marcano–Tour's method is that the mixture is cooled to room temperature and poured onto ice (400 mL) with 30% H_2O_2 (3 mL) [18]. The mixture is then purified following the previous protocol of sifting, filtering, centrifugation, and decanting with multiple washings followed by a final vacuum drying to give IGO II.

2.2. Reduction

HGO (500 mg) was loaded in a 500 mL round-bottom flask and water (200 mL) was then added, yielding an inhomogeneous yellow-brown dispersion. This dispersion was sonicated using a Fisher Scientific FS60 ultrasonic bath cleaner (150 W) until it became clear with no visible particulate matter. Sodium borohydride (500 mg) was then added and the solution heated in an oil bath at 80 °C under a water-cooled condenser for 2 h over which the reduced HGO (r-HGO) gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed copiously with water (5×100 mL) and methanol (5×100 mL), and dried on the funnel under a continuous air flow through the solid product cake. Reduced IGO I (r-IGO I) and reduced IGO II (r-IGO II) were also prepared with the above-mentioned procedure.

2.3. Characterization

The structures of HGO, IGO I, IGO II, r-HGO, r-IGO I and r-IGO II were analyzed by X-ray diffraction (XRD, 1.54059 Å Cu Kα 1 as wavelength), as well as Raman (RENISHAW in Via Raman Microscope, recorded using 514 nm laser excitation with a power of 5 mW), and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

3. Results and discussion

3.1. Oxidation degree

For GO, the interlayer spacing of the materials is proportional to the degree of oxidation [10,18]. The XRD spectra of HGO, IGO I, and IGO II are shown in Fig. 1. There are two diffraction peaks for HGO and IGO I at $2\theta = 12.0^\circ$ ($d = 0.74$ nm) and 26.4° ($d = 0.34$ nm). The relatively weak diffraction peak with $d = 0.34$ nm corresponds to the normal graphite spacing. The stronger peak with $d = 0.74$ nm should come from the inter-GO diffraction, corresponding to the typical diffraction peak of GO. Compared with HGO and IGO I, the interlayer spacing of IGO II is larger, implying more extensive oxidation due to the fact that increased oxidative intercalation of $KMnO_4$ and H_3PO_4 in H_2SO_4 is much more highly exothermic. Furthermore, the pattern of the water addition in Marcano–Tour's method is likely to play a much more important role to expand the graphite oxide GO than the other two. The increased interlayer spacing brought by the extensive intercalation of water molecules in Marcano–Tour's method may also decrease the difficulties in exfoliating the GO. In addition, the total disappearance of the typical graphite interlayer diffraction peak in IGO II strongly supports the full oxidation in Marcano–Tour's method. It should be a promising method for the production of graphene oxide nanosheets with a high percent of monolayers.

XRD patterns of the reduced GO are recorded in Fig. 2. For r-HGO, the diffraction peak at $2\theta = 26.4^\circ$ is stronger than that for r-IGO and r-IGO+, indicating the rather limited oxidation of HGO. Due to the introduction of a mass of oxygen-containing groups in the IGO II, the spectrum of r-IGO II shows a diffraction peak for the reduced IGO+ at 12°, implying more obstacles in the

Table 1
Chemical reagents and reaction conditions of HGO, IGO I and IGO II.

Method	Product	Reagents				Reaction conditions
		$NaNO_3$	H_2SO_4	$KMnO_4$	H_3PO_4	
Hummers' method [7]	HGO	0.5	1	3	/	The mixture is cooled using a water bath for 10 min. Additional water (400 mL) and 30% H_2O_2 (3 mL) are added.
Improved method I	IGO I	/	9	6	1	The mixture is poured into water (400 mL) with 30% H_2O_2 (3 mL).
Improved method II [15]	IGO II	/	9	6	1	The mixture is cooled to room temperature and poured onto ice (400 mL) with 30% H_2O_2 (3 mL)

