Electrochemical Exfoliation of Graphite: Effect of Temperature and Hydrogen Peroxide Addition

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Abstract:

Controlling the defect density in graphene is critical to manipulate materials properties and functionality through synthesis and processing. In this work, graphene was prepared by electrochemical exfoliation method at different temperatures from 25 to 95 °C with and without the addition of H₂O₂. The effect of both the exfoliation temperature and H₂O₂ addition on governing the defect density and oxygen functional groups in graphene was investigated using Raman spectroscopy analysis and thermogravimetric analysis (TGA), respectively. The number of defects, which can be edge defect or oxygen functional groups, decreases with the increase of exfoliation temperature from 25 to 95 °C. This can be explained by nucleophilicity of hydroxyl ions and peroxide ions. The thermal stability of the as-synthesized graphene increases with increasing exfoliation temperature and the amount of H₂O₂ addition. Transmission electron microscopy (TEM) was performed to characterize the morphology and the layer number of the as-synthesized graphene.

1. Introduction:

The wonder material called graphene, which is a two-dimensional monolayer carbon material arranged in a hexagonal lattice, is rapidly getting more attention since 2004 due to its superior electrical, thermal, optical properties and high surface area.^{1,2,3} Great efforts have been made to synthesize high quality and low-defect density graphene for various applications, such as energy storage and conversion devices,^{4,5} composite materials,⁶ semiconductor devices,^{7,8} and sensors.⁹ Different methods, such as chemical vapor deposition (CVD),^{10, 11, 12} micromechanical exfoliation,¹³ sonochemical liquid phase exfoliation,¹⁴ microwave,^{15,16} Hummers method,¹⁷ Tour method,¹⁸ and electrochemical exfoliation^{19,20} etc. have been used to make low-defect graphene. Among these, Hummers and Tour methods are used to produce graphene oxide first by chemically exfoliating, and then it needs to be reduced chemically or thermally to reestablish electronic properties. After reduction of graphene oxide, reduced graphene can still have a large number of defects.¹⁸ CVD method, which is not cost effective, can be useful to yield better quality graphene.¹⁹ Kim et al.²¹ conducted work on surface wave plasma CVD to synthesize graphene at low temperature (400°C), which had a large amount of defects as shown in their Raman spectra.

Parvez et al.¹⁹ studied the electrochemical exfoliation of graphite using different aqueous inorganic salts, such as ammonium sulfate, ammonium chloride, sodium sulfate, sodium nitrate, potassium sulfate and sodium chlorate as the electrolyte. They suggested that sulfate ions showed better exfoliation even at low reduction voltage. A high yield ($>85\%$, ≤ 3 layers) with an improved chemical and electronic properties of graphene were obtained at room temperature by electrochemical exfoliation. Sanjeeva et al.²⁰ investigated the electrochemical exfoliation behavior of graphite, using sodium hydroxide with the addition of hydrogen peroxide (H_2O_2) as an electrolyte solution. They proposed that addition of hydrogen peroxide can yield better exfoliation process and produce multilayered, low-defect graphene. However, it is still challenging to produce single layer low-defect graphene using electrochemical exfoliation method. The increasing temperature during exfoliation can give extra energy to speed up the reaction rate of hydrogen peroxide with hydroxyl ions, which can be a key to produce high-quality graphene. The information available in the literature seems insufficient on the electrochemical exfoliation of graphite to synthesize graphene at elevated temperature. In this project, we investigated the electrochemical exfoliation process of graphite at different temperatures with and without the addition of H_2O_2 .

