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PII: S0001-8686(15)00125-6  
DOI: doi: [10.1016/j.cis.2015.07.011](https://doi.org/10.1016/j.cis.2015.07.011)  
Reference: CIS 1556

To appear in: *Advances in Colloid and Interface Science*



Please cite this article as: Mohamed Ahmed A., Salmi Zakaria, Dahoumane Si Amar, Mekki Ahmed, Carbonnier Benjamin, Chehimi Mohamed M., Functionalization of nanomaterials with aryldiazonium salts, *Advances in Colloid and Interface Science* (2015), doi: [10.1016/j.cis.2015.07.011](https://doi.org/10.1016/j.cis.2015.07.011)

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## Functionalization of nanomaterials with aryldiazonium salts

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**Abstract.** This paper reviews the surface modification strategies of a wide range of nanomaterials using aryldiazonium salts. After a brief history of diazonium salts since their discovery by Peter Griess in 1858, we will tackle the surface chemistry using these compounds since the first trials in the 1950s. We will then focus on the modern surface chemistry of aryldiazonium salts for the modification of materials, particularly metallic, semiconductors, metal oxide nanoparticles, carbon-based nanostructures, diamond and clays. The successful modification of  $sp^2$  carbon materials and metals by aryldiazonium salts paved the way to innovative strategies for the attachment of aryl layers to metal oxide nanoparticles and nanodiamonds, and intercalation of clays. Interestingly, diazotized surfaces can easily trap nanoparticles and nanotubes while diazotized nanoparticles can be (electro)chemically reduced on electrode/materials surfaces as molecular compounds. Both strategies provided organized 2D surface assembled nanoparticles. In this review, aryldiazonium salts are highlighted as efficient coupling agents for many types of molecular, macromolecular and nanoparticulate species, therefore ensuring stability to colloids on the one hand, and the construction of composite materials and hybrid systems with robust and durable interfaces/interphases, on the other hand. The last section is dedicated to a selected fistful of patents and industrial products based on aryldiazonium-modified nanomaterials. After nearly 160 years of organic chemistry, diazonium salts have entered a new, long and thriving era for the benefit of materials, colloids, and surface scientists. This tempts us to introduce the terminology of “diazonics” we define as the science and technology of aryldiazonium salt-derived materials.

**Keywords:** aryldiazonium salts, coupling agents, carbon nanomaterials, colloids, nanoparticles, clays, catalysts, coatings, fillers, nanocomposites, sensors, adsorbents.

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## 1. Introduction

The surface chemistry of aryldiazonium salts is well renowned [1,2,3] since the pioneering work of Jean Pinson and co-workers in 1992 pertaining to the mechanisms of electrochemical reduction and concerted attachment of aryl radicals to glassy carbon electrodes [4]. The discovery of true covalent bonding at the substrate-aryl interface was a decisive step in establishing aryldiazonium salts as key surface modifiers and coupling agents in materials science. Much has been said since then on the role of aryldiazonium salts in surface modification in view of many applications: corrosion control [5], molecular electronic junctions [6,7] and complexing layers for the removal of heavy metals [8]. Aryldiazonium salts have also been shown to act as true coupling agents for polymers [9], adhesive resins [10], biomacromolecules [11], nanoparticles for catalysis [12] and optical sensing purposes [13]. Besides the academic achievements, surface chemistry of aryldiazonium salts has permitted the design of novel, industrially produced materials, namely modified carbon blacks and drug eluting stents [14].

Aryldiazonium salts could be reduced using a wide range of methods leading to aryl layers which act as true coupling agents as they adhere to surfaces with energies high enough to ensure stability [15]. The energies were reported to be over 50 kcal/mol [16,17,18], a requisite for considering compounds as coupling agents [19].

Modern surface chemistry of aryldiazonium salts has been from the start a rich field for electrochemists researching on planar electrode substrates, but it soon became clear that divided materials can also be modified either electrochemically if they are conductive (e.g. CNTs) or via chemical and other radiation-assisted processes for either conductive or insulating nanomaterials. Modification of nanomaterials by aryldiazonium salts offers unique opportunities for tuning optical properties [20], providing specialty fillers for polymers [21], constructing polymer nanocomposites [9,22], enhancing the performance of polymeric sensing layers [23], and designing nanorobots for cancer probes [24] and drug delivery [25].

