



## Morphological and chemical features of nano and macroscale carbons affecting hydrogen peroxide decomposition in aqueous media

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### ABSTRACT

Chemical and structural factors of carbon materials affect their activity in adsorption and surface reactions in aqueous media. Decomposition of hydrogen peroxide studied is a probe reaction for exploring parameters of carbons that might be involved, such as specific surface area, nitrogen and oxygen doping and conformational changes. To date, a detailed comparison of the behavior of carbon nanoscale (Carbon Nanotubes, CNT, Single Layer Graphene Oxide, SLGO) with macroscale (Activated carbons, AC) materials in this reaction has not been forthcoming. Herein, we demonstrate that on their first cycle, ACs in doped and undoped forms outperform all nanoscale carbons tested in the H<sub>2</sub>O<sub>2</sub> decomposition. Among the nanocarbons, nitrogen-doped CNT exhibited the highest activity in this reaction. However, subsequent recycling of each carbon, without chemical regeneration between uses, reveals SLGO exhibits greater reaction rate stability over an extended number of cycles ( $n > 8$ ) than other carbons including nitrogen-doped CNT and ACs. The effects of pH, temperature and concentration on the reaction were analyzed. Quantum-chemical modeling and reaction kinetics analysis reveal key processes likely involved in hydrogen peroxide decomposition and show evidence that the reaction rate is linked to active sites with N- and O-containing functionalities.

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### 1. Introduction

Numerous carbon materials are used in a variety of applications, including adsorption, catalysis, filling of polymers for strength, conductivity and so forth [1–3]. In the case of the adsorption of reactive compounds to carbons, chemical transformation of both components is possible; however, this depends on the composition of the adsorbent and the adsorbate, temperature, pH, adsorbent porosity, etc. Hydrogen peroxide is a simple but interesting active adsorbate and can be used to study the interfacial behavior of carbons in aqueous media under a variety of conditions.

Hydrogen peroxide, which is a useful reagent in the oxidative decontamination of organic chemicals in waste and groundwater, is decomposed on addition of ferric ions (Fenton reaction), to form strongly oxidizing hydroxyl radicals. The drawback of homogeneous Fenton-like chemical processes in the oxidative treatment of wastewater is the need for strict pH control and difficulty of separating a homogeneous catalyst from the reaction mixture [4]. The

use of carbon materials as catalysts as an alternative to metal-based systems has been the subject of much consideration [5,6]. Among the host of carbon materials utilized in heterogeneous catalysis, activated carbons (ACs) are exploited most frequently because of several key factors, including their large specific surface area ( $S_{\text{BET}} = 1000\text{--}3500 \text{ m}^2/\text{g}$ ), type and number of active surface sites containing O, N and other heteroatoms, large pore volume, narrow or zero electron bandgap and comparatively low cost [1–3,7–9]. ACs have been demonstrated to catalyze chlorination and dechlorination, oxidation and/or decomposition of a variety of organic and inorganic compounds [10]. Carbon nanomaterials, including CNTs, graphenes, carbon nanoparticles, on the other hand embody many such features, providing additional advantages over macroscale carbon systems due to their nanosized dimensions and topology [11]. CNTs have been shown to catalyze numerous organic chemical reactions [12,13], where they outperform ACs [14]. Furthermore, single layer graphenes (SLG) have additional advantages over CNTs as catalysts due to their outstanding thermal conductivity, large surface-to-mass ratio and extremely high mobility of electrons [15–17]. It is recognized that some of these properties may be diminished in oxidized SLG, but their facile and large-scale preparation capability makes them a worthy candi-

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date for this investigation and it has been shown that SLG oxide (SLGO) is an active oxygen donor in oxidation and hydration reactions [18].

In this study, we investigated the activity of SLGO in  $H_2O_2$  decomposition in comparison with pure (CNT), acid-oxidized ( $CNT_{ox}$ ) and N-doped carbon nanotubes (N-CNT) and activated carbon (AC) and AC doped by nitrogen (N-AC) or oxidized ( $AC_{ox}$  and  $N-AC_{ox}$ ).

## 2. Materials and methods

Initial multiwall carbon nanotubes, CNT (TekhSpetsMash, Kiev, Ukraine) were oxidized by treatment with 70%  $HNO_3$  at 100 °C for 4 h. The oxidized CNT ( $CNT_{ox}$ ) samples were purified from immobilized fulvic acids formed upon oxidation by refluxing in NaOH solution. Subsequently the protonated form of covalently attached surface acidic groups was regenerated by treatment of  $CNT_{ox}$  with dilute HCl. Catalytic metal particles used in the chemical vapor deposition growth of CNTs were removed from pure and oxidized samples [19]. CNT samples were also doped with nitrogen using a fusion process with 10% urea in an inert atmosphere (700–800 °C, 1 h). Chemical (Table 1) and XPS (Table 2) analysis data confirmed the presence of nitrogen in the final sample (N-CNT).

Single-layer graphene oxides (SLGO, about 10% O) were obtained from Cheap Tubes Inc. (USA). Their structure confirmed through AFM and TEM analysis can be found at the website of the company [20]. Samples were dispersed in aqueous solution and monitored over time for possible leaching of acids and also washed in both acid and alkaline solutions. No impurities were detected by UV–Visible or fluorescence spectroscopic analysis of the leachates implying that the as-supplied samples were clean. SLGO used behaved in a similar fashion to that reported elsewhere in terms of solubility and sheet size [21,22].