2. Experimental:

2.1 Materials synthesis:

The electrolyte solution was prepared using 1.06 g $(\text{NH}_4)_2\text{SO}_4$ in 80 mL DI water.¹⁹ The solution was stirred for 1 min on a magnetic stirrer. Then 5 mL or 10 mL H_2O_2 was added to make different solutions and, in some cases, no H_2O_2 was used. The solutions were kept at different temperatures (25, 50, 75, 95 °C) in a heated water bath. The maximum water bath temperature of 95 °C was used because boiling temperature of water is about 100 °C, and H_2O_2 in aqueous solution starts to decompose at 114 °C. Two graphite rods were used as cathode and anode, serving as the carbon source for each electrolyte solution. The rods were dipped into the solutions at a distance of 4 cm between them as shown in Figure 1. The graphite rods were connected to the negative and positive source from a BK Precision 1760a triple output DC power supply. To start the electrochemical exfoliation on positive rods, 10 V of power was supplied and the process was conducted for 2 hrs. Then the solution was cooled down to room temperature if in case it was heated. The samples were filtered and washed with DI water several times to remove any ammonium ion left in graphene. Finally, the samples were dried at 75 °C for 12 hrs. The samples are designated as EG- XH_2O_2 -T or EG- XH_2O_2 , where EG is exfoliated graphene, X is the amount of H_2O_2 addition, and T is the solution temperature. EG- XH_2O_2 is referred to the samples for EG synthesized with the addition of X mL of H_2O_2 at different temperatures.

2.2 Characterization:

The X-ray diffraction (XRD) of powder samples was conducted in Rigaku MiniFlex II from 5° to 90° of 2θ with a scan rate of 0.5° per min. Horiba iHR320 Raman spectrometer was used to

record Raman spectrum with a laser at an excitation wavelength of 532 nm. The 5-second exposure time and 10 spectrum accumulation number were used for each of the samples. Before the measurement, the spectrometer was calibrated, using a Si single crystal wafer as a reference peaked at 520 cm^{-1} . TA Q50 Thermogravimetric analyzer (TGA) was used to test thermal stability of the as-synthesized samples. TGA was done from room temperature to $900\text{ }^{\circ}\text{C}$ at a temperature ramp rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. JEOL 2100 Transmission electron microscope (TEM) at an acceleration voltage of 200 KV was used to investigate the morphology and structure of the samples. The powder samples were added in ethanol and then were sonicated for 30 seconds. Holey carbon copper grids from Ted Pella were dipped into the solutions to prepare TEM samples.

3. Results and Discussion:

3.1 Production amount and XRD analysis:

As described earlier, each experiment was conducted for 2 hrs under different conditions. The surface area of immersed graphite rods was 782 mm^2 . When the experiment was conducted at high temperature, the surface area decreased gradually due to the evaporation of water. Table 1 shows the amount of produced graphene by electrochemical exfoliation process under different conditions. The production of graphene increases from 223 mg to 276 mg as the amount of the addition of H_2O_2 increases from 0 to 10 mL in the solution at $25\text{ }^{\circ}\text{C}$. Similar increment can be seen for the temperatures at 50, 75 and $95\text{ }^{\circ}\text{C}$. This increment in production happens due the increasing of the exfoliation rate, which is described later. The production of graphene starts decreasing as the temperatures are increased for the same amount of H_2O_2 addition. This occurs due to the decrease of the surface area of immersed graphite rods.

Figure 2 displays the XRD patterns of graphite and as-prepared graphene synthesized at $95\text{ }^{\circ}\text{C}$ with and without the addition of H_2O_2 . For graphite, three peaks are found at 2θ of 26.5° , 44.5° and 54.4° for the corresponding planes (002), (101) and (004), respectively.²² A single peak with very low intensity compared to a similar peak of graphite is found at $2\theta = 26.6^{\circ}$ for each graphene sample.^{23,24} This peak suggests that as-prepared graphene sheets have either good crystallinity or multiple layers.²⁵ Wazir et al.²⁶ and Sun et al.²⁷ showed a broad peak at $2\theta = 26.5^{\circ}$ for graphene layers. This broad peak can be a proof of the presence of amorphous graphene layers. Thus, XRD patterns of graphene can be ambiguous and because of this researchers have been relying on other characterization techniques, such as Raman and TEM analysis, to verify more precisely the presence of a single or multi-layers graphene.

3.2 Raman analysis:

Raman spectroscopy was carried out to characterize the defect-activated band information in exfoliated graphene (EG). Raman spectra are shown in Figure 3. Raman spectra of EG synthesized without the addition of H_2O_2 (EG-0 H_2O_2) are displayed in Figure 3a. There are three major peaks at 1325 , 1568 and 2736 cm^{-1} , which are called D band, G band, and 2D band,