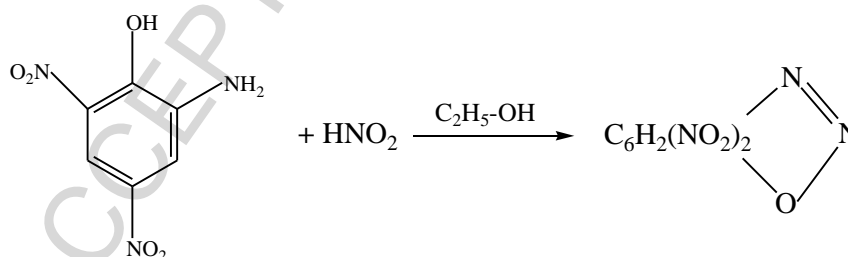
The new challenges in the surface chemistry of aryldiazonium salts and their applications to nanoparticles have motivated this review paper which is structured into the following sections:

- Concise history of diazonium salts from their discovery and use in organic chemistry to their modern surface chemistry,
- Summary of the traditional synthesis methods of aryldiazonium salts and description of new strategies,
- Surface grafting of aryl layers to nanoparticles from either isolated or *in situ* generated salts,

- Attachment of aryl layers to metal and metal oxide nanoparticles,  $sp^2$  carbon nanomaterials, nanodiamonds and clays,
- Reactivity of diazotized surfaces with particles and attachment of diazotized nanoparticles to surfaces,
- Summary of patents and industrial applications of aryldiazonium-modified nanoparticles.

## 2. Brief history of aryldiazonium salts: From organic to surface chemistry

Aryldiazonium compounds were discovered in 1858 by Peter Griess when he synthesized a product was coined “diazonitrophenol” (Fig. 1), a diazotized dinitrophenol [26]. The term “diazo” stems from the French origin “diazote” and means dinitrogen. Reading his article with interest, A. W. von Hoffman thought the subject would occupy the whole lifetime of Peter Griess [27]. Hoffman was right to predict enormous avenues in organic chemistry that would be paved by the pioneering work of the young investigator Peter Griess. Rightly, aryldiazonium salts have been playing a major role in organic synthesis of many important classes of compounds [28,29] such as the long known azo dyes [30].



**Figure 1.** Diazotization reaction of dinitrophenol by Peter Griess.

The versatility of aryldiazonium salts has attracted electrochemists for more than half a century to understand the electron transfer process during electroreduction. For example in 1958, and one century after Griess' discovery, Elofson [31] found that the electroreduction of aryldiazonium salts on hanging mercury drop electrode (HMDE) resulted in the formation of phenylmercuric chloride and diphenyl mercury. Obviously, these are surface chemical reactions but, at that time, they were not defined as such. The electrochemical investigations continued sparsely in the 1960s and 1970s for various purposes until the early 1980s when a Norwegian group, led by Vernon Parker [32], observed the passivation of metal electrodes upon electrochemical reduction of

1-naphthalenediazonium tetrafluoroborate (NDT). They stated that deactivation of electrodes during oxidation or reduction of organic compounds is not an unusual observation and the fact that the phenomenon occurs during the electrochemical reduction of NDT is not of interest. After ruling out the electrode deactivation by the adsorbed molecular nitrogen released from the aryldiazonium reduction, they suspected a reaction between a supposedly generated radical and the metal, however without any spectroscopic evidence for the existence of the resulting interfacial product. The authors stated that, though the surface blockage is of considerable interest, the study was beyond the scope of their paper. Ironically, after a decade the modern surface chemistry of aryldiazonium salts has at last taken off following the understanding passivation of electrodes, previously experienced by the Norwegian group in their study of metal electrodes. Indeed, in 1992, Pinson and co-workers [4] studied the mechanisms of electrochemical reduction of nitrobenzenediazonium tetrafluoroborate on a glassy carbon (GC) electrode. They observed the passivation of electrodes as in the case of metals but the phenomenon was interpreted in terms of attachment of nitrophenyl as evidenced by the surface specific technique XPS (X-ray photoelectron spectroscopy). Nitrogen region indeed indicated the presence of an N1s peak centered at 406 eV assigned to the nitro group in the aryl layer.