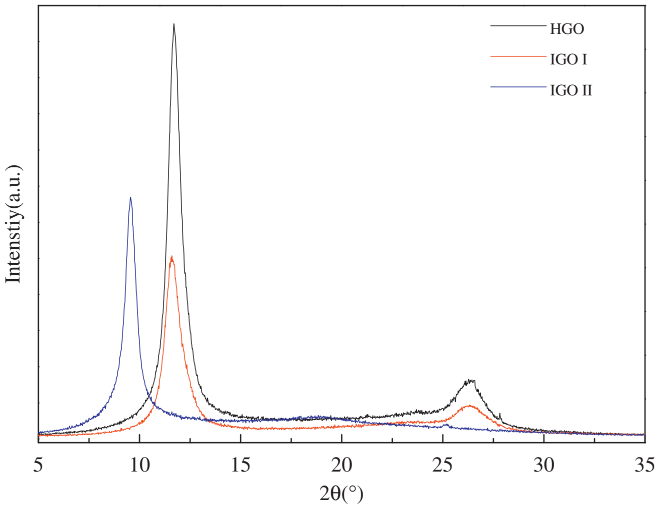

Fig. 1. XRD spectra of HGO, IGO I and IGO II.

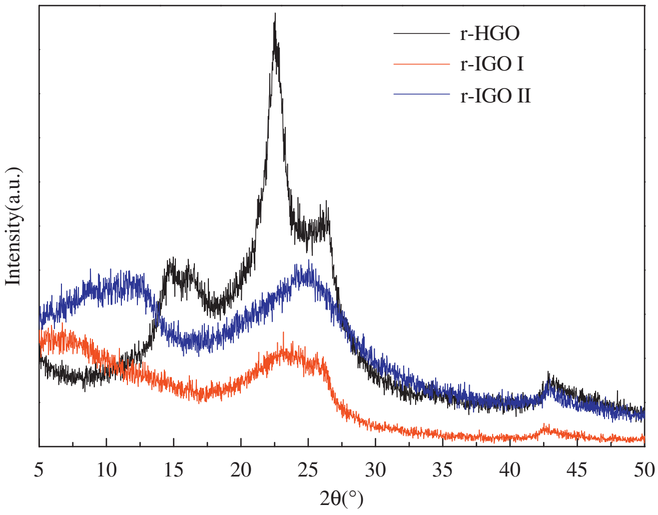

Fig. 2. XRD spectra of r-HGO, r-IGO I and r-IGO II.

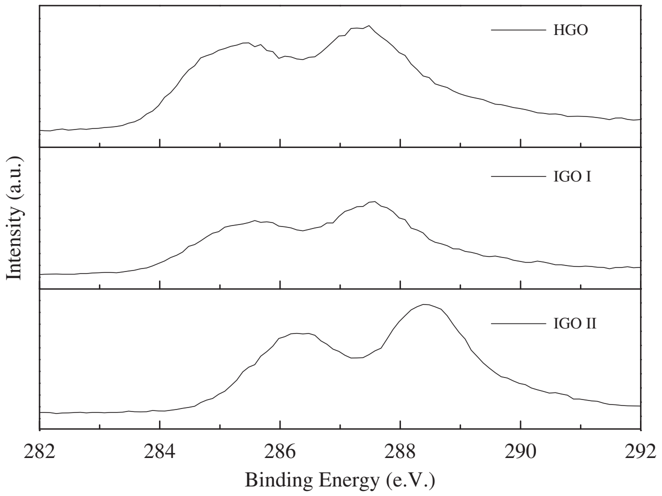

Fig. 3. C1s XPS spectra of HGO, IGO I and IGO II.