respectively.²⁸ D peak at 1325 cm^{-1} is activated due to different kinds of disordered defects, such as edges, functional groups and structural groups.²⁹ G peaks at 1568 cm^{-1} correspond to transverse optical (TO) and longitudinal optical (LO) phonon mode.²⁰ The intensity of D band and G band decreases with increasing the electrolyte solution temperatures as shown in Figure 3a. A small D-band peak typically suggests a low concentration of disorder structures in graphene and/or a high purity of graphene, indicating that increasing the electrolyte solution temperature during the electrochemical exfoliation process resulted in a better quality of graphene. This is also confirmed by the following TGA analysis. The ratio of the intensity of D and G band decreases with increasing the temperature. The peak at 2170 cm^{-1} corresponds to the linear carbon chains.^{30,31} However, carbon chains are not stable in air at room temperature.³¹ The Raman G^* bands found at 2355 cm^{-1} are attributed to the combination of two phonon modes: in-plane longitudinal acoustic (iLA) and in-plane transverse optical (iTO) modes. The position of G^* bands do not change for few layers of graphene; though, G^* bands can shift to the left for graphite due to a large amount of layers.³² Another important peak 2D found at 2736 cm^{-1} is the second order two-phonon process. The observed single 2D band suggests that the samples have single or few layers of graphene.²⁹ Figures 3b and 3c show Raman spectra of the EG synthesized with the addition of 5 mL (EG-5H₂O₂) and 10 mL H₂O₂ (EG-10H₂O₂), respectively. These figures show a similar trend as shown in Figure 3a for the samples without addition of H₂O₂.

The intensity ratio of D and G band relates to the mean distance between defects (L_D). It can be estimated by using the equation below.³³

$$L_D^2 (\text{nm}^2) = (1.8 \pm 0.5) \times 10^{-9} \lambda^4 (I_D/I_G)^{-1} \quad (\text{i})$$

Here, λ is the excitation laser wavelength in nm, and I_D and I_G are the intensity of D band and G band, respectively. Furthermore, the number of defects (N_D) can also be estimated based on the equation below.³³

$$N_D (\text{cm}^{-2}) = 10^{14} / (\pi L_D^2) \quad (\text{ii})$$

Figure 4a shows that the mean distance between defects increases with increasing the electrolyte solution temperatures for the samples with and without the addition of H₂O₂. The EG-0H₂O₂ has the lowest L_D value at room temperature. As the temperature of electrolyte solution increases, the L_D value for the EG-0H₂O₂ starts increasing more rapidly than it does for both EG-5H₂O₂ and EG-10H₂O₂. Thus, EG-0H₂O₂ has the highest L_D value compared to the L_D value for the EG synthesized with the addition of H₂O₂ (EG-5H₂O₂ and EG-10H₂O₂) for each of the following temperatures: 50, 75 and 95 °C. The number of defect (N_D) decreases with increasing the electrolyte solution temperatures for all three samples shown in Figure 4b. This illustrates the exactly opposite trend of the mean distance between defects shown in Figure 4a. In other words, EG-0H₂O₂ has the lowest N_D value at 50, 75 and 95 °C. This can be explained by the effectiveness of interaction of different ions with graphite discussed later. The ratios of I_D and I_G for the graphene synthesized at the electrolyte solution temperature of 95°C with addition of 0, 5

and 10 mL H_2O_2 are 0.32, 0.39 and 0.38, respectively, which are significantly lower than for those in the graphene prepared by either chemically or thermally reduction of graphene oxide ($1.1 \sim 1.4$)³⁴ and in electrochemically exfoliated graphene at room temperature (0.67).²⁰ Since the ratio of I_D and I_G is related to the defect density of graphene, it can be concluded that the graphene synthesized at a higher electrolyte solution temperature in electrochemical exfoliation method shows lower defect density than the graphene synthesized using other methods.

3.3 Thermogravimetric analysis:

To further understand the effect of H_2O_2 addition and exfoliation temperature, TGA was carried out to evaluate the thermal stability and decomposition of the residual functional groups in the as-synthesized graphene shown in Figures 5 and 6. Figure 5 depicts the TGA and first derivative (DTG, the rate of change of mass) curves of **EG-0H₂O₂-25**, where three major weight loss steps are observed. As shown in Figure 5, the sample initially undergoes the first major weight loss of 4.9% below 150 °C due to the water removal. Then, the second weight loss occurs between 150-400 °C centered at 184 °C with an observed weight loss of 15.2% corresponding to the removal of oxygen functional groups, such as -OH and =O.³⁵ **Chen et al.,³⁶ Park et al.³⁷ and Naebe et al.³⁸ showed that oxygen functional groups were removed over 200 °C for both graphene and graphene oxide.** No obvious weight loss is observed from 400 to 500 °C. The third weight loss step is detected at over 600 °C, which relates to the unstable carbon remaining in the structure.³⁵