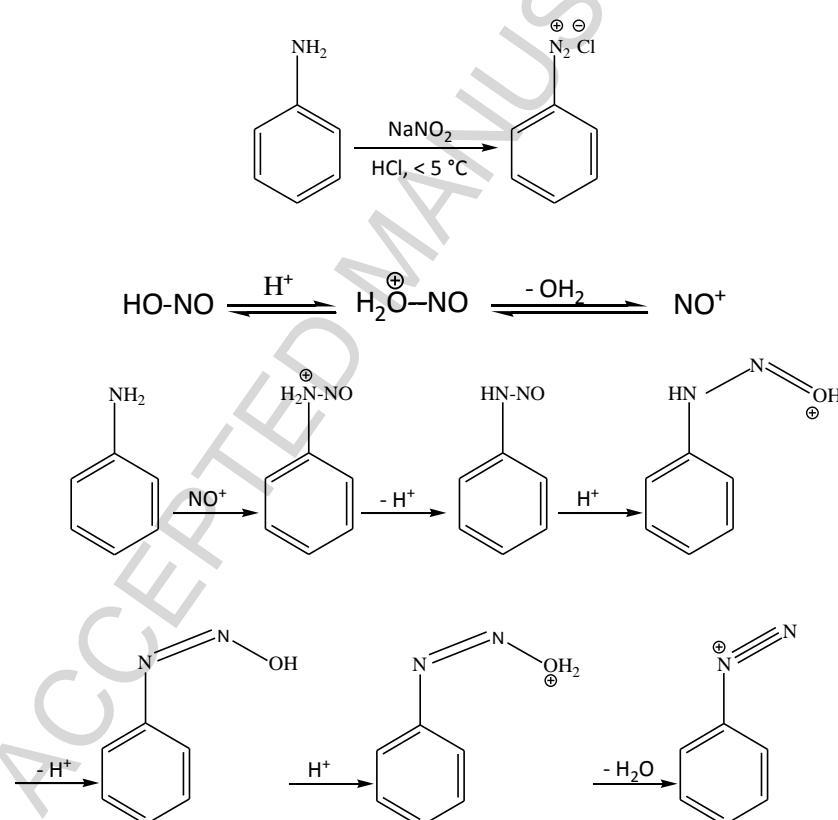
In our fair opinion, as Peter Griess discovered the diazonium salts in 1858, Jean Pinson could also be credited as the father of the modern surface chemistry of aryldiazonium salts. Since its advent in 1992, this chemistry has progressed at an astonishing pace. Although it is still in its infancy but the achievements around the globe have been phenomenal. Actually, since aryldiazonium chemistry started to “go surface”, in only 23 years, this versatile surface process has attracted several researchers who efficiently modified a large panel of substrates through a plethora of approaches [1,2,3]. However, in the following and as we indicated above, the scope of this review is restricted to nanomaterials rather than the frequently investigated macroscopic planar plates.

### 3. Synthesis of aryl diazonium salts

There are only few commercially available aryldiazonium salts such as 4-nitrobenzenediazonium tetrafluoroborate, 4-bromobenzenediazonium tetrafluoroborate, 4-formylbenzenediazonium hexafluorophosphate and 4-aminodiphenylaminediazonium sulfate. This makes a very small choice for constructing new multicomponent materials with robust interfaces. Particularly, the most used diazonium salt has always been the 4-nitrobenzenediazonium tetrafluoroborate because it gives characteristic peaks in infra-red (IR) and XPS spectroscopies and

can be tracked electrochemically as its  $\text{NO}_2$  group is reduced into  $\text{NH}_2$ . This salt has thus become a model diazonium salt for the demonstration of proof of new concepts: surface modification [1,2,3,4], biosensors [33], intercalated clay-based nanofillers [34], etc. However, this is by far not enough and most of the time materials chemists have to cope with the synthesis of aryl diazonium salts that have particular structure not available in the short list of commercial diazonium compounds.

The synthesis of aryldiazonium salts can be conducted by the addition of an aqueous solution of  $\text{NaNO}_2$  to a solution of an aromatic amine in the presence of excess  $\text{HCl}$  which is cooled in an ice bath to keep the temperature below  $5^\circ\text{C}$ . The general reaction scheme is displayed in Figure 2.



**Figure 2.** General synthesis and mechanism of formation of aryldiazonium salts. Example is given for benzenediazonium chloride.

Despite the wide applications of aryldiazonium salts in fundamental and materials chemistry, there are many serious drawbacks: their intrinsic instability at room temperature, the difficulty to isolate and purify, and their explosive nature [35]. In order to avoid some of these limitations, aryldiazonium salts must undergo the targeted application in the same medium without isolation. This can be achieved by *in situ* diazotization of aryl amines followed by reductive grafting [36].

