

Device And Method For Electro-Fenton Process Using a Carbon Electrode And Its Application For Removal Of Organic Pollutants

Field of Invention

The invention relates to a green electrochemical advanced oxidation process, known as the electro-Fenton process, as applied to industrial wastewater treatment. More specifically, the invention relates to a carbon cathode (e.g. graphene foam, or carbon fiber/carbon cloth coated with graphene) and their use in the electro-Fenton process.

Background

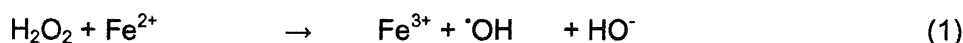
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Water quality is a growing concern, not only at a societal level but also technologically. In particular, various industries currently release large amounts of synthetic organic pollutants in their wastewater streams. These contaminants often cannot be significantly removed in conventional wastewater treatment plants because the vast majority of these contaminants consist of persistent organic pollutants (POPs), which are resistant to microbial degradation. Current interest in the field of wastewater treatment focuses on the development of simple, safe, effective, environmentally-friendly and economical physicochemical technologies for the total removal of such POPs.

Among physicochemical processes, advanced oxidation processes (AOPs) have become popular because they allow the generation of the hydroxyl radical ($\cdot\text{OH}$), a non-selective oxidant that can react very quickly with many biorefractory organic compounds. Traditional AOPs consist of hydrogen peroxide photolysis ($\text{H}_2\text{O}_2/\text{UV}$), ozone photolysis (O_3/UV), Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) and photo-Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$) techniques. However, these techniques rely on the addition of high amounts of expensive chemical reagents and especially hydrogen peroxide (H_2O_2). Moreover, ozone-based processes are difficult to implement because this molecule is explosive and so is hard to handle on scale, and the Fenton processes typically produce large amounts of sludge.

Electrochemical advanced oxidation processes (EAOPs) have become increasingly investigated because they offer a means to replace the use of chemicals by a clean reagent

(electrons) in combination with enhanced removal efficiency. These processes allow the continuous electrochemical generation of $\cdot\text{OH}$ and offer the advantage of a broad range of applications, thanks to their high flexibility in terms of organic load ($0.01 < \text{COD} < 100 \text{ g-O}_2 \text{ L}^{-1}$). Electro-Fenton (EF) has recently emerged as the most promising EAOP by generating $\cdot\text{OH}$ radicals through the Fenton's reaction (Eq. 1):



In contrast with the conventional Fenton process, H_2O_2 is generated electrocatalytically and *in situ* at the cathode through O_2 reduction (Eq. 2), while Fe^{2+} is only required at a catalytic concentration – if not originally present in the wastewater – thanks to its electrochemical regeneration through Fe^{3+} reduction (Eq. 3) [10]:



In other words, the electro-Fenton technology is an electrochemical variant of the Fenton process, in which Fenton's reagent(s) (H_2O_2 and Fe^{2+}) are generated electrocatalytically and *in situ* at the cathode of the reactor, provided that there is at least a catalytic amount of iron provided in the reaction medium (either present *in situ* or added to the medium). The Fenton reaction takes place thereafter, during which H_2O_2 reacts with Fe^{2+} to produce hydroxyl radicals ($\cdot\text{OH}$) (i.e. $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$). Hydroxyl radicals are a very highly oxidizing species ($E^\circ = 2.80 \text{ V/SHE}$), second only to fluorine. This makes them very efficient for advanced removal of persistent organic pollutants. As such, the electro-Fenton process and other variations of the Fenton process have been used frequently in the treatment of wastewaters.

A review of current attempts to make use of the electro-Fenton process all show that the conventional processes are all inefficient and make use of expensive electrode materials (e.g. see Brillas, E., *et al.*, 2009. *Chem. Rev.* 109, 6570–6631; Nidheesh, P.V., and Gandhimathi, R., 2012. *Desalination* 299, 1–15; and Sirés, I., *et al.*, 2014. *Environ. Sci. Pollut. Res. Int.* 21, 8336–67).

Summary of Invention

Aspects and embodiments of the current invention are provided in the following numbered clauses.

1. An electro-Fenton apparatus comprising:
 - a cathode; and
 - an anode, wherein
 - the cathode is a non-graphene carbon substrate coated with graphene or is graphene.

2. The apparatus of Clause 1, wherein:
 - (a) the graphene has a sheet resistance of from 4.0 to 5.5 k Ω sq⁻¹, such as from 4.4 to 5.1 k Ω sq⁻¹; and/or
 - (b) the graphene-coated cathode has a resistance value of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω , such as less than or equal to 0.1 Ω ; and/or
 - (c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, has a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or
 - (d) the cathode has an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²); and/or
 - (e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode; and/or
 - (f) when the cathode is a non-graphene carbon substrate coated with graphene, the graphene coating further comprises a graphene and a binder material where the weight ratio of graphene to binder material is from 1:1 to 1:10, optionally wherein the binder material is a fluorocarbon polymer (e.g. the fluorocarbon polymer may be selected from one or more of the group consisting of perfluorosulfonic acid, polytetrafluoroethylene, polyvinylfluoride, polyvinylidene fluoride, fluorinated ethylene propylene, polyethylenetetrafluoroethylene, polyethylenechlorotrifluoroethylene, polychlorotrifluoroethylene, poly(chlorotrifluoroethylene-co-vinylidene fluoride), poly(chlorotrifluoroethylene-co-tetrafluoroethylene-co-vinylidene fluoride), poly(hexafluoropropylene-co-vinylidene fluoride), poly(tetrafluoroethylene-co-hexafluoropropylene-co-vinylidene fluoride), polychlorotrifluoroethylene and a polysulfonated tetrafluoroethylene, such as a polysulfonated tetrafluoroethylene or perfluorosulfonic acid).

3. The apparatus of Clause 1 or Clause 2, wherein:
 - (a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or

(b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene (e.g. from 2 to 800 layers, such as 3 to 5 layers), optionally wherein:

(i) the resistance of the cathode is from 0.1 to 2 Ω (e.g. 1.6 Ω) when the cathode is a graphene foam;

(ii) the resistance of the cathode is from 500 to 5000 Ω (e.g. from 1500 to 4000 Ω , such as 3651 Ω) when the cathode is a monolayer graphene; or

(iii) the resistance of the cathode is from 1.0 to 200 Ω (e.g. from 50 to 150 Ω , such as 123 Ω) when the cathode is a multilayer graphene.

4. The apparatus of Clause 3, wherein the non-graphene carbon substrate is a carbon cloth or a carbon fiber brush.

5. The apparatus of any one of the preceding clauses, wherein the anode is a boron doped diamond anode.

6. The apparatus of Clause 5, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate for the boron doped diamond coating is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

7. An electro-Fenton process to treat a wastewater, comprising:
contacting a wastewater with a cathode and an anode in a vessel under electro-Fenton conditions, wherein the cathode is a non-graphene carbon substrate coated with graphene or is graphene, optionally wherein the process further comprises adding a catalytic amount of an iron (II) and/or (III) salt to a wastewater in need thereof.

8. The process of Clause 7, wherein:

(a) the graphene has a sheet resistance of from 4.0 to 5.5 $\text{k}\Omega \text{ sq}^{-1}$, such as from 4.4 to 5.1 $\text{k}\Omega \text{ sq}^{-1}$; and/or

(b) the cathode has a resistance value of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω , such as less than or equal to 0.1 Ω ; and/or

(c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, as a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or

(d) the cathode has an electroactive surface area of from 2,000 cm^2 to 10,000 cm^2 , such as from 3,500 cm^2 to 5,000 cm^2 (e.g. 4,665 cm^2); and/or

(e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode.

9. The process of Clause 7 or Clause 8, wherein:

(a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or

(b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene (e.g. from 2 to 800 layers, such as 3 to 5 layers).

10. The process of Clause 9, wherein the non-graphene carbon substrate is a carbon cloth or a carbon fiber brush.

11. The process of any one of Clauses 7 to 10, wherein the anode is a boron doped diamond anode.

12. The process of Clause 10, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

13. Use of a non-graphene carbon substrate coated with graphene or graphene as a cathode in an electro-Fenton process.

14. The use of Clause 13, wherein the electro-Fenton process relates to the treatment of a wastewater.

15. The use of Clause 13 or Clause 14, wherein:

(a) the graphene has a sheet resistance of from 4.0 to 5.5 $\text{k}\Omega \text{ sq}^{-1}$, such as from 4.4 to 5.1 $\text{k}\Omega \text{ sq}^{-1}$; and/or

(b) the cathode has a resistance value of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω , such as less than or equal to 0.1 Ω ; and/or

(c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, as a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or

(d) the cathode has an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²); and/or

(e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode.

16. The use of any one of Clauses 13 to 15, wherein:

(a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or

(b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene (e.g. from 2 to 800 layers, such as 3 to 5 layers).

17. The use of Clause 16, wherein the non-graphene carbon substrate is a carbon cloth or a carbon fiber brush.

18. The use of any one of Clauses 13 to 17, wherein the use further comprises the use of a boron doped diamond anode.

19. The use of Clause 18, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

Drawings

Fig. 1. Structural characterization of electrochemically-exfoliated graphene: (a) TEM (left) and HRTEM (right) images; (b) Raman spectrum.