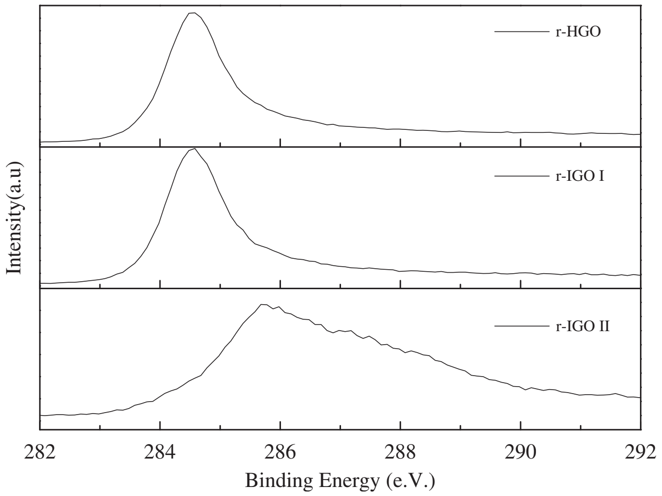

Fig. 4. C1s XPS spectra of r-HGO, r-IGO I and r-IGO II.

reduction process than in the other two reduced GOs. In addition, compared with r-HGO and r-IGO II, the structure of r-IGO I displays much more graphitic characteristics, which was mainly attributed to the medium reagents and reaction procedures in the oxidation procedure [25].

3.2. *Element composition*

In brief, the C1s XPS spectrum of GO clearly indicates a considerable degree of oxidation with four components that correspond to carbon atoms in different functional groups: the nonoxygenated ring C (284.8 eV), the C in C–O bonds (286.2 eV), the carbonyl C (287.8 eV), and the carboxylate carbon (O–C=O, 289.0 eV) [18]. The C1s XPS spectra (Fig. 3) show that IGO II contains a higher fraction of well-oxidized hydrophilic carbon materials than HGO and IGO I. Moreover, the apparent peak at ~288.5 eV, corresponding to the oxidized carbon for IGO II, is sharper than those for HGO and IGO I. This suggests the most extensive oxidation of IGO II in these three GOs. Highly re-hybridized carbon sheets bearing hydroxyl and carboxyl moieties are found to be produced between the IGO II interlayers compared with HGO and IGO. In addition, Marcano–Tour's method does not generate toxic gases such as NO_2, N_2O_4 and ClO_2 and the temperature is more easily controlled compared with the traditional methods [18]. Fig. 4 shows the XPS spectra of r-HGO+, r-IGO I and r-IGO II. The reduction degree of CCG can be determined by the binding energy of each XPS spectrum. In XPS spectrum of r-IGO II, the binding energy at the peak is higher than that in the spectra of r-HGO and r-IGO I, indicating the least intensive reduction in these three CCGs. Both of these observations from Figs. 3 and 4 are consistent with the XRD results and suggest considerable oxygenation of IGO II as well by the H_3PO_4 incorporation and the procedure alternation.

3.3. *Defects and graphitic structures*

Raman spectroscopy is a noninvasive technique, which is widely used to characterize the structural and electronic properties of the carbon-based materials such as carbon nanotubes, diamond, graphite, and diamond-like carbons. The G band is usually assigned to the E_{2g} phonon of C sp^2 atoms, while the D band is a breathing mode of k-point phonons of A_{1g} symmetry [29]. The Raman spectra of HGO, IGO I and IGO II are shown in Fig. 5. The G band (sp^2-hybridized carbon) at 1590 cm^{-1}, and the D band (sp^3-hybridized carbon) at 1350 cm^{-1} are recorded. The position and the intensity ratio of D to G band (I_D/I_G) of these GOs are grossly similar to each other, indicating rare changes in size of the sp^2 domains, and can be little influenced by some factors such

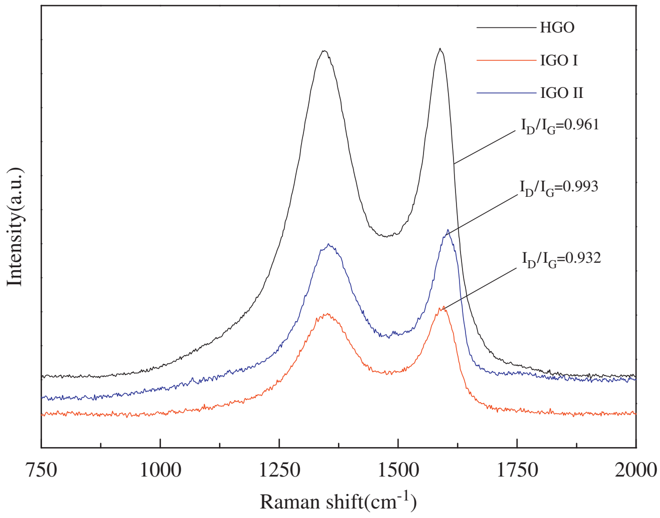

Fig. 5. Raman spectra of HGO, IGO I and IGO II.