The electron density model described the bonding in aryldiazonium by synergistic  $N \rightarrow C$   $\sigma$ -bonding and  $C \rightarrow N$   $\pi$ -back-bonding [37]. A stabilizing effect for the C-N bond includes the formation of charge-transfer complexes, metal-based anion and coordination [38,39,40,41]. Based on the relative size of aryldiazonium and the void of the polyether ring, basicity of the oxygen atoms, and steric hindrance in the ring, it is possible to affect the stabilization of the aryldiazonium salts by macrocyclic polyethers [38,39]. The formation of aryldiazonium ion-crown ether complexes increases the thermal and photochemical stabilities of aryldiazonium ions in solution and solid state. Metal-based anion approach was also utilized in order to stabilize the C-N bond [40]. A complex of aryldiazonium with the anion  $[ZnCl_4]^{2-}$  was synthesized and its X-ray structure was determined [40]. Moreover, coordination of the *in situ* generated diazonium is a plausible route for stabilization of aliphatic diazonium salts [41].

Several aryldiazonium salts have been isolated in the last few decades and their X-ray structures described [42]. The structure of benzenediazonium chloride showed  $N \equiv N \cdots Cl$  distance of 3.22-3.56 Å. The first example of diazonium stabilization by multiple and close contacts with tosylate anion shows the shortest distances between the outer diazonium nitrogen and the tosylate oxygen of 2.673-2.770 Å [43], shorter than the sum of van der Waals radii of 2.90 Å [44]. The ionic structures of metal-based aryldiazonium complexes  $[R-4-C_6H_4N \equiv N]X$  ( $X = SbCl_6, FeCl_4, CuBr_2$ ) and  $[R-4-C_6H_4N \equiv N]_2ZnCl_4$  show the shortest interionic distances between the diazonium and the metal-based anion occur between the halide and the outer diazonium nitrogen than to the ammonium nitrogen. Metal-based aryldiazonium salts structurally characterized so far indicate that the bond order in the diazonium nitrogen-nitrogen is close to a triple bond distance of approximately 1.1 Å.

From acetonitrile solvent at room temperature, well-shaped yellow crystals of aryldiazonium tetrachloroaurate(III) salts were obtained [45,46]. The  $N \equiv N$  distance is typical of diazonium, approximately 1.10 Å. Each diazonium group is surrounded by four  $[AuCl_4]^-$  normal to the  $N \equiv N$  axis. The  $N(\text{outer}) \cdots Cl$  distances are 3.217, 3.267, 3.300, and 3.468 Å. The close proximity to the  $N \equiv N$  group,  $Cl \cdots N \equiv N$  interaction, and the fact that the chloride is less nucleophilic in  $[AuCl_4]^-$  than the free chloride, are presumably contributing factors in the increased stability of the new gold-based aryldiazonium salts.



#### 4. Methods of attachment of aryl layers to particles

Two general approaches can be envisaged with nanomaterials: modification with (i) isolated aryldiazonium salts and (ii) *in situ* generated aryldiazonium salts from aromatic amines in the presence of  $\text{NaNO}_2$  in acidic medium. Alternatively, *in situ* generated aryldiazonium salts can be prepared in pure isoamyl nitrite medium, a method which ensures high grafting density of aryl groups onto CNTs [47]. This solvent-free approach technique provided functionalized carbon nanotubes with high solubility in organic solvents and processibility in polymeric blends. The approach is scalable therefore paving the way for its use in bulk applications such as the development of structural materials.

Although electrochemistry has been for years the privileged method for modification of surfaces, it became clear that it presented limitations when applied to non-conductive substrates. Conductive particles can be assembled on electrodes and electrochemically modified electrodes but other approaches might prove more general as they can be applied either to conductive or insulating suspended or immobilized particles. It is worth to note that several studies reported on spontaneous attachment of aryl layers to surfaces resulting in true covalent bonds at interfaces. In these approaches, no chemical reductants are required nor electrochemical / radiation-induced radical processes are employed. The reduction of the diazonium occurs by simple contact of the salt with the material provided this latter has sufficient reducing power; this is the case of carbon materials and metals such as gold. Via either spontaneous or chemically, electrochemically or radiation-induced grafting, covalent bonds were reported to be of the following natures: C-C [48,49,50], C-O-Aryl [48], C-N=N-Aryl [49,48], metal-C [9,51,52], metal-N=N-Aryl [52], and metal-O-C for the interaction of diazonium salts with metal oxides [53].