Fig. 2. Picture of carbon fiber brush used in embodiments of the invention as a cathode.

Fig. 3. Comparison of the sheet resistance of graphene produced by electrochemical and chemical methods.

Fig. 4. Optimization of graphene ink coating method by varying: (a) the percentage of NafionTM (with [Graphene] = 2 g L⁻¹) and (b) the concentration of graphene (with 0.05% (w/v) of NafionTM). Values in brackets correspond to NafionTM to graphene mass ratio. Conditions: Pt anode, V = 400 mL, pH = 3, [K₂SO₄] = 50 mM, J = 1.25 mA cm⁻².

Fig. 5. Optical micrographs ($\times 20$ magnification) of (a) uncoated brush and (b) Gr-brush at the optimal ink coating conditions (NafionTM = 0.05% (w/v) and [graphene] = 1.5 g L⁻¹).

Fig. 6. H₂O₂ electrogeneration efficiency of uncoated brush and Gr-Brush: (a) evolution of H₂O₂ concentration and (b) CE mean value after 90 min of electrolysis. Conditions: Pt anode, V = 400 mL, pH = 3, [K₂SO₄] = 50 mM, J = 1.25 mA cm⁻².

Fig. 7. ORR activity of uncoated brush and Gr-Brush determined by LSV in N₂- and O₂-saturated solution at a scan rate of 5 mV s⁻¹. Conditions: Pt anode, V = 400 mL, pH = 3, [K₂SO₄] = 50 mM, J = 1.25 mA cm⁻².

Fig. 8. Hydrogen peroxide production rate performance of carbon fiber brush coated with graphene compared to uncoated brush, graphene foil (multi layers) and graphene (single layer). Operating conditions: Pt anode, current density: 1.25 mA cm⁻², [Fe²⁺] = 0 mM, [K₂SO₄] = 0.05 M, pH_{init} = 3, pH_{final} = 3.

Fig. 9. BDD anode performance compared to carbon cloth and Pt anodes regarding the degradation (a) and mineralization (b) evolution of phenol (1 mM) as a function of electrolysis time. Operating conditions: carbon fiber brush cathode, [Fe²⁺] = 0.1 mM, [K₂SO₄] = 0.05 M, pH_{init} = 3, pH_{final} = 3, air bubbling all along (0.2 L min⁻¹), current density: 1.25 mA cm⁻².

Fig. 10. Performance of Gr-Brush and uncoated brush cathode on phenol (0.33 mM) degradation by EF: phenol decay vs electrolysis time (k_{app} determination in inset panel, assuming a pseudo-first order reaction between phenol and [•]OH). Conditions: Pt anode, V = 400 mL, [Fe²⁺] = 0.1 mM, pH = 3, [K₂SO₄] = 50 mM, J = 1.25 mA cm⁻².

Fig. 11. Performance of Gr-Brush and uncoated brush cathode on phenol (0.33 mM) mineralization by EF: (a) TOC decay expressed in percentage of the initial TOC (TOC₀) vs electrolysis time and (b) calculated MCE values vs electrolysis time (E_{consum} (in kWh g-TOC⁻¹) to reach 75% mineralization in inset panel). Conditions: Pt anode, V = 400 mL, [Fe²⁺] = 0.1 mM, pH = 3, [K₂SO₄] = 50 mM, J = 1.25 mA cm⁻².

Fig. 12 Performance of graphene coating as measured by H₂O₂ electrogeneration performance.

Fig. 13. Performance of PTFE-carbon cloth anode compared to other carbon anode (carbon fiber brush, carbon felt, graphite), by comparing the kinetics of H_2O_2 accumulation in the bulk solution. Operating conditions: carbon fiber brush cathode, current density: 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0 \text{ mM}$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH}_{\text{init}} = 3$, $\text{pH}_{\text{final}} = 3$.

Fig. 14. Performance of Gr-Brush cathode combined with BDD anode (Gr-Brush/BDD) over other electrode combinations (Gr-Brush/Pt, Brush/BDD, Brush/Pt). Operating conditions: current density: $V = 400 \text{ mL}$, 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0.1 \text{ mM}$, $\text{pH} = 3$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$.

Description

Surprisingly, it has been found that the use of a graphene-coated carbon substrate or graphene itself as a cathode in an electro-Fenton process results in an unexpectedly significant increase of Fe(II) regeneration rate and H_2O_2 production yield, resulting in increased reaction speed, reduced energy usage and reduced costs.

Thus, there is provided an electro-Fenton apparatus comprising:

a cathode; and

an anode, wherein

the cathode is a non-graphene carbon substrate coated with graphene or is graphene.

As will be appreciated by a person in the art, an Electro-Fenton apparatus requires a vessel that is fitted with at least one cathode and anode and a power supply attached to the electrodes. In addition, the system may also require a supply of oxygen into the vessel (e.g. as air or oxygen) and a mixing means (e.g. a mechanical stirrer, or use of a pump to recirculate the fluid within the vessel). The system may also contain additional components, such as monitoring equipment and control systems (e.g. pH, temperature, and dissolved oxygen monitors and control systems).

As noted herein, the apparatus is intended to be used to treat wastewater. As such, the system is scalable and is intended to be used on an industrial scale, that is, to treat the wastewater produced from an industrial plant. When used herein, the term “wastewater” is intended to relate to any water that is contaminated by organic and/or inorganic pollutants that may be treated by the Electro-Fenton process. Examples of such wastewaters include those produced by as electronics, pharmaceutical, mining, chemical, refining, food processing, and textile industries. Other wastewaters that may be treated using the current

apparatus and process include hospital, commercial (e.g. restaurant) and domestic wastewaters.

The apparatus may be operated in any suitable configuration for handling wastewaters. For example, there may be a single cathode and anode, or there may be multiple cathodes and anodes in a single vessel. There may also be multiple vessels, each operating in sequence or parallel. Further, each vessel may be operated in a continuous batch mode or in a flow mode. It will be appreciated that the skilled person will consider the kind of wastewater and scale of operation and use these in determining the most suitable configuration for any particular application of the apparatus and process described herein.

When used herein, "graphene" may refer to a monolayer of graphene (i.e. a thickness of 0.37 nm), a foil (i.e. multilayer) of from 2 to 800 layers of graphene in thickness (e.g. around 230 nm, which is around 621 layers of graphene, particular values that may be mentioned herein include from 3 to 5 layers of graphene) or a graphene foam. The graphene used in the current invention may be a high-quality graphene (i.e. substantially no graphene oxide) or pristine graphene (i.e. substantially without defects). In other words, the graphene may have a sheet resistance of from 4.0 to 5.5 k Ω sq⁻¹, such as from 4.4 to 5.1 k Ω sq⁻¹. The resulting graphene-coated cathode may have a resistance of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω or less than or equal to 0.1 Ω and/or the cathode may have an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²). In additional or alternative embodiments, the graphene-coated cathode may show a decrease in resistance of greater than or equal to 90% (e.g. greater than or equal to 92.8%) when compared to an equivalent uncoated cathode, and/or the graphene-coated cathode may show an increase in electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode. It will be appreciated that the details provided above relate to individual cathodes. As such, if an apparatus uses multiple cathodes, the values may change accordingly. For example, when multiple cathodes are used in an apparatus, the total electroactive surface area will be a multiple of the electroactive surface areas values provided above.

When the cathode is graphene, the graphene may be in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene (e.g. from 2 to 800, such as from 3 to 5 layers). Suitable substrates for a monolayer of graphene include, but are not limited to, quartz, glass, silicon, silicon dioxide and nickel. When a graphene cathode is used, the resistance of the cathode may be from:

- (i) 0.1 to 2 Ω (e.g. 1.6 Ω) when the cathode is a graphene foam;

(ii) 500 to 5000 Ω (e.g. from 1500 to 4000 Ω , such as 3651 Ω) when the cathode is a monolayer graphene; or

(iii) from 1.0 to 200 Ω (e.g. from 50 to 150 Ω , such as 123 Ω) when the cathode is a multilayer graphene.

In embodiments where the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush. In particular embodiments that may be mentioned herein, the cathode may be a carbon cloth or a carbon fiber brush coated with a graphene as described hereinbefore. In embodiments of the invention mentioned herein, the carbon cloth may be a carbon cloth treated with polytetrafluoroethylene to provide 50% wetproofing (e.g. as measured using ASTM D7490).

A further advantage associated with the cathodes mentioned above is that, as demonstrated herein, the use of this electro-Fenton apparatus produces much more H_2O_2 from O_2 reduction at its surface than alternative materials. Since no iron electrode is employed, no sludge is produced. While this is true for the use of a carbon fiber brush coated with graphene, it is also true for the other graphene-coated cathodes and, indeed, for a cathode made from graphene itself. In addition, the use of certain of these cathode materials results in a cathode that is flexible and not fragile, but with high scalability and which is demonstrably more efficient than other cathode materials (e.g. uncoated carbon felt, graphite etc...).

When the cathode is a non-graphene carbon substrate coated with graphene, the graphene coating may comprise both graphene and a binder material. In embodiments of the invention that may be mentioned herein, the weight ratio of graphene to binder may be from 1:1 to 1:10, such as from 1:2 to 1:5, such as from 1:3 to 1:4. In particular embodiments that may be mentioned herein the non-graphene carbon substrate may be a carbon-fibre brush or a carbon cloth (e.g. a cloth treated with polytetrafluoroethylene), wherein the weight ratio of graphene to binder is 1:3 or 1:4, respectively.

