Claims:

[Claim 1]. An apparatus for functionalizing graphene or graphene oxide, the apparatus comprising:

a plasma generator;

a treatment chamber connected to the plasma generator;

a substrate holder, positioned to hold a substrate for electron microscopy, preferably cryogenic electron microscopy, having a graphene or graphene oxide layer thereon within the treatment chamber, and having a mounting area configured to have a substrate mounted therein;

a shutter movable between an open position, in which the mounting area of the substrate holder is exposed to the treatment chamber, and a closed position, in which the mounting area of the substrate holder is concealed;

an injector, for injecting a functionalizing compound into the treatment chamber; and

a helium source, for supplying helium to the plasma generator.

[Claim 2]. An apparatus according to claim 1, wherein the apparatus further comprises a mask for masking an area of the substrate.

[Claim 3]. An apparatus according to claim 2, wherein the mask is moveable.

[Claim 4]. An apparatus according to claim 2 or claim 3, wherein the mask is removable from the remainder of the apparatus.

[Claim 5]. An apparatus according to any one of claims 2-4, wherein the apparatus is configured such that the mask is not in contact with the graphene or graphene oxide layer of the substrate when the substrate is held in the substrate holder.

[Claim 6]. An apparatus according to claim 5, wherein the apparatus is configured such that the mask is positioned less than 200 μm above the surface of the substrate when the substrate is held in the substrate holder.

[Claim 7]. An apparatus according to any one of claims 1-6, further comprising a hydrogen source, for supplying hydrogen to the plasma generator.

[Claim 8]. An apparatus according to any one of claims 1-7, further comprising a viewport opening into the treatment chamber and a UV-vis spectrometer configured to analyse radiation emitted from the treatment chamber through the viewport.

[Claim 9]. An apparatus according to any one of claims 1 to 8, further comprising one or more functionalizing compound sources, each being connected to the injector, for supplying the functionalizing compound or compounds to the injector.

[Claim 10]. An apparatus according to any one of claims 1 to 9, comprising a plurality of injectors, each injector being connected to a respective functionalizing compound source for supplying the functionalizing compound to the respective injector.

[Claim 11]. An apparatus according to any one of claims 1 to 10, wherein the injector or injectors is/are gas injector/s.

[Claim 12]. A method of functionalizing graphene or graphene oxide on a substrate for use in electron microscopy using an apparatus according to any one of claims 1-11, the method comprising:

- placing a substrate having a layer of graphene or graphene oxide thereon, for use in electron microscopy, in the substrate holder;
- supplying helium to the plasma generator to form a helium plasma in the treatment chamber;
- injecting a functionalizing compound into the treatment chamber; and
- exposing the substrate to the plasma comprising helium and the functionalizing compound.

[Claim 13]. A method according to claim 12, wherein , before exposing the substrate to the plasma comprising helium and the functionalizing compounds, a mask is applied to the substrate, to selectively expose only a part of the substrate.

[Claim 14]. A method according to claim 13, wherein the mask is moved during exposure of the substrate to the plasma comprising helium and the functionalizing compound.

[Claim 15]. A method according to any one of claims 13 or 14, further comprising, after exposing the substrate to the plasma comprising helium and the functionalizing compound,

- ceasing injection of the functionalizing compound;
- unmasking the substrate;
- masking a different area of the substrate;
- injecting a further functionalizing compound into the treatment chamber;
- exposing the substrate to the plasma comprising helium and the further functionalizing compound;

and, optionally, repeating these steps using a different functionalizing compound in each repeat, to form a substrate with multiple zones each having different functionalization.

[Claim 16]. A method according to any one of claims 12-15, wherein the time of exposure of the substrate to the plasma is controlled by use of the shutter of the apparatus.

[Claim 17]. A method according to any one of claims 12-16, wherein the or each functionalizing compound is one or more selected from compounds of the following general formula (I):



Formula (I)

wherein each of R1 and R2 are independently selected from the group consisting of H, halo (for example –F, -Cl, -Br), thiol (-SH), amino (-NH2), carboxyl (-COOH) and hydroxyphenyl (-C6H4OH); one of R1 and R2 is not H; and
n is an integer from 1 to 10.

[Claim 18]. A method according to any one of claims 12-17, wherein the or each functionalizing compound is one or more selected from the group consisting of amylamine, hexanoic acid, 1-pentanethiol and 4-pentylphenol.

[Claim 19]. A method according to any one of claims 12-18, wherein the method comprises a further step of exposing the substrate to a plasma comprising hydrogen to effect hydrogenation of the graphene or graphene oxide layer or a portion of the graphene or graphene oxide layer.

[Claim 20]. A method according to any one of claims 12-19, wherein the substrate is a gold cryoEM grid.