Activated carbon (AC) and nitrogen-containing AC (N-AC) were obtained from the Institute for Sorption and Problem of Endoecology (NAS of Ukraine). The AC used is an activated carbon derived from natural raw materials (apricot stones) and N-AC was synthesized from vinylpyridine copolymer (Table 1). Oxidation of AC was carried out using the same procedure as in the case of CNT samples. The amount of surface acidic groups on each carbon material was determined using the Boehm titration method (Table 3) [23,24].

Hydrogen peroxide (Aldrich, 50 vol.%) was used without additional purification. The decomposition of hydrogen peroxide was conducted in phosphate buffers at pH 4–8,  $C_{H_2O_2} = 0.2–15$  vol.% and 20–50 °C. To analyze the activity of carbons in the  $H_2O_2$  decomposition, a volumetric method was used with a microburette array to measure the quantity of released oxygen. The ratio of the  $H_2O_2$  solution to AC, N-AC and  $AC_{ox}$  was 50 ml per 0.1 g; to CNT and  $CNT_{ox}$  – 25 ml per 0.05 g; to N-CNT and SLGO – 25 ml per 0.005 g. In a blank experiment without a carbon, the oxygen yield was too small to be measured. Therefore, the total  $O_2$  yield can be attributed to the  $H_2O_2$  decomposition at the surface of the carbons.

For analysis, quantitative assessment and comparison of the activity of carbons, the rate constant ( $k$ ,  $min^{-1}$ ), distribution function of the rate constant ( $f(k)$ ) and activation energy ( $E_a$ , kJ/mol)

**Table 2**  
XPS analysis of CNTs.

Sample	$C_{1s}$		$O_{1s}$		$N_{1s}$	
	Atom%	wt.%	Atom%	wt.%	Atom%	wt.%
CNT	98.78	98.38	1.22	1.62	–	–
$CNT_{ox}$	97.94	97.28	2.06	2.72	–	–
N-CNT	98.27	97.80	1.11	1.47	0.62	0.72

were determined as described below. The rate of hydrogen peroxide decomposition can be described by the first-order equation:

$$-dC/dt = kC, \quad (1)$$

Additionally, the reaction (see ESI) can be described by a sum of the first and second order equations

$$C/C_0 = a_1 \exp(-k_1 t) + a_2 / (1 + C_0 k_2 t), \quad (2)$$

where  $a_1$  and  $a_2$  are the weight coefficients. As the activity of the studied carbons may change over time, for example, due to the chemical oxidation of the surface by hydrogen peroxide, it will affect the  $k$  value. Therefore instead of using a single constant  $k$  value (or two  $k_1$  and  $k_2$  values), this process should be more correctly characterized by a certain distribution function of  $k$ , i.e.  $f(k)$ . On the basis of Eq. (1), an integral equation can be written as:

$$\frac{C(t)}{C_0} = \int_{k_{min}}^{k_{max}} f_d(k) \exp(-kt) dk \quad (3)$$

where  $C_0$  is the  $H_2O_2$  concentration at  $t = 0$ ,  $k_{max}$  ( $10^2 min^{-1}$ ) and  $k_{min}$  ( $10^{-10} min^{-1}$ ) are the boundary values of the rate constant on the integration. The integral equation based on Eq. (2) can be written as:

$$\frac{C(t)}{C_0} = \int_{k_{min}}^{k_{max}} f_d(k) (a_1 \exp(-kt) + a_2 / (1 + kt)) dk \quad (4)$$

The  $a_1$  and  $a_2$  values can be determined using the functional minimization method for the best fitting of the experimental  $C(t)/C_0$  curves with Eq. (2). The boundary values in Eqs. (3) and (4) are established on the basis of the experimental data for the lowest and highest reaction rates. The differential  $f_d(k)$  distribution functions were calculated using a constrained regularization procedure at non-negativity condition ( $f_d(k) \geq 0$  at any  $k$ ) and unfixed regularization parameter [25]. For all samples, non-zero  $f_d(k)$  values were in a broad range at  $10^{-8} < k < 3 min^{-1}$ .

## 3. Results and discussion

### 3.1. Morphology and chemical structure of carbons

CNTs are thin and long tubes (Fig. 1a) or wrapped or cylindrical graphene, which typically possess closed ends, pores in the external walls and a non-smooth surface depending on their production and treatment methodology. Though under aggressive oxidation conditions it is possible to decap them leaving open access to their central cavity (Fig. 1a). SLGO with about 10% of oxygen [20] represent large and very thin (1–3 single layers) carbon sheets (Fig. 1b) which are highly flexible, according to PM6 modeling of a single layer (Fig. 1c). The flexibility of SLGO sheets is clearly observed under TEM imaging (Fig. 1b) showing many bends and folds in a single sheet. Additionally, this image shows that SLGO is composed with 1–3 layers that are observed in the left part of the image as thin lines and changes in the color, which is in agreement with data obtained from the manufacturing company [20]. Activated carbons (ACs) represent hierarchical structures with nanoporous particles often tightly bound in aggregates forming visible beads

**Table 1**  
HCNO-element analysis of carbons.

Sample	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)
N-CNT	98.63	0.16	0.14	1.07
AC	99.415	0.21	0.32	0.055
$AC_{ox}$	96.33	1.015	0.55	2.105
N-AC	91.243	0.955	1.315	6.487

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