Any suitable binder material may be used. Examples of such binder materials include, but are not limited to a fluorocarbon polymer. Suitable fluorocarbon polymer include, but are not limited to perfluorosulfonic acid, polytetrafluoroethylene, polyvinylfluoride, polyvinylidene fluoride, fluorinated ethylene propylene, polyethylenetetrafluoroethylene, polyethylenetrifluoroethylene, polychlorotrifluoroethylene, poly(chlorotrifluoroethylene-co-vinylidene fluoride), poly(chlorotrifluoroethylene-co-tetrafluoroethylene-co-vinylidene

fluoride), poly(hexafluoropropylene-co-vinylidene fluoride), poly(tetrafluoroethylene-co-hexafluoropropylene-co-vinylidene fluoride), polychlorotrifluoroethylene and a polysulfonated tetrafluoroethylene. Particular fluorocarbon polymers that may be mentioned herein include a sulfonated tetrafluoroethylene polymer (Nafion™) and polytetrafluoroethylene.

When the cathode is a non-graphene carbon substrate coated with graphene, the coating may be applied by forming a graphene ink solution and immersing the substrate in the solution for a period of time (e.g. from 1 hour to 24 hours, such as from 3 hours to 16 hours) at a temperature of from 20°C to 60°C (e.g. from 35°C to 59°C, such as 55°C), followed by drying the coated substrate to remove the solvent used in the graphene ink solution. This drying period may be from 10 minutes to 16 hours, such as from 30 minutes to 2 hours (e.g. 1 hour)) at a temperature sufficient to ensure almost complete removal of the solvent (e.g. from 100°C to 500°C, such as from 250°C to 350°C).

The graphene ink used herein may be prepared by adding graphene and the binder material (in amounts to provide the desired wt:wt ratios mentioned hereinbefore in the coated substrate) to an appropriate solvent (e.g. water and ethanol in a 1:1 v/v ratio) followed by agitation to obtain a well-dispersed ink. The agitation may be by any suitable method, for example by ultrasonication or by mechanical stirring.

In embodiments of the invention, the anode of the apparatus may be any suitable anode that can be used in an electro-Fenton reaction. Suitable anode materials include, platinum, carbon cloth, a boron doped diamond material on a substrate, a dimensionally stable anode made of iridium and/or ruthenium oxide coated on a substrate (e.g. titanium). In particular embodiments of the invention, the use of a boron doped diamond anode is preferred in the apparatus described hereinbefore. The boron doped diamond may be formed on a substrate, which may be any suitable conductive metal or metalloid substrate. Examples of suitable substrate materials for boron doped diamond include, but are not limited to, tantalum, tungsten, or more particularly, silicon, titanium and niobium.

When the cathode described herein is used in conjunction with a carbon cloth anode, the degradation power is unexpectedly higher than would have been expected, as is the lifetime of the cathode (as described below). In addition, when the cathode described herein is used in conjunction with a boron doped anode, there is an unexpected increase in the mineralization power of the apparatus. Further, as no iron electrode is employed, no sludge is produced.

As will be appreciated, the above apparatus is intended for use in the electro-Fenton process itself. Thus, there is also provided an electro-Fenton process to treat a wastewater, comprising:

contacting a wastewater with a cathode and an anode in a vessel under electro-Fenton conditions, wherein the cathode is a non-graphene carbon substrate coated with graphene or is graphene, optionally wherein the process further comprises adding a catalytic amount of an iron (II) salt to a wastewater in need thereof.

The above process uses the apparatus described above and so it is intended that all functional variations of the apparatus described herein above may be used.

The process may be conducted in any suitable vessel at a temperature of from 20°C to 55°C (e.g. from 25°C to 40°C, such as less than 40°C) and at a pH of from 2.0 to 9.0, such as 3.0 with a current density of from 0.5 mAcm⁻² to 20.0 mAcm⁻², such as from 1.0 mA cm⁻² to 15.0 mAcm⁻², e.g. 1.25 mAcm⁻², with air (or oxygen) being bubbled (e.g. at a flow rate of from 0.1 L min⁻¹ to 1 L min⁻¹, such as 0.2 L min⁻¹) into a wastewater to be treated during the reaction. The reaction may be conducted under continuous agitation. If the wastewater to be treated does not contain a sufficient source of iron, any suitable iron source may be added to the reaction (e.g. as an iron (II) or iron (III) salt (e.g. FeSO₄) to the wastewater in a sufficient quantity to enable the electro-Fenton reaction to take place (e.g. from 0.05 mM to 0.5 mM, such as 0.1 mM). If the ionic strength of the wastewater is not sufficient (e.g. less than 0.1 M, such as less than 0.15 M), an electrolyte (e.g. K₂SO₄, Na₂SO₄, NaCl, KClO₄, Na₂PO₄) may be added to the wastewater to provide sufficient ionic strength.

In a further aspect of the invention, there is provided a use of a non-graphene carbon substrate coated with graphene or graphene as a cathode in an electro-Fenton process. This electro-Fenton process may relate to the treatment of a wastewater as defined hereinbefore. It will be appreciated that the cathode used in this aspect is as described hereinbefore.

In embodiments of the invention, the use of a non-graphene carbon substrate coated with graphene or graphene as a cathode in an electro-Fenton process may make use of any suitable anode. For example, a carbon cloth anode, a platinum anode or, more particularly, a boron doped diamond anode. When the anode is a boron doped diamond anode it may be a boron doped diamond coating on a substrate, optionally wherein the substrate is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

Hereinafter, the embodiments are illustrated in more detail with reference to the following examples, and although specific terms are employed, they are used and are to be interpreted in a generic and descriptive sense only and not for purpose of limitation. In some instances, as would be apparent to one of ordinary skill in the art as of the filing of the present application, features, characteristics, and/or elements described in connection with a particular embodiment may be used singly or in combination with features, characteristics, and/or elements described in connection with other embodiments unless otherwise specifically indicated. Accordingly, it will be understood by those of skill in the art that various changes in form and details may be made without departing from the scope of the present invention as set forth in the following claims.

Examples

Materials

TiCl₄ (99.9%), phenol (> 99%), acetic acid (> 99%) and H₂O₂ (30% (v/v)) were purchased from Sigma-Aldrich (Singapore). Potassium sulphate (99%) was provided by Nacalai Tesque (Singapore). FeSO₄·7H₂O (> 99%), sulphuric acid (95% v/v) and ortho-phosphoric acid (85% (v/v)) were supplied by Merck (Singapore), methanol (99.9%) by Fisher Scientific (Singapore) and potassium permanganate (98%) by Acros Organics (Singapore). Nafion™ (sulfonated tetrafluoroethylene; 5% (w/v)) and ascorbic acid (> 99%) were purchased from GasHub Technology (Singapore) and Goodrich Chemical Enterprise (Singapore), respectively. All the chemicals were of analytical grade and were used as is. In all experiments, the solutions were prepared with ultrapure water from a Millipore system (Singapore, resistivity > 18 MΩ cm at room temperature).

Unless otherwise stated herein, any reference to “medium” in the examples below relates to the ultrapure water mentioned above.

Graphene foil sheets were obtained from Graphene Supermarket, with the following properties: size of 20.32x10.16 cm (8x4 inches); 97% carbon content; 25 micrometers thickness; density of 2 g/cm³; thermal conductivity of x-y plane, 1300-1500 W/(m)x(k); z plane, 13-15 W/(m)x(k); tensile strength of 30 MPa; and sheet resistance of 2.8 x 10⁻² ohm/square. (<https://graphene-supermarket.com/Conductive-Graphene-Sheets.html>)

Monolayer graphene was obtained from Graphene Supermarket on a quartz substrate (<https://graphene-supermarket.com/Monolayer-Graphene-film-on-Quartz-Size-1-x1.html>).

The carbon cloth used herein was obtained from Fuel Cell Earth (US) as Carbon Cloth CC6 Wet Proofed with 50% wet-proofing, and is a carbon cloth treated with polytetrafluoroethylene.

Preparation 1

Electrochemical Synthesis of Graphene

The electrochemical exfoliation technique made use of an inert piece of platinum (Pt) (30 cm²) obtained from Manilal Maganlal & Co (India) as a cathode and of a graphite anode, consisting of a pencil rod (Staedtler, Singapore), immersed in 150 mL of an aqueous sulphuric acid electrolyte (0.1 M). A low voltage of 2.5 V was applied at the anode for 5 minutes using a power supply (HAMEG 7042-5, Germany). After 5 minutes, the voltage was ramped up to about 10 V for 20 minutes to obtain exfoliated graphene in the electrolyte. The mixture of graphene and electrolyte was then centrifuged (Kubota 6500, Japan) at 4000 rpm for 30 minutes. After centrifugation, the top half of the solution was decanted into another beaker. A two-step filtration process was then applied in order to obtain a thin film of graphene coated over the filter; the solution was first filtered through a mesh of 6.5 μm before being subjected to vacuum filtration using a 0.45 μm -mixed cellulose ester filter (Pall Corporation, USA).