Figure 6a compares the thermal stability of **EG-0H₂O₂** at different exfoliation temperatures: 25, 50, 75 and 95 °C. Clearly, the sample obtained at 25 °C reveals the highest weight loss of ~50% up to 880 °C and other samples obtained at higher temperatures (50, 75, 95 °C) exhibits a much smaller weight loss. The sample obtained at 95 °C demonstrates the best thermal stability and only shows ~1% weight loss in this temperature range. It can be concluded that the weight loss of the EGs synthesized without the addition of H_2O_2 decreases with increasing the exfoliation temperature. The samples obtained at 50 and 75 °C exhibit a similar three major steps of weight loss compared to the sample obtained at 25 °C as discussed above in Figure 5. The sample acquired at 90 °C shows a continuous weight loss with a relatively small weight change (~1%) below 700 °C seen in Figure 6d, which demonstrates high thermal stability up to 880 °C. **Figures 6b and 6c display the thermal stability of EG-5H₂O₂ and EG-10H₂O₂ which were synthesized at the same temperatures, respectively. The first two weight loss steps are also observed for these two samples at all temperatures; however, the amount of weight losses is low compared to EG-0H₂O₂ samples. In Figures 6b and 6c, EG-5H₂O₂-25 and EG-10H₂O₂-25 samples confirm ~27% and ~14% of total weight loss, respectively, and they show the similar weight loss trend as EG-0H₂O₂ at higher exfoliation temperatures. It is also evident that the second step of weight loss decreases with increasing the exfoliation temperature for both EG-5H₂O₂ and EG-10H₂O₂ samples. Because the second weight loss step is assigned to the removal of residual oxygen functional groups, this result indicates that the addition of H_2O_2 and the increase of reaction temperature during electrochemical exfoliation greatly decreases the oxygen-containing**

functional groups, which improves the thermal stability of the EGs. Table 2 compares the weight percentage of calculated oxygen functional groups present in the temperature range from 150 to 400 °C based on the weight loss measurement. It also should be noted that the third step of weight losses due to the unstable carbon remaining in the structure is observed at over 600°C for both **EG-0H₂O₂** and **EG-5H₂O₂** seen in Figures 6a and 6b. However, the third weight loss step can hardly be seen for the **EG-10H₂O₂** samples shown in Figure 6c. As the exfoliation temperature increases, the thermal stability of **EG-10H₂O₂** increases; nevertheless, it does not show any unstable carbon weight loss at any exfoliation temperature. It is clear that the addition of H₂O₂ reduces the amount of the unstable carbon during the electrochemical exfoliation.

To observe this even precisely, Figure 6d was drawn in a narrow range to show the weight loss corresponding to the removal of the unstable carbon for **EG-0H₂O₂**, **EG-5H₂O₂** and **EG-10H₂O₂** synthesized at 95°C. The unstable carbon can be observed in graphene synthesized by Brodie³⁹ method. In this study, **EG-10H₂O₂-95 sample** shows the highest thermal stability with having extremely low (<1%) amount of unstable carbon in the structure.

The advantage of the addition of H₂O₂ and higher temperature electrochemical exfoliation can be understood as follows. It is known that OH⁻ and O₂²⁻ interact with graphite edges and grain boundaries, and this helps to expand carbon layers.²⁰ The reactions 1 and 2 explain how the hydroxyl ions (OH⁻) come to the solution from **the reduction of water at negative electrode**, and the peroxide ions (O₂²⁻) are formed when H₂O₂ is added.¹⁹ SO₂ and O₂ gases are also produced from the residual SO₄²⁻ ions and water oxidation, respectively, during the process shown below in the reactions 3 and 4.^{19,35} These gases intercalate with graphite layers and peel each layer off by applying force on the layers.¹⁹ A possible exfoliation process is shown in a schematic representation in Figure 7.