Table 1 summarizes methods of surface modification of nanoparticles using aryldiazonium salts and the underlying mechanisms of reactions.

**Table 1. Main methods and mechanisms for grafting of aryl layers derived from diazonium compounds.**

Method	Materials	Mechanism	Refs.
Spontaneous	Au NPs SWCNTs suspended in SDS	Radical reaction Radical coupling	[54] [55]
Ion exchange	Clay	Ion exchange of sodium by aryldiazonium cations	[34]
Chemical	Au and other metal NPs  Graphite powder  TiO <sub>2</sub> NPs  CNTs  Carbon black  SW- and MWCNTs	Phase transfer followed by radical reaction  Reduction of aryldiazonium by hypophosphorous acid  Reduction of aryldiazonium by ascorbic acid  Reduction of aryldiazonium by hypophosphorous acid  <i>In situ</i> generated aryldiazonium in water using NaNO <sub>2</sub> followed by addition of HCl  <i>In situ</i> generated aryldiazonium in pure isoamyl nitrite Reaction at 60 °C resulting in heterolytic cleavage of N <sub>2</sub> -aryl bond	[56]  [57]  [58]  [59]  [60]  [47, 61]
Electrochemical	Immobilized Au NPs  SWCNT-pucky paper electrode  SWCNTs immobilized on Teflon filter  Aligned CNTs on Si wafer  SWCNT-COOH assembled on GC electrode	Radical reaction with gold NPs  Electrochemical reduction and reaction of radicals with the nano-objects  Idem  Idem  Electrochemical reduction and radical reaction	[23]  [62]  [63]  [64]  [65]
Photochemical	MWCNTs	UV-assisted production of aryl radicals which react with MWCNTs in acetonitrile	[20]
Sonochemical	O-ND	Possible reaction of ultrasonically produced radicals with C sp <sup>2</sup> surface defects of O-ND	[66,67]
Thermal	SWCNTs	No mechanism was mentioned in the manuscript	[68]
Microwave	MW- and SWCNTs	Arene radical addition	[69,70]
	C60@SWCNT peapods	<i>In situ</i> generated aryldiazonium in pure isoamyl nitrite reaction at 10 W and 30 min	[71]
Mechanochemical	GC spheres	Possible radical reaction. If grinding provokes heat, heterolytic cleavage could be possible resulting in a reaction between cationic aryl and carboxylates from the spheres	[72]

CNTs: Carbon nanotubes, Au: Gold, NP: Nanoparticle, GC: Glassy carbon, CF: Carbon fibres, MWCNTs: Multi-walled carbon nanotubes, ND: Nanodiamond, O-ND: Oxidized nanodiamond, SDS: Sodium dodecyl sulphate, SWCNTs: Single-walled carbon nanotubes, UNCD: Ultrananocrystalline diamond.

In most of the methods described in Table 1, diazonium salts yield aryl multilayers on the supports. This “graft-oligomerization” of the aryl groups at the surface has been described in detail by Pinson and Podvorica [2]. It yields an ultrathin grafted film of 3-5 nm (or more) depending on the underlying support and on the experimental conditions. It has been shown that the grafting of aryl group monolayer can be achieved if the grafting experiments are conducted in ionic liquids [73] or in the presence of a radical scavenger [74]. Attachment of aryl monolayers can also be obtained with aryldiazonium salts bearing two bulky tert-butyl groups in meta positions of the diazonium group [75].

## 5. Modification of nanomaterials

### 5.1. sp<sup>2</sup> carbon nanomaterials

The reader should be aware that it is unfeasible to include a comprehensive review on the modification of sp<sup>2</sup> carbon (Csp<sup>2</sup>) nanomaterials by aryldiazonium salts. It would take a whole book as this interfacial chemistry takes its source from the original work by Pinson *et al.* on glassy carbon electrodes [4] followed by studies on electrochemical modification of carbon felts [76] and carbon fibers [10]. Obviously and as a follow up of the work by Pinson *et al.*, much time and energy have been devoted to carbon nanotubes (CNTs) for their modification by aryldiazonium salts and uses thereof (see Table 1). Current literature shows enormous interest in the modification and exfoliation of graphene by aryldiazonium salts [77]. Less investigated is the modification of carbon nano-horns [78] and nano-onions [79]. Besides carbon nanomaterials, aryldiazonium surface modification of the industrially important carbon beads will be highlighted. Clearly, there is not enough space for the aryldiazonium modification of Csp<sup>2</sup> nano-objects. Instead, we will select studies that reflect a wide range of modification methods using aryldiazonium salts and highlight some of their applications.