A picture of graphene obtained by transmission electronic microscopy (TEM) is shown in Fig. 1a.

Preparation 2

Chemical Exfoliation of Graphite

Graphene oxide was prepared in accordance with the procedure set out in *ACS Nano*. 4 (2010) 4806–4814 (the Tour's method, which is a modified Hummers method). The resultant graphene oxide (GO) was reduced with ascorbic acid (0.1 g L⁻¹) using the procedure set out in *Chem. Commun.* 46 (2010) 1112–1114. The reduced graphene oxide (rGO) solution obtained was then subjected to vacuum filtration using a 0.45 μm -mixed cellulose ester filter.

Preparation 3

Preparation of Carbon-Fibre Brush

The substrate consisted of polyacrylonitrile (PAN)-carbon fibers (SGL group, USA) shaped as a brush with stainless steel as current collector. In other words, carbon fibers (PAN)-carbon fibers were deposited on a stainless steel wire (the wire optionally coated with an inert polymer like PVC to prevent corrosion) and the coated wires were then twisted in order to obtain a brush shape (Fig. 2). While stainless steel wire has been used herein, it will be appreciated that any suitable conductive material may be used, such as a titanium wire, which will not corrode even if no additional coating is applied to its surface.

Preparation 4

Preparation of Carbon-Fiber Brush Coated With Graphene

Graphene powder was mixed with a binder (Nafion™) and an organic solvent (ethanol) in order to provide a graphene ink solution. The carbon fibre brush of Preparation 3 was immersed in the graphene ink solution to provide a carbon-fibre brush coated with graphene and then dried. Further details are provided below.

In order to proceed with the ink-coating method, conductive graphene ink was first synthesized, consisting of (i) graphene made as per the electrochemical method (Preparation 1) and used as a conductive functional material, and (ii) a mixture of ultrapure water/ethanol with Nafion™ as dispersant and binder. The conductive ink was prepared by mixing graphene at different concentrations (from 0 to 2 g/L) with different concentrations of Nafion™ (from 0 to 0.2% (w/v)) in a mixture of ultrapure water/ethanol (5 mL:5 mL; i.e. a 1:1 (v/v) ratio). The mixture was then sonicated for 10 min to ensure a homogenous and dispersed ink suspension.

The carbon-based substrate was then immersed in the graphene-ink suspension overnight in an oven (55°C) and, the following day, the graphene coated material was heated in a furnace at 360°C for 1h to ensure complete evaporation of the solvent. Alternatively, the drying step may involve placing the coated brush in an oven at 100°C for 1 h, followed by 370°C overnight.

The procedure was repeated to prepare a graphene-coated brush using chemical exfoliation technique discussed in Preparation 2.

Preparation 5

Preparation of Carbon Cloth Coated With Graphene

Different conductive inks (10 mL) were prepared by mixing various concentrations of Nafion™ (from 0% to 0.15% (w/v)) and graphene (from 0 to 3 mg mL⁻¹) in a solution of water/ethanol (5 mL:5 mL; i.e. 1:1 (v/v) ratio). Next, the graphene inks were ultrasonicated for 1 h to obtain a well-dispersed graphene suspension. Then, the raw carbon cloth was soaked in the prepared ink for 3 h at 55 °C and, subsequently, heated in the furnace for 1 h at 250 °C to remove residual moisture. To determine the final loading of graphene on the carbon cloth, the carbon cloth and dish (used to soak the cloth) were weighed before and after coating. The differences in initial and final weight were taken and used to calculate the weight of graphene transferred to cloth and remained in the dish. The weight of Nafion™ was previously subtracted to the weight of both cloth and dish.

The resulting coated cloth materials were then tested in the manner described below in Example 1 and it was found that a weight ratio of 1:4 graphene:Nafion™ was optimal for the cloth, with a graphene loading on cloth equivalent to 0.27 mg cm⁻² considering a 50% of graphene yield transfer to the cloth (the other 50% remained in the dish). Unless otherwise stated, any reference to graphene-coated cloth materials in the examples below refers to a weight ratio of 1:4 graphene:Nafion™.

Comparison Example 1

Characterization of the properties of graphene

The quality of the graphene produced by electrochemical (Preparation 1) and chemical methods (Preparation 2) was assessed functionally by determining its electrical properties. The sheet resistance, which is commonly used to assess the conductivity of graphene sheets, was determined using a custom two-point probe sheet resistance device using a Fluke (USA) multimeter in accordance with D.K. Schroder, *Semiconductor material and device characterization*, Third Ed., John Wiley & Sons, New-York, 2006.

The structural characterization of graphene was monitored (i) by a Horiba Jobin Yvon Modular Raman spectrometer at a laser excitation wavelength of 514 nm (Green) and a laser power of 50 mW and; (ii) by field transmission electron microscopy (TEM) (model JEM-2010F, JEOL (USA)) at an accelerating voltage of 200 kV.

Results

The resistances of the graphene sheets produced by the electrochemical (Preparation 1) and chemical methods (Preparation 2) are depicted in Fig. 3. The sheet resistance of electrochemical graphene was around 6-fold lower ($5.1 \pm 0.6 \text{ k}\Omega \text{ sq}^{-1}$) than that of rGO ($30 \pm 1.1 \text{ k}\Omega \text{ sq}^{-1}$). The electrical conductivity of rGO was in the usual range of values obtained by most of the GO reduction methods (from 14 to 52 $\text{k}\Omega \text{ sq}^{-1}$).

The electrochemical method offered several other advantages over the chemical approach. First, the time taken to produce electrochemical graphene ($\sim 2 \text{ h}$) was much shorter than that of chemical graphene ($\sim 1 \text{ week}$). The rate of graphene production averaged $30.0 \pm 0.6 \text{ mg h}^{-1}$ with electrochemical method against $1.2 \pm 0.5 \text{ mg h}^{-1}$ chemically. Second, the electrochemical technique was achieved in a diluted electrolyte (H_2SO_4 at 0.1 M in 150 mL), whereas the chemical method required a mixture of highly concentrated acids: H_2SO_4 (180 mL at 18 M), H_3PO_4 (20 mL at 12 M) and highly concentrated oxidants: H_2O_2 (1.5 mL at 10 M) and KMnO_4 (9 g in 200 mL equivalent to 0.3 M) (Fig. S2). Third, the chemical method required heating the solution at 50°C , which increased the energy consumption. In conclusion, the electrochemical exfoliation method was safer, more environmentally friendly and required less energy.

To further investigate the characteristics of the graphene obtained via the electrochemical method, TEM analysis and Raman spectroscopy were performed and the results are shown in Fig. 1. In Fig. 1a (left), a graphene sheet is clearly seen with a size of around $7.5 \mu\text{m}$. A high resolution TEM (HRTEM) micrograph of the edge of the graphene sheet is also displayed in Fig. 1a (right). The graphene sheet consists of 5 layers (2 nm in total) with an interlayer distance of 0.4 nm, close to the distance of 0.34 nm that corresponds to the theoretical mean thickness of a graphene monolayer.

The Raman spectrum of the electrochemically-exfoliated graphene is shown in Fig. 1b. The G peak at $\sim 1580 \text{ cm}^{-1}$ is representative of the sp^2 -hybridized carbon-carbon bonds in graphene, the 2D peak at $\sim 2689 \text{ cm}^{-1}$ is relevant to a stacking orders and the D peak at $\sim 1353 \text{ cm}^{-1}$ provides information on defects. The 2D/G intensity ratio is related to the degree of recovery of $\text{sp}^2 \text{ C}=\text{C}$ bonds (graphitization) in graphitic structures and further constitutes an indicator of the electrical properties of graphene. The 2D/G intensity ratio of the electrochemically-exfoliated graphene was 0.92, which was significantly higher than that of rGO (0.13-0.34) [42]. These results confirm the high quality and excellent electrical properties of the electrochemically-exfoliated graphene produced herein. The defects

observed were probably due to the overoxidation of graphite caused by sulphuric acid and by the application of a positive electrical potential for exfoliation.

Based upon these results, electrochemically-exfoliated graphene was used herein.

Example 1

Optimisation of Graphene/Binder Content in Graphene-coated brush

Method

The performance of the Gr-Brush cathodes (as prepared in Preparation 4) were evaluated by monitoring H_2O_2 electrogenerated at the electrode surface from O_2 reduction (Eq. 2). Electrolysis experiments were run at controlled temperature (35 ± 0.1 °C), in a 0.40 L open undivided glass reactor under current-controlled conditions for 2 h. The electrochemical cell was monitored with a power supply (HAMEG 7042-5, Germany). The current density was calculated by normalizing the applied current intensity to the projected surface area of the cathode – the working electrode – and was set at 1.25 mA cm^{-2} . The anode employed in all experiments was a piece of Pt (30 cm^2).

The distance between the cathode and the anode was kept constant at 3 cm. An electrolyte (K_2SO_4 at 0.050 M) was added into the medium in order to ensure constant ionic strength (0.15 M). The solutions were continuously stirred at 500 rpm. The initial pH of the solution was adjusted to 3, the optimal value for EF. In all experiments, compressed air was bubbled into the solution at a flow rate of 0.2 L min^{-1} for 20 min in order to reach saturation before starting the electrolysis. The bubbling was extended until the end of the electrolysis treatment to provide a continuous O_2 source for H_2O_2 production.