OH⁻ has low nucleophilicity. Thus, it does not interact with graphite effectively. This leads to less chance of intercalation of SO₂ and O₂ in the absence of H₂O₂. Less interaction of these gasses with graphite layers causes the remaining of some unstable carbons. However, the oxidation of water happens more frequently at a higher temperature, which leads to less amount of OH⁻ in the solution. The amount of oxygen functional groups decreases drastically with increasing exfoliation temperature due to the decrease of OH⁻; thus, the number of defects decreases as oxygen functional groups are one kind of defects. Peroxide ions are better nucleophilic than hydroxyl ions and, thus, O₂²⁻ can interact with graphite effectively. However, the effectiveness of interaction of O₂²⁻ depends on the rate of the reaction 2. Kodepelly S. Rao et

al.²⁰ showed that the exfoliation rate increases drastically with increasing the concentration of H₂O₂. For the addition of 5 mL H₂O₂, the effectiveness of interaction of O₂²⁻ is still low enough to produce unstable carbons due to the slower rate of the reaction. The rate of reaction increases with increasing temperature and, thus, the amount of O₂²⁻ increases with increasing exfoliation temperature which eventually leads to the presence of less amount of unstable carbon in graphene. On the other hand, for the addition of 10 mL H₂O₂ the rate of reaction increases due to the increment of H₂O₂ concentration in the solution, and it produces enough O₂²⁻ to increase the effectiveness of intercalation with graphite.

OH⁻ produces most oxygen functional groups in the layers during intercalation with graphite, and O₂²⁻ produces fewer amounts of oxygen functional groups due to its high nucleophilic behavior. In the absence of H₂O₂, oxidation of water increases with increasing temperature, which leads to fewer amounts of OH⁻, and this process yields fewer amounts of oxygen functional groups. For 5 mL H₂O₂ addition both OH⁻ and O₂²⁻ participate in producing oxygen functional groups. As the exfoliation temperature increases, the amount of OH⁻ decreases due to a higher water oxidation rate. Although the amount of OH⁻ decreases at the same rate for both cases (0 mL and 5 mL of H₂O₂) there is still OH⁻ left along with O₂²⁻ for 5 mL H₂O₂ case, and both OH⁻ and O₂²⁻ produce oxygen functional groups during interaction with graphite. For 10 mL H₂O₂ addition, only O₂²⁻ produces oxygen functional groups. Thus, the amount of oxygen functional groups is the lowest in this case.

3.4 TEM analysis:

TEM analysis was done on electrochemically exfoliated graphene to observe the number of layers shown in Figure 8. The TEM images of EG synthesized at 50°C with and without the addition of H₂O₂ were taken at the same magnification (×4000) shown in Figure 8a–c. Typically it was observed that multi-layer (≥3) graphene was obtained for the samples without the addition of H₂O₂. Figure 8a shows a usual TEM image of three layers of graphene synthesized without the addition of H₂O₂ at 50°C. Many wrinkles of graphene sheets are observed in the samples without the addition of H₂O₂. Figure 8b and 8c show TEM images of double-layer or overlap of two single-layer graphene sheets with uniform contrast for both **EG-5H₂O₂-50** and **EG-10H₂O₂-50 samples**, respectively. The uniform or homogeneous contrast in TEM images indicates less folded or crumpled regions within these graphene sheets. As H₂O₂ was added, it is clear that the number of graphene sheet layers decreased due to the interaction of highly nucleophilic O₂²⁻. In Figure 8d, TEM image of **EG-10H₂O₂-95 sample** shows a double-layer graphene at a magnification of ×30K, and these graphene layers have fewer wrinkles. The selected area electron diffraction (SAED) was recorded and shown with index in the inset of Figure 8d. It shows the typical six-fold symmetry corresponding to the hexagonal carbon lattice in graphene. The electron diffraction spots were indexed/labeled using Miller-Bravis (hkl) indices. An identification method of graphene layers by electron diffraction pattern was proposed by Meyer et al.⁴⁰ using the intensity ratio of the {1-210} and {1-100} spots. The ratio of I(1-210)/I(1-100) for **EG-10H₂O₂-95** is 0.61 shown in Figure 9 and confirms that as-synthesized graphene is a

single layer in fact. Kodepelly S. Rao et al.²⁰ reported getting three or more layers of graphene sheets, using electrochemical exfoliation method, by adding H_2O_2 in the electrolyte solution kept at room temperature. In our experiment, double-layer or overlap of two single-layer graphene sheets was obtained due to the increase of the electrolyte solution temperature during the electrochemical exfoliation. The heating of electrolyte solution causes the increase of the rate of reaction of hydrogen peroxide with hydroxyl ion, which helps to exfoliate graphene layers more efficiently as discussed above.