#### 5.1.1. Multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs)

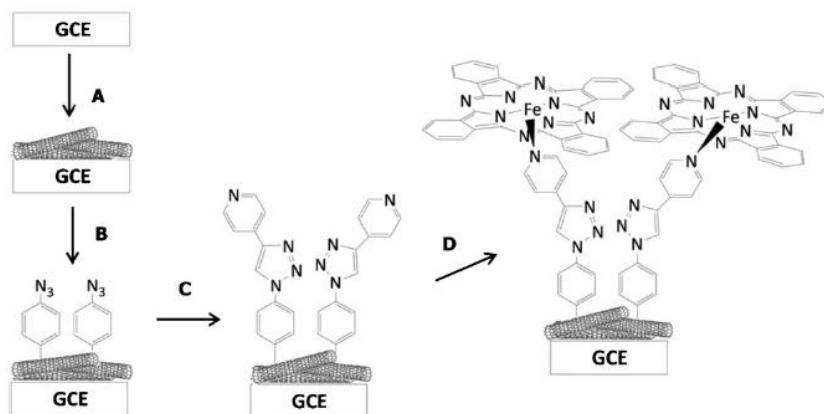
Aryldiazonium modification of SWCNTs and MWCNTs is the subject of numerous fundamental and applied studies. James Tour has published at length on the topic. In addition, other groups described not only chemical and electrochemical approaches but also innovative radiation induced diazonium modification of MWCNTs or SWCNTs.

### 5.1.1.1. Electrochemical modification of MWCNTs and SWCNTs

#### a. With isolated aryldiazonium salts

Using electrochemistry, the modification of CNTs depends on the assembling approach. Bahr *et al.* [62] prepared a bucky paper by filtration of CNTs suspension in 1,2-dichloroethane over a poly(tetrafluoroethylene) membrane. The bucky paper was detached from the membrane and held with an alligator. A colloidal silver paste was used to ensure electrical contact. The bucky papers were treated with 0.01-0.05 M aryldiazonium in acetonitrile. The aryls were grafted via the electrochemical reduction of diazonium salts (for example, R = F, Cl, Br, NO<sub>2</sub>, PEG for polyethylene glycol) with an achieved grafting density of up to one aryl group per 20 carbon atoms. In a similar approach, Marcoux *et al.* [63] electrochemically modified the CNTs film-coated membranes with R = SO<sub>3</sub><sup>-</sup>, COOH, Br, and CH<sub>2</sub>Cl. Surface modification is readily visible by XPS and the grafting densities are fairly high and are in line with what has been achieved elsewhere [62], except for *p*-sulfonatebenzenediazonium which could not be solubilized in acetonitrile.

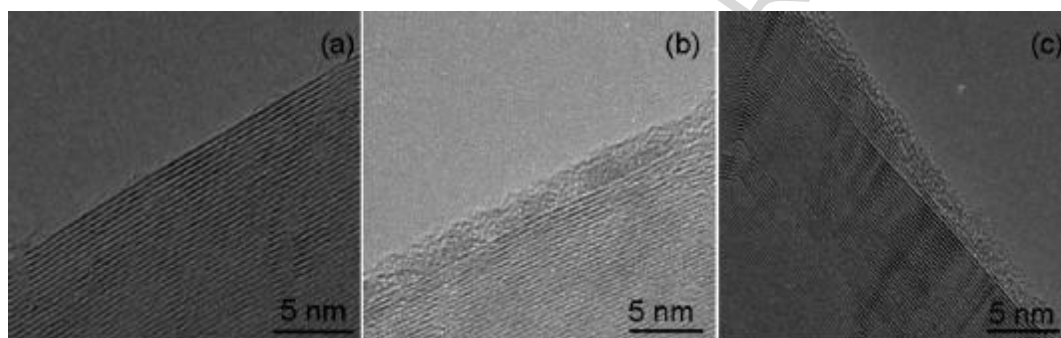
Carboxylated SWCNTs were adsorbed onto GC electrodes and subjected to electrochemical reduction of 4-azidobenzenediazonium resulting in clickable azide-functionalized SWCNTs. The immobilized SWCNTs were then reacted with 4-ethynylpyridine for the axial ligation of iron phthalocyanine [80] as shown in Figure 3. The system served in the detection of hydrazine with a limit of detection (LOD) of  $1.10 \pm 0.06 \mu\text{M}$ , ten-fold lower than LOD found for GC without SWCNTs.