H_2O_2 was quantified by colorimetry using $TiCl_4$ as previously described by Brillas *et al.* in *J. Electrochem. Soc.* 143 (1996) 2–6. The absorbance of the complex was measured with a DR 5000 (HACH, USA) spectrophotometer at a wavelength of 410 nm. An external calibration curve was performed with a standard of H_2O_2 .

The efficiency of H_2O_2 electrogeneration with Gr-Brush compared to uncoated Brush ($\eta(H_2O_2)$) was calculated as follows:

$$\eta(H_2O_2) = \frac{[H_2O_2]_{Gr-Brush} - [H_2O_2]_{Brush}}{[H_2O_2]_{Brush}} \quad (4)$$

where $[H_2O_2]_{Gr-Brush}$ and $[H_2O_2]_{brush}$ are the maximal H_2O_2 concentration ($[H_2O_2]$) (mM) electrogenerated following 2 h of electrolysis at the surface of the Gr-Brush cathode and at the uncoated brush cathode, respectively.

The current efficiency (CE) for H_2O_2 production was calculated according to the following equation (Eq. 5):

$$CE = \frac{nF[H_2O_2]V}{It} \quad (5)$$

where n represents the stoichiometric number of electrons transferred for O_2 reduction to H_2O_2 (Eq. 2), F is the Faraday constant ($96\,487\text{ C mol}^{-1}$), $[H_2O_2]$ represents the concentrations of H_2O_2 (M), V is the volume of solution (L), I is the applied current intensity (A) and t is the electrolysis time (s).

In addition, the H_2O_2 electrocatalytic activity of both coated and uncoated materials was assessed by linear scanning voltammetry (LSV). These experiments were carried out at a scan rate of 5 mV s^{-1} and the potential scan range varied from 0 to -1.2 V vs Ag/AgCl. The solution consisted of 400 mL of electrolyte (K_2SO_4) at 50 mM and was acidified at pH 3.0. The solution was saturated with N_2 or O_2 by feeding with pure N_2 gas or compressed air for 20 min before the measurement.

Results

The conductive ink consisted of a mixture of graphene and NafionTM as a dispersant and binder. Since H_2O_2 is required to produce $\cdot OH$ (Eq. 1), which in turn are responsible for the oxidation of organic pollutants, it is a good indicator of the cathode efficiency. Therefore, the performance of the graphene coating was evaluated by monitoring the rate of H_2O_2 electrogenerated at the surface of Gr-Brush compared to an uncoated brush. The results are expressed as $\eta(H_2O_2)$ (Eq. 4).

First, the NafionTM concentration was optimized by varying its concentration from 0 to 0.2% (w/v) and the resulting values of $\eta(H_2O_2)$ are displayed in Fig. 4a. The corresponding NafionTM to graphene ratio is shown in brackets in Fig. 4a and varied from 0 to 1:1 (w/w). In the absence of NafionTM, $\eta(H_2O_2)$ was very close to zero ($-0.5 \pm 0.5\%$), meaning that graphene alone did not improve the raw brush in any way. Upon visual inspection, in those conditions Gr-Brush was shown to release graphene into the solution during electrolysis. Interestingly, at 0.025% (w/v) and 0.05% (w/v) NafionTM – equivalent to an increase from 1:8

(w/w) to 1:4 (w/w) – $\eta(\text{H}_2\text{O}_2)$ rose from $5 \pm 2\%$ to $16 \pm 3\%$. With increasing NafionTM concentrations, the graphene coating therefore improved, which was further confirmed by the absence of graphene being released at 0.05% (w/v) of NafionTM. However, at NafionTM concentrations higher than 0.05% (w/v), Fig. 4a shows that $\eta(\text{H}_2\text{O}_2)$ dropped down to negative values. The H_2O_2 production efficiency therefore decreased with Gr-Brush when the NafionTM concentration became too high. Visual inspection showed that the microfibers formed aggregates as the NafionTM concentration increased to very high values. This resulted in a decrease of the surface area of the raw brush, which in turn lowered the efficiency of Gr-brush. Therefore a 0.05% (w/v) NafionTM concentration was found to be optimal.

In order to optimize the coating efficiency, the concentration of graphene was then varied from 0 to 2.0 g L^{-1} at the optimal NafionTM concentration and the results are depicted in Fig. 4b. When no graphene was added into the NafionTM solution, $\eta(\text{H}_2\text{O}_2)$ approached 0 ($-0.5 \pm 1.2\%$), demonstrating that NafionTM on its own had no direct influence on the accumulation rate of H_2O_2 . This fact acts as another indirect evidence of the role of graphene in the enhancement of H_2O_2 electrocatalytic activity. As the concentration of graphene increased from 0.1 to 0.5 g L^{-1} , $\eta(\text{H}_2\text{O}_2)$ remained close to zero, meaning that the graphene concentration was too low to improve the brush performance. From 1.0 to 1.5 g L^{-1} of graphene, $\eta(\text{H}_2\text{O}_2)$ increased from $6 \pm 2.1\%$ to $40 \pm 4.2\%$, as a result of increasing specific surface area and conductivity of the raw brush. When the graphene concentration increased further to 2.0 g L^{-1} , $\eta(\text{H}_2\text{O}_2)$ decreased to $16 \pm 3\%$, indicating that the NafionTM concentration became limiting and unable to adequately disperse the sheets of graphene and bind them onto the brush. As a consequence, the graphene sheets started to aggregate, leading to a decrease of specific surface area and therefore a decrease of H_2O_2 accumulation. Applying a concentration of NafionTM higher than 0.05% (w/v) would likely avoid the aggregation of graphene sheets; however, this would result in the sticking of the brush microfibers, as previously described. Thus, a NafionTM to graphene mass ratio of 1:3 was considered to be optimal and was maintained in all other examples using a graphene-coated brush, unless otherwise stated.

In order to visualize the quality of the coating, optical micrographs of uncoated brush and Gr-Brush at the optimal ink coating conditions were taken (Fig. 5). The raw material clearly appears to be made of microfilaments with a diameter of around $15 \mu\text{m}$, resulting in a large specific surface area (Fig. 5a). Following coating with graphene, many nanoscale clusters of agglomerated sheets with a diameter ranging from 500 to $1,000 \text{ nm}$ were seen on the

surface of the fibers (Fig. 5b), which further enhanced the surface area and increased the gas-liquid contact interface in the modified samples.

Example 2

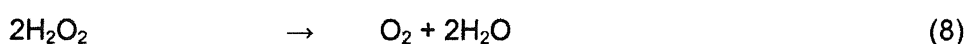
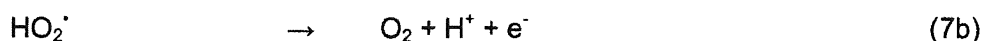
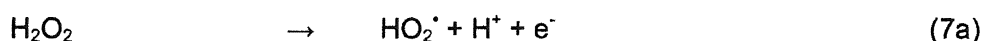
Hydrogen peroxide electrogeneration -Comparison of Graphene-coated and uncoated brushes

Method

The method used in Example 1 was repeated here using a graphene-coated carbon brush (Preparation 1; graphene:NafionTM mass ratio of 1:3) and compared with an uncoated carbon fiber brush (8 cm length and 5 cm diameter) obtained using Preparation 3.

Results

The H₂O₂ concentration evolution of Gr-Brush, as compared to the uncoated brush cathode, is displayed in Fig. 6a. A plateau was reached after around 90 min of electrolysis with both cathodes. This phenomenon could be explained by the occurrence of three waste reactions – (i) H₂O₂ reduction at the cathode (Eq. 6); (ii) H₂O₂ oxidation at the anode (Eqs. 7a-7b) and; (iii) to a lesser extent, H₂O₂ self-decomposition in the bulk solution (Eq. 8) – which counterbalanced the production rate of H₂O₂:



Thus, the maximum H₂O₂ concentration, determined from Fig. 6a for the uncoated brush and Gr-Brush, averaged 5.0 ± 0.2 mM and 7.0 ± 0.3 mM, respectively. Since these yields are strongly dependent upon the surface area of the cathode, they were normalized to the projected surface area of the brush in order to provide a comparison with the literature. Maximal H₂O₂ electrogeneration yields of 3.00 ± 0.12 mg-H₂O₂ L⁻¹ cm⁻² and 4.23 ± 0.18 mg-H₂O₂ L⁻¹ cm⁻² were obtained with the uncoated brush and Gr-Brush, respectively, showing the superiority of Gr-Brush, which outperformed the uncoated brush by 40%. Such increase in H₂O₂ production could be attributed to graphene adhesion onto the raw brush. The maximal H₂O₂ yields obtained with Gr-Brush is much higher than would be anticipated (e.g. graphite felt, which has a maximal yield of 1.05 mg-H₂O₂ L⁻¹ cm⁻²).

The improved H_2O_2 production efficiency with Gr-Brush was consistent with the *CE* calculations showcased in Fig. 6b. Both *CE* values were high at 0.83 ± 0.02 and 0.95 ± 0.01 for the uncoated brush and Gr-Brush, respectively, after 90 min of electrolysis, the time to reach the H_2O_2 concentration equilibrium. This high *CE* value confirmed the adequate performance of the uncoated brush itself to promote the generation of H_2O_2 , while inhibiting its decomposition.