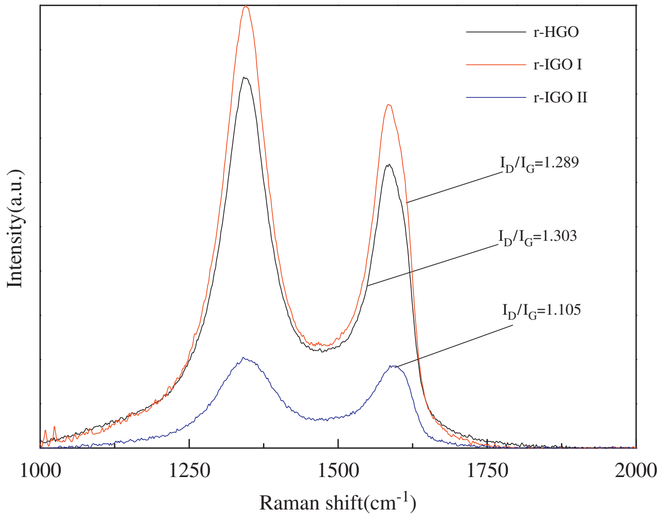

Fig. 6. Raman spectra of r-HGO, r-IGO I and r-IGO II.

as the time under low reaction temperature, reagents contents, the way of adding water under high reaction temperature and so on. We also characterize our reduced GOs by means of Raman spectroscopy and the spectra are shown in Fig. 6. The I_D/I_G of r-IGO II is found to be smaller than those of r-HGO and r-IGO+, suggesting a lower defect density in r-IGO II, which may be attributed to the less intensive reduction induced by the fundamental oxidation in Marcano–Tour's method.

3.4. Effect mechanisms of the chemical agents

Compared with Hummers' method, the excessive oxidative intercalation of $KMnO_4$ in H_2SO_4 in the improved method and Marcano–Tour's method is much more highly exothermic so that the products composed of more highly re-hybridized carbon sheets bearing hydroxyl and carboxyl moieties have been prepared successively [30]. Also, the way of water addition seems to affect the oxidation effect significantly. The water molecules are found to intercalate in IGO II more easily than in the other two products to make an extensively expanded GO. Unfortunately, extensive oxidation in Marcano–Tour's method has brought more difficulties in the reduction process. Lots of oxygen functional groups are found to be deposited on the IGO II basal plane so that extensive reduction is hard to be realized. Interestingly, the amounts of defects and graphitic structures of GO are found to be little affected by altering the content of chemical reagents and the way of adding water. It may be attributed to the extreme damage on the GO lattice so that even the addition of the chemical reagents cannot increase the defects significantly.

4. Conclusions

To investigate the way how the various reagents and the alternation procedure affect graphene nanosheet structures, we cited three methods [10,18] (which all have been widely used in graphene production) to prepare GO. The interlayer spacing of IGO II is found to be increased significantly by the incorporation of H_3PO_4, addition of excessive H_2SO_4 and $KMnO_4$ and alternation of the water into ice in reaction procedure. Owing to increased amount of oxygen groups between the product interlayers, the oxidation of IGO II is also seen to be more extensive than in HGO and IGO. Moreover, Raman spectroscopy shows that r-IGO II has the least defects in these three CCGs. Due to the medium oxidation effect, r-IGO I displays much more satisfying reduction than the other two outcomes because of the extensive reduction effect. It can be concluded that Marcano–Tour's method is a more promising method for preparing graphene nanosheets with high percent of monolayers and low defects than the other two methods. In addition, the improved method is shown to produce sufficiently reduced graphene nanosheets.

Acknowledgments

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