**Figure 3.** Attachment of FePc through: (A) adsorption of single-walled carbon nanotubes, (B) grafting of the GCE-SWCNT by electrochemical reduction of 4-azidobenzenediazonium, (C) click chemistry with 4-ethynylpyridine, and (D) axial ligation of FePc. Reproduced from ref. [80]. Copyright (2013) Elsevier.

Vertically aligned CNTs, grown on silicon wafers, are easily modified, through an electrochemical approach, with aryls as the growth of the CNTs is achieved on a conductive

substrate. Matrab *et al.* [64] grafted aryls that served as initiators for atom transfer radical polymerization (ATRP) of methyl methacrylate and styrene. The aryl and polymer layers form a protruding amorphous coating that can be easily distinguished from the crystalline nature of the underlying MWCNTs (Fig. 4). In a similar approach, MWCNTs were synthesized by CVD (Chemical vapour deposition) on carbon paper then electrochemically functionalized by aryldiazonium salts prior to the adsorption of Pt ions and their *in situ* reduction to Pt nanoparticles (NPs) [81].



**Figure 4.** HRTEM images of untreated MWCNTs (a), MWCNTs-PMMA (b), and MWCNTs-PS (c). Reprinted from ref. [64]. Copyright (2006) Elsevier.

#### **b. With *in situ* generated aryldiazonium salts**

Electrochemical modification of carbon materials with *in situ* generated aryldiazonium salts takes its origin in the work by Baranton and Bélanger [82] who derivatized glassy carbon electrode surfaces. The aryldiazonium salts were synthesized in the electrochemical cell by the reaction of  $\text{NaNO}_2$  in aqueous HCl with the corresponding amines. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were used to confirm the barrier properties. This approach has been extended to carbon nanomaterials. For example, carboxylated SWCNTs were vertically anchored on the top of covalently modified GC substrate with a mixed layer of 4-aminophenyl and phenyl by electrochemical reduction of *in situ* generated aryldiazonium salts in acidic solutions for the subsequent attachment of endosulfan and its antibody [83]. The fabricated electrochemical immunosensor was successfully used for the detection of endosulfan over 0.01–20 ppb range by a displacement assay. The lowest detection limit of this immunosensor is 0.01 ppb endosulfan in 50 mM phosphate buffer at pH 7.0.

In another biomedical application, Tasca *et al.* [84] electrochemically modified SWCNTs adsorbed on GC via *in situ* generation of aryldiazonium salts from either *p*-aminobenzoic acid or *p*-phenyldiamine. The electrode was then placed in an electrochemical cell with an acidic electrolyte solution and left to interact with PsCDH, a cellobiose dehydrogenase (CDH) from the basidiomycete

*Phanerochaete sordida* (Ps). When a potential was applied, a highly direct electron transfer (DET) was produced and high current densities were induced. The DETs could have a potential effect in reducing the interference between oxidizable matrix components in biosensors, on the one hand, and increasing the open circuit potential in biofuel cells, on the other hand.

#### 5.1.1.2. Chemical modification of carbon nanotubes

##### a. With isolated aryldiazonium salts

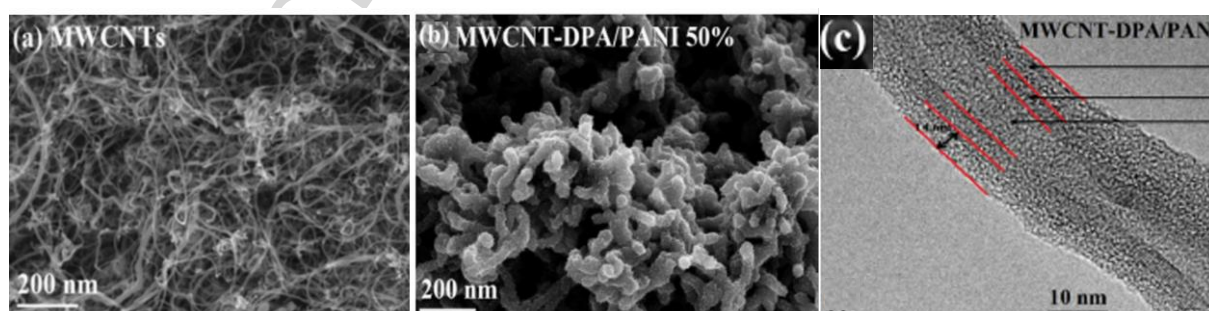
Aryldiazonium salts can be reduced spontaneously on carbon nanotubes in the presence or absence of surfactants leading to aryl modified CNTs [55]. Mévellec *et al.* [85] utilized the chemical reduction of aryldiazonium salts by iron powder approach to attach organic coatings to vertically aligned MWCNTs. The approach called *diazonium-induced anchoring process* (DIAP) involves the reduction of aryldiazonium salts in the presence of vinylic monomers. The generated radicals from the reduction process are readily anchored to the CNT surface; the so-anchored radicals initiate radical polymerization in solution of vinylic monomers such as 2-hydroxy ethyl methacrylate (HEMA). The growing polymer chain radicals provide a homogeneous and thick organic coating. The interface structure is constructed as follow: CNT surface-aryl layer-*P*(monomer-co-aryl) where the top layer wrapping the nanotubes is actually a copolymer of vinylic monomer and aryls from the reduction of diazonium salts. Note, however, that the relative concentration of aryl units in the copolymer grafts can be minimized.