4. Conclusion:

The experimented electrochemical exfoliation method at elevated temperatures has several major advantages, such as (i) simple operation setup, (ii) ecofriendly, (iii) one step method, (iv) low temperature (maximum 95 °C). The layer number of the graphene, the number of defects and the amount of oxygen functional groups can be controlled using a different amount of H_2O_2 at different temperatures. The amount of oxygen functional groups decreases with increasing the exfoliation temperature of electrolyte and the amount of H_2O_2 addition in the electrolyte solution. The number of defects decreases as well due to the increase of the exfoliation temperature and the concentration of H_2O_2 in the solution. Increasing the concentration of H_2O_2 produces fewer amounts of unstable carbon, and as for the addition of 10 mL H_2O_2 , there was less than 1% unstable carbon in graphene. Increasing both the exfoliation temperature and the concentration of H_2O_2 causes the decrease in layer number of graphene. Electrochemical exfoliation of graphite at 95°C with the addition of 10 mL H_2O_2 produced low-defect, double-layer or overlap of two single-layer graphene. This research showed a crucial role of both temperature and H_2O_2 addition in producing high-quality graphene, which is significant for future applications.

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Figure 1. Schematic of a typical electrochemical exfoliation process to prepare graphene.

Figure 2. XRD patterns of graphite, and exfoliated graphene synthesized at 95°C with the addition of 0, 5 and 10 mL of H₂O₂.

Figure 3. Raman spectra of the exfoliated graphenes synthesized using electrochemical exfoliation (a) without the addition of H_2O_2 and with the addition of (b) 5 mL H_2O_2 and (c) 10 mL H_2O_2 at different temperatures in the range of 25 to 95°C.

Figure 4. Comparison of (a) the mean distances between defects and (b) the number of defects in the exfoliated graphene synthesized with and without the addition of H_2O_2 at different temperatures.

Figure 5. TGA and DTG curves of the EG synthesized at 25°C without the addition of H₂O₂. Black and blue profiles represent the weight loss and first derivative of weight loss with respect to temperature, respectively.

Figure 6. TGA curves for the exfoliated graphene synthesized using electrochemical exfoliation (a) without addition of H_2O_2 and with addition of (b) 5 mL H_2O_2 and (c) 10 mL H_2O_2 at different temperatures in the range of 25 to 95°C. (d) TGA curves for the graphene synthesized at 95°C with and without addition of H_2O_2 .

Figure 7. Schematic representation of the proposed exfoliation process.

Figure 8. TEM images of the exfoliated graphenes synthesized using electrochemical exfoliation at 50°C (a) without the addition of H_2O_2 and with the addition of (b) 5 mL H_2O_2 and (c) 10 mL H_2O_2 . (d) Electrochemical exfoliation at 95°C with the addition of 10 mL H_2O_2 and the corresponding selected area electron diffraction pattern (inserted).

(a)

(b)

Figure 9. Selected area diffraction pattern (a) of the EG sample synthesized at 95 °C with the addition of 10 mL H_2O_2 and (b) diffraction intensity $I(1-100)$ and $I(1-210)$ of the (1-100) and (1-210) diffraction spots.

Table 1. The amount of exfoliated graphene synthesized at different conditions.

Temperature (°C)	0 mL H₂O₂ (mg)	5 mL H₂O₂ (mg)	10 mL H₂O₂ (mg)
25	223	240	276
50	215	232	265
75	201	225	247
95	182	212	228

Table 2. The percentage of oxygen functional groups present in the temperature range from 150 to 400°C in the EGs synthesized at different exfoliation temperatures with and without the addition of H₂O₂.

Temperature (°C)	0 mL H₂O₂ (%)	5 mL H₂O₂ (%)	10 mL H₂O₂ (%)
25	15.22	9.35	6.66
50	14.80	5.46	5.26
75	0.93	2.10	1.44
95	0.00	0.00	0.17

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