To further investigate the ORR activity that was responsible for H_2O_2 generation at the uncoated brush and Gr-Brush cathodes, LSV measurements were obtained in N_2 - and O_2 -saturated solutions of K_2SO_4 (50 mM) electrolyte adjusted to pH 3 – the optimal pH for EF (Fig. 7). When the solution was saturated with N_2 , the absence of dissolved O_2 prevented any ORR activity and only the parasitic H_2 evolution reaction (HER) was possible (Eq. 9):



At a given cathode, a difference of current between N_2 -saturated and O_2 -saturated solutions therefore represents the net current involved in the ORR activity via the 2-electron reaction pathway that generates H_2O_2 (Eq. 2). Therefore a higher net current implies higher ORR activity and higher H_2O_2 production. The ORR activity of Gr-Brush was compared quantitatively to that of the uncoated brush electrode at -1.0 V vs Ag/AgCl, a value that was found optimal to electrogenerate H_2O_2 at a carbon fiber brush cathode, while higher voltages were found to trigger HER (Eq. 12) and to increase the rates of the other waste reactions that decompose H_2O_2 (Eqs. 9-11). In these conditions, Fig. 7 shows that the net current exhibited with Gr-Brush and the uncoated brush equaled 1.25 mA cm^{-2} and 0.4 mA cm^{-2} , respectively, which represents a 3.1-fold improvement of ORR activity in the presence of graphene. The better performance of Gr-Brush can be explained by the presence of graphene, which increased the conductivity and the electroactive surface of the Gr-Brush cathode, as stated above. The higher conductivity increased the rate transfer of electrons at the cathode surface and therefore the rate of H_2O_2 production (Eq. 2). The improved ORR activity of Gr-Brush, as compared to the uncoated brush, corroborates its higher *CE* as well as the higher H_2O_2 production rates and yields observed.

These electrocatalytic properties of the Gr-Brush emphasize the unexpected benefits of graphene in the electro-Fenton process.

Example 3

Comparison of Cathode Materials

Methodology:

Electro-Fenton (EF) experiments are performed in an undivided electrochemical reactor under current-controlled conditions. The electrochemical cell was connected to a power supply. The cathode material was:

- a carbon fiber brush coated with graphene as prepared in Preparation 4 - the graphene:Nafion™ ratio was 1:3;
- an uncoated carbon fiber brush as prepared in Preparation 3;
- graphene foil (multiple layers of graphene); and
- monolayer graphene on a quartz substrate.

A platinum anode material was used.

Electrolysis experiments were performed using a platinum-based anode material under the following operating conditions: *current density*: 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0 \text{ mM}$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH}_{\text{init}} = 3$, $\text{pH}_{\text{final}} = 3$. The experiments were monitored by monitoring H_2O_2 formation, since a higher concentration of H_2O_2 guarantees a higher production of hydroxyl radicals through the Fenton reaction and therefore a higher process efficiency.

The reaction was run using ultrapure water as medium. No iron was added in this example, as this example was aimed at measuring the production of hydrogen peroxide only.

Results

Figure 8 displays the performance of various cathodes using a platinum-based anode material under the following operating conditions: *current density*: 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0 \text{ mM}$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH}_{\text{init}} = 3$, $\text{pH}_{\text{final}} = 3$. As shown in Figure 8, the performance of the cathode material that has a graphene coating on a carbon fiber brush was compared to graphene itself (single or multi-layer(s) (i.e. graphene foil)) and the carbon fiber brush itself. No iron was added in to this experiment since the monitoring of H_2O_2 concentration was chosen as the best criteria for cathode material selection. This is because the addition of iron would react with H_2O_2 to form $\cdot\text{OH}$, obscuring the desired comparative data. The H_2O_2 production rate of the graphene coated carbon fiber brush ($0.065 \text{ mM min}^{-1}$) was much

higher compared to the other materials tested, i.e., uncoated brush ($0.043 \text{ mM min}^{-1}$), graphene foil ($0.0008 \text{ mM min}^{-1}$) and single layer graphene ($0.0002 \text{ mM min}^{-1}$). This translates to a H_2O_2 production yield instead of the production rate, with the following production yields:

- Gr-Brush: $4.23 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$;
- Uncoated Brush: $3.00 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$;
- Graphene foil: $0.048 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$; and
- Graphene single layer: $0.032 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$.

The enhancement observed for the graphene-coated brush as compared to single layer graphene, graphene foil and uncoated brush is 32,253%, 7512% and 49%, respectively. It is clear that a synergistic effect is observed when graphene is combined with the carbon fiber brush. The great increase in performance of the graphene-coated carbon fiber brush can be explained by the high specific surface area of the brush that is further (synergistically) enhanced by the presence of graphene.

Example 4

Comparison of Anode Materials

Methodology:

The degradation and mineralization of phenol (0.33 mM) – chosen as a model pollutant – was conducted by using an Electro-Fenton process. Electrolysis experiments were run at controlled temperature ($35 \pm 0.1 \text{ }^\circ\text{C}$), in a 0.40 L open undivided glass reactor at current controlled conditions during 2 h . The electrochemical cell was monitored by a power supply HAMEG 7042-5 (Germany). The current density was calculated by normalizing the applied current intensity with the projected surface area of the cathode – the working electrode - and was set at 1.25 mA cm^{-2} . The anode employed was varied as described below. The Gr-Brush was employed as cathode and was compared with the performance of the uncoated Brush (7 cm length and 4 cm diameter). The distance between the cathode and the anode was kept to 3 cm . An electrolyte (K_2SO_4 at 0.050 M) is added to the medium in order to ensure constant ionic strength (0.15 M). The solutions were continuously stirred at 500 rpm . The initial pH of the solution was adjusted to 3, the optimal value for EF. In all experiments, compressed air was bubbled into the solution at a flow rate of 0.2 L min^{-1} for 20 min in order to reach saturation before starting the electrolysis. The bubbling was extended until the end of the electrolysis treatment to provide a continuous O_2 source for H_2O_2 production. FeSO_4

(0.1 mM) was added into the medium as a source of Fe^{2+} to implement the Fenton's reaction (Eq. 1).

The decay of phenol was followed by reversed phase high performance liquid chromatography (HPLC) (Shimadzu SCL-10A, Japan) coupled with a UV-absorbance detector (Shimadzu SPD-M10A, Japan). A Zorbax® C-18 column (15 cm length, 5 μm of stationary phase thickness) (Agilent, USA) was used and placed in an oven and set at 40.0 °C. The mobile phase consisted of a mixture of ultrapure water and acetic acid (1%)/methanol (75:25 (v/v)) and the flow rate was set at 0.25 mL min⁻¹. Analyses were carried out at isocratic elution mode. The UV detection was set at 280 nm.

Total organic carbon (TOC) was monitored to quantify the degree of mineralization during the EF treatment of phenol. The TOC values were determined by thermal catalytic oxidation (680°C) using a Shimadzu V_{CSH} TOC analyzer (Japan). The mineralization current efficiency (MCE) was calculated as follows (Eq. 10):

$$MCE = \frac{nF\Delta(\text{TOC})V}{4.32 \times 10^7 mIt} \quad (10)$$

where n is the number of electrons exchanged per phenol molecule mineralized, $\Delta(\text{TOC})$ the experimental TOC decay (mg-C L⁻¹), 4.32×10^7 is the conversion factor to homogenize the units ($= 3600 \text{ s h}^{-1} \times 12,000 \text{ mg-C mol}^{-1}$), m is the number of carbon atoms that the phenol molecule contains.

Finally, the Energy consumption (E_{consum} expressed in kWh g-TOC⁻¹) was calculated following the method of Brillas *et al.* (Eq. 11):

$$E_{\text{consum}} = \frac{E_{\text{cell}}It}{\Delta(\text{TOC})V} \quad (11)$$

where E_{cell} is the average cell voltage (V).

All of the experiments were performed in duplicate and the results are given in the text at a 95% confidence interval by using the Student's t-distribution.

The anode was varied as follows:

- a platinum plate anode;
- a single-sided BDD plate (2.5×8 (cm)) coated on a niobium substrate (0.2 cm thick) - the plate purchased from Condias, Germany; and
- a carbon cloth (5×13.5 (cm)).

Results

Figures 9a and 9b compare BDD anode performance to a carbon cloth anode and to a Pt anode, regarding the degradation and mineralization evolution of phenol (1 mM) as a function of the electrolysis time, respectively. BDD gives better kinetics of degradation and mineralization compared to carbon cloth and Pt anodes since heterogeneous $\cdot\text{OH}$ are also produced at the surface of BDD anode. The kinetics of the carbon cloth and Pt materials are similar, but Pt is much more expensive than carbon cloth, which makes carbon cloth a very promising anode. Therefore, the combination of graphene-coated carbon brush cathode and carbon cloth anode is promising, as is the combination of the graphene-coated carbon brush cathode with a BDD anode.

Conclusions:

Based upon the above examples, graphene coated on carbon fiber brush cathode displays improved performance compared to graphene alone or brush alone. Moreover, carbon cloth anode as well as BDD anode displayed better performance than other electrode materials conventionally employed for electrochemical techniques.

Example 5

Assessment of graphene-based electrode performance in Electro-Fenton process

The degradation and mineralization of phenol (0.33 mM) – chosen as a model pollutant – was conducted by using an Electro Fenton process. Electrolysis experiments were run at controlled temperature (35 ± 0.1 °C), in a 0.40 L open undivided glass reactor at current controlled conditions during 2 h. The electrochemical cell was monitored by a power supply HAMEG 7042-5 (Germany). The current density was calculated by normalizing the applied current intensity with the projected surface area of the cathode – the working electrode - and was set at 1.25 mA cm^{-2} . The anode employed in all the experiments was a piece of Pt (30 cm^2). The Gr-Brush was employed as cathode and was compared with the performance of the uncoated Brush (7 cm length and 4 cm diameter). The distance between the cathode

and the anode was kept to 3 cm. An electrolyte (K_2SO_4 at 0.050 M) is added to the medium in order to ensure constant ionic strength (0.15 M). The solutions were continuously stirred at 500 rpm. The initial pH of the solution was adjusted to 3, the optimal value for EF. In all experiments, compressed air was bubbled into the solution at a flow rate of 0.2 L min^{-1} for 20 min in order to reach saturation before starting the electrolysis. The bubbling was extended until the end of the electrolysis treatment to provide a continuous O_2 source for H_2O_2 production. FeSO_4 (0.1 mM) was added into the medium as a source of Fe^{2+} to implement the Fenton's reaction (Eq. 1).

The decay of phenol and TOC were measured as described in Example 4.

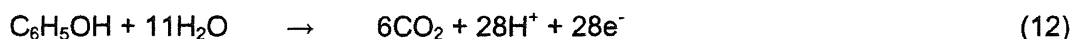
Results

Phenol is not only a contaminant found in industrial wastewater streams from oil refineries, petrochemical and coal conversion plants, and chemical industries in general, but it is also a very commonly used model molecule for testing and comparing the efficacies of AOPs. Phenol was added at a concentration of 0.33 mM with FeSO_4 as a source of Fe^{2+} , in order to generate $\cdot\text{OH}$ through the Fenton's reaction (Eq. 1) (Fig. 10). After 2 h of treatment, the phenol removal yield reached $99.0 \pm 0.4\%$ and $91.4 \pm 0.7\%$ with Gr-Brush and the uncoated brush, respectively. The pseudo-first order kinetic constants (k_{app}) were compared for the coated and uncoated cathodes, assuming a quasi-stationary state for $\cdot\text{OH}$ concentration. The linear regression of the semi-logarithmic plots depicted in the inset panel of Fig. 10 shows k_{app} values of $0.0600 \pm 0.0003 \text{ min}^{-1}$ and $0.0261 \pm 0.0002 \text{ min}^{-1}$ for Gr-Brush and the uncoated brush, respectively. Correspondingly, the half-life time ($t_{1/2}$) of phenol degradation decreased from 26.5 min to 11.5 min. The excellent correlation coefficients ($R^2 > 0.990$) highlight the good fitting between the experimental data and the pseudo-first order kinetic model and the overall superiority of Gr-Brush. Faster H_2O_2 production and Fe(II) regeneration led to enhanced production of $\cdot\text{OH}$, which in turn was responsible for improved phenol degradation.

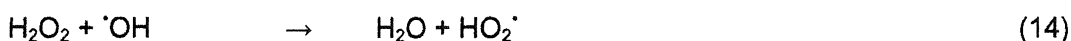
TOC was monitored to determine the mineralization efficiency of Gr-Brush and of the uncoated brush by EF and the results are displayed in Fig. 11a. The decrease of TOC was much faster with Gr-Brush and the final TOC decay averaged $98.5 \pm 1.0\%$, following 6 h of EF treatment, vs. $78.0 \pm 1.3\%$ using an uncoated brush. Consequently, the remaining TOC equaled $0.34 \pm 0.24 \text{ mg-C L}^{-1}$ and $5.28 \pm 0.31 \text{ mg-C L}^{-1}$, with Gr-Brush and the uncoated brush, respectively. The superiority of Gr-Brush could again be attributed to the improved

properties of the electrochemically-exfoliated graphene, leading to a mineralization yield of 20.5%.

The *MCE* was calculated according to Eq. 10 in order to compare the energy efficiency of Gr-Brush and of the uncoated brush (Fig. 11b). The number of electrons transferred per molecule of phenol mineralized can be determined through the following equation (Eq. 12):



Thus, 28 moles of electrons (n) were required for the complete mineralization of 1 mol of phenol. During the 6-h EF treatment, *MCE* decreased from 0.60 ± 0.03 to 0.22 ± 0.02 and from 0.48 ± 0.02 to 0.17 ± 0.01 with Gr-Brush and the uncoated brush, respectively. The continuous decrease could be explained by the occurrence of several waste reactions (Eqs. 13-14) favored by the increasing concentration of carboxylic acids, as the easily mineralized aromatic intermediates concentration decreased:



These waste reactions played a scavenging role by competing with the Fenton's reaction (Eq. 1). Besides, $\cdot\text{OH}$ generation required the mass transport of reactants, which affected the efficiency of mineralization and this could explain why all *MCE* values were below 1.

The energy consumed to achieve 75% phenol mineralization was calculated according to Eq. 11. The E_{consum} values are depicted in the inset of Fig. 11b. The energy requirements were 0.250 ± 0.008 kWh g-TOC⁻¹ and 0.080 ± 0.005 kWh g-TOC⁻¹ with the uncoated brush and Gr-Brush, respectively, meaning that the use of Gr-Brush led to a 3.1-fold reduction of energy consumption. This difference was partly accredited to the lower E_{cell} applied to perform experiments with Gr-Brush as compared to the uncoated brush. The increase of surface area in the presence of graphene may also play an important role in the enhanced treatment efficiency.

In addition to the above, the resistance of the coated brush to the uncoated brush was 0.1Ω to 1.40Ω (a 93% decrease) and the electroactive surface area was $4,665 \text{ cm}^2$ to 416 cm^2 (a 1021% increase), respectively.

Example 6

Graphene-coated cloth as cathode

Methodology

Phenol was again chosen as a synthetic and representative pollutant. The ink-coating technique and the electrochemical setup are identical to Example 5. The following carbon cloths were tested:

- raw cloth;
- pyrolysed raw cloth;
- graphene cloth; and
- pyrolysed graphene cloth.

The graphene-based carbon cloth was prepared as described in Preparation 5, with a weight ratio of 1:4 graphene:NafionTM. The pyrolysing treatment was applied at 1000°C on the raw cloth or after coating the graphene on the cloth. The carbon cloths described above were each individually used as the cathode while an inert piece of platinum (15 cm²) was used as the anode and the distance between them was 4 cm.

Results

Carbon cloth was used as raw material and the quality of the coating was assessed by visual observation as well as by monitoring H₂O₂ production, as described in Example 1. The graphene-coated cloth (Gr cloth) and the pyrolysed Gr cloth were able to produce 2 and 2.3-times more H₂O₂ than the uncoated equivalents, respectively, (Figure 12) demonstrating performance enhancement in the presence of graphene combined with the application of thermal treatment. Thus, graphene-coated carbon cloth may be a suitable cathode for electro-Fenton treatment of wastewater.

In addition to the above, the resistance of the coated cloth to the uncoated cloth was 2.45 Ω to 81.08 Ω (a 97% decrease) and the electroactive surface area was 6.31 cm² to 0.57 cm² (a 1007% increase), respectively. Moreover, by following the electro-Fenton setup from Example 5, the phenol (1.4 mM) degradation rate of the coated cloth to the uncoated cloth was 0.0157 min⁻¹ to 0.0051 (a 208% increase) while the mineralization yield after 8h was 56.6% to 41.2% (a 16% increase) and the energy consumption at 40% mineralization was 0.20 kWh g-TOC⁻¹ to 0.31 kWh g-TOC⁻¹ (a 36% decrease).

Example 7

Carbon fiber brush as cathode with carbon cloth as anode compared to other carbon-based electrodes combinations

Methodology:

Electro-Fenton (EF) experiments are performed in an undivided electrochemical reactor under current-controlled conditions. The electrochemical cell was connected to a power supply. The anode material was:

- an uncoated carbon fiber brush as prepared in Preparation 3;
- a raw carbon cloth;
- a carbon felt; and
- a graphite plate.

A carbon fiber brush cathode material was used as prepared in Preparation 3.

Electrolysis experiments were performed using a carbon fiber brush cathode material under the following operating conditions: *current density*: 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0 \text{ mM}$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH}_{\text{init}} = 3$, $\text{pH}_{\text{final}} = 3$. The experiments were monitored by monitoring H_2O_2 formation, since a higher concentration of H_2O_2 guarantees a higher production of hydroxyl radicals through the Fenton reaction and therefore a higher process efficiency.

The reaction was run using ultrapure water as medium. No iron was added in this example, as this example was aimed at measuring the production of hydrogen peroxide only.

Results

Figure 13 displays the performance of various carbonaceous anodes using a carbon fiber brush cathode material under the following operating conditions: *current density*: 1.25 mA cm^{-2} , $[\text{Fe}^{2+}] = 0 \text{ mM}$, $[\text{K}_2\text{SO}_4] = 0.05 \text{ M}$, $\text{pH}_{\text{init}} = 3$, $\text{pH}_{\text{final}} = 3$. As shown in Figure 13, the performance of the anode material that has PTFE coating on a carbon cloth was compared to other raw carbonaceous material (i.e. uncoated carbon fiber brush, carbon felt and graphite plate)). No iron was added in to this experiment since the monitoring of H_2O_2 concentration was chosen for electrode materials combination selection.

It would be expected that all the kinetics of H_2O_2 concentration evolution would be similar, since the H_2O_2 production is governed by the cathode (which is the same in all experiments, i.e. uncoated brush). However, different maximum H_2O_2 production yield were obtained according to the electrode combination, with the following production rates (cathode/anode):

- Uncoated Brush/Cloth: $3.00 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$;
- Uncoated Brush/Graphite plate: $1.14 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$;
- Uncoated Brush/Carbon felt: $0.55 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$; and
- Uncoated Brush/Uncoated Brush: $0.072 \text{ mg-H}_2\text{O}_2 \text{ L}^{-1} \text{ cm}^{-2}$.

The H_2O_2 production yield of the uncoated Brush/Cloth combination ($0.065 \text{ mM min}^{-1}$) was much higher compared to the other materials combination tested.

The enhancement observed for the uncoated Brush/Cloth combination as compared to uncoated Brush/Graphite plate, uncoated Brush/Carbon felt, and uncoated Brush/uncoated Brush combinations is 163%, 445% and 4066%, respectively. It is clear that a synergistic effect is observed when uncoated Brush cathode is combined with the carbon cloth anode. The great increase in performance of the uncoated Brush/Cloth combination can be explained by the PTFE coated on the cloth that limit the oxidation of carbonaceous material when used as anode, giving a longer lifetime to the cloth anode as compared to the felt, the graphite and the brush anodes.

Example 8

Graphene-coated brush as cathode with BDD as anode compared to other electrode combinations

Methodology

Phenol was again chosen as a synthetic and representative pollutant. The ink-coating technique and the electrochemical setup are identical to Example 5. The following electrode combinations were tested (cathode/anode):

- Gr-Brush/BDD;
- Gr-Brush/Pt;
- Uncoated brush/BDD; and
- Uncoated brush/Pt.

The graphene-based carbon fiber brush was prepared as described in Preparation 4, with a weight ratio of 1:3 graphene:Nafion™.

Results

The phenol degradation and mineralization during an electro-Fenton treatment were monitored - as described in Example 5 - with different electrodes combinations (cathode/anode), i.e. Gr-Brush/BDD, Gr-Brush/Pt, Uncoated brush/BDD and Uncoated brush/Pt (Figure 14). As shown in Figure 14, the following phenol degradation efficiency rank was obtained: Gr-Brush/BDD (0.0936 min^{-1}) > Brush/BDD (0.0807 min^{-1}) > Gr-Brush/Pt (0.0623 min^{-1}) > Brush/Pt (0.0275 min^{-1}). In addition, the following mineralization efficiency rank was given: Gr-Brush/BDD (0.9275 h^{-1}) > Gr-Brush/Pt (0.8076 h^{-1}) > Brush/BDD (0.7573 h^{-1}) > Brush/Pt (0.32 h^{-1}).

In any case it is observed higher improvement with Gr-Brush/BDD (compared to Gr-Brush/Pt, Brush/BDD and Brush/Pt) in degradation and mineralization during an electro-Fenton treatment with the following percentage increase:

- Gr-Brush/BDD vs Brush/BDD: 22% (mineralization) and 16% (degradation)
- Gr-Brush/BDD vs Brush/Pt: 190% (mineralization) and 240% (degradation)
- Gr-Brush/BDD vs Gr-Brush/Pt: 15% (mineralization) and 50% (degradation)
- Gr-Brush/Pt vs Brush/Pt: 152% (mineralization) and 126% (degradation)

Moreover, by comparing Brush/BDD and Brush/Pt, the superiority of BDD anode compared to Pt anode is again highlighted as in Example 4, with an increased phenol degradation rate constant of 193%, while an increase in the mineralization rate constant of 137% was noticed.

Claims

1. An electro-Fenton apparatus comprising:
a cathode; and
an anode, wherein
the cathode is a non-graphene carbon substrate coated with graphene or is graphene;
the graphene has a sheet resistance of from 4.0 to 5.5 kΩ sq⁻¹; and
when the cathode is a non-graphene carbon substrate coated with graphene the graphene coating comprises a graphene and a binder material where the weight ratio of graphene to binder material is from 1:1 to 1:10.
2. The apparatus of Claim 1, wherein:
 - (a) the graphene has a sheet resistance of from 4.4 to 5.1 kΩ sq⁻¹; and/or
 - (b) the graphene-coated cathode has a resistance value of less than or equal to 3.0 Ω, such as less than or equal to 0.2 Ω, such as less than or equal to 0.1 Ω; and/or
 - (c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, has a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or
 - (d) the cathode has an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²); and/or
 - (e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode; and/or
 - (f) the binder material is a fluorocarbon polymer.
3. The apparatus of Claim 1, wherein:
 - (a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or
 - (b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene.
4. The apparatus of Claim 3, wherein the non-graphene carbon substrate is a carbon cloth (e.g. carbon cloth treated with polytetrafluoroethylene) or a carbon fiber brush.
5. The apparatus of Claim 1, wherein the anode is a boron doped diamond anode.

6. The apparatus of Claim 5, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate for the boron doped diamond coating is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

7. An electro-Fenton process to treat a wastewater, comprising:

contacting a wastewater with a cathode and an anode in a vessel under electro-Fenton conditions, wherein:

the cathode is a non-graphene carbon substrate coated with graphene or is graphene,

the graphene has a sheet resistance of from 4.0 to 5.5 k Ω sq⁻¹; and

when the cathode is a non-graphene carbon substrate coated with graphene the graphene coating comprises a graphene and a binder material where the weight ratio of graphene to binder material is from 1:1 to 1:10,

optionally wherein the process further comprises adding a catalytic amount of an iron (II) salt to a wastewater in need thereof.

8. The process of Claim 7, wherein:

(a) the graphene has a sheet resistance of from 4.4 to 5.1 k Ω sq⁻¹; and/or

(b) the cathode has a resistance value of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω , such as less than or equal to 0.1 Ω ; and/or

(c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, has a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or

(d) the cathode has an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²); and/or

(e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode.

9. The process of Claim 7, wherein:

(a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or

(b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene.

10. The process of Claim 9, wherein the non-graphene carbon substrate is a carbon cloth or a carbon fiber brush.
11. The process of Claim 7, wherein the anode is a boron doped diamond anode.
12. The process of Claim 11, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.
13. Use of a non-graphene carbon substrate coated with graphene or graphene as a cathode in an electro-Fenton process, wherein:
 - the graphene has a sheet resistance of from 4.0 to 5.5 k Ω sq⁻¹; and
 - when the use is a use of a non-graphene carbon substrate coated with graphene as a cathode in an electro-Fenton process, the graphene coating comprises a graphene and a binder material where the weight ratio of graphene to binder material is from 1:1 to 1:10.
14. The use of Claim 13, wherein the electro-Fenton process relates to the treatment of a wastewater.
15. The use of Claim 13, wherein:
 - (a) the graphene has a sheet resistance of from 4.4 to 5.1 k Ω sq⁻¹; and/or
 - (b) the graphene-coated cathode has a resistance value of less than or equal to 3.0 Ω , such as less than or equal to 0.2 Ω , such as less than or equal to 0.1 Ω ; and/or
 - (c) the graphene-coated cathode, when compared to an equivalent uncoated cathode, has a decrease in its resistance value of greater than or equal to 90%, such as greater than or equal to 92.8%; and/or
 - (d) the cathode has an electroactive surface area of from 2,000 cm² to 10,000 cm², such as from 3,500 cm² to 5,000 cm² (e.g. 4,665 cm²); and/or
 - (e) the cathode has an electroactive surface area of greater than or equal to 1000% in comparison to an equivalent uncoated cathode.
16. The use of Claim 13, wherein:
 - (a) when the cathode is a non-graphene carbon substrate coated with graphene, the non-graphene carbon substrate is selected from the group consisting of a carbon cloth, a carbon felt, a carbon fiber wire, graphite or a carbon fiber brush; or

(b) when the cathode is graphene, the graphene is in the form of a graphene foam, a monolayer of graphene on a substrate or a multilayer graphene (e.g. from 2 to 800 layers).

17. The use of Claim 16, wherein the non-graphene carbon substrate is a carbon cloth or a carbon fiber brush.

18. The use of Claim 13, wherein the use further comprises the use of a boron doped diamond anode.

19. The use Claim 18, wherein the boron doped diamond anode comprises a boron doped diamond coating on a substrate, optionally wherein the substrate is selected from one or more of the group consisting of tantalum, tungsten, silicon, titanium and niobium.

20. The apparatus according to any one of Claims 1 to 6, wherein the cathode is a non-graphene carbon substrate coated with graphene; or

the process according to any one of Claims 7 to 12, wherein the cathode is a non-graphene carbon substrate coated with graphene; or

the use according to any one of Claims 13 to 19, wherein the use is a use of a non-graphene carbon substrate coated with graphene as a cathode in an electro-Fenton process.