Another chemical approach consisting on the reduction of aryldiazonium salt with hypophosphorous acid was described by Compton's group [59]. This is a one-electron chemical reduction mechanism of the aromatic diazonium using hypophosphorous acid. The reaction produces highly reactive aryl radicals which bind to the CNTs, and other  $sp^2$  carbon materials, by C-C interfacial bond.

##### b. With *in situ* generated aryldiazonium salts

One of the elegant and ecofriendly chemical approaches to modify CNTs consists in directly employing aromatic amines which are *in situ* transformed into their corresponding diazonium salts in the presence of  $Csp^2$  nanomaterials. This approach has proven effective in its positive impact on the CNTs functionalization reaction efficacy in the sense it permitted to reduce the solvent amount and to shorten the reaction time. In organic solvents, the reaction of aromatic amines with isoamyl nitrite

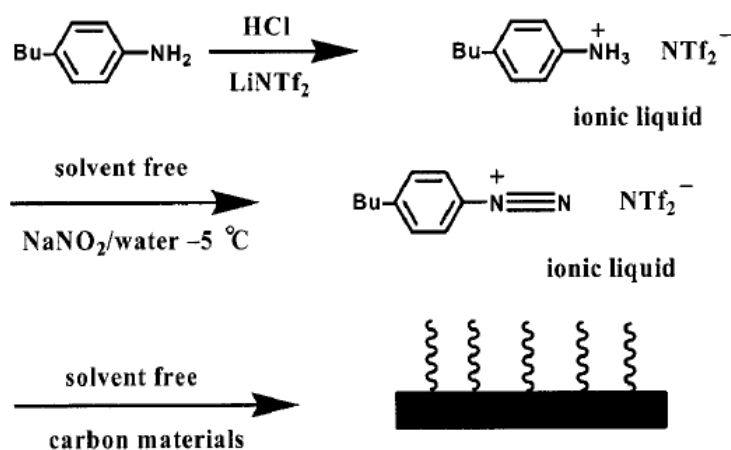
generates the corresponding aryldiazonium salts which, in turn, are reduced to aryl groups that graft to CNTs with a degree of functionalization of one out of 20 carbon atoms [86]. The reaction can even be conducted without solvent [87] as described by Dyke *et al.* [88]. The authors grafted organic addends on the sidewalls of CNTs by conducting the reaction at 60 °C in isoamyl nitrite which, in turn, reacts with the appropriate aniline to form the derived aryldiazonium salt. The approach permits the functionalization of CNTs with a grafting density of one carbon atom over nine. The alkyl nitrite can be easily substituted with  $\text{NaNO}_2$  and  $\text{H}^+$  source. The process opened new avenues for other authors to design hybrid nanomaterials with controlled architectures. For example, Mahouche-Chergui *et al.* [61] modified CNTs surfaces by 4-ethynylbenzenediazonium salt that served to click azide functionalized polymer to give CNT@polymer hybrids forming “hairy” CNTs. The latter served as efficient platforms for loading Pd nanoparticles to form a hetero-nanostructure that catalyzed C-C Suzuki coupling reaction in a high yield. Castelain *et al.* [89] reported CNTs and graphene surface modification using similar approach but they used a variant of the protocol described by Mahouche-Chergui *et al.* [61]. The results suggest that the same synthetic protocol in both cases leads to a certain degree of covalent modification, whilst a proportion of the modifying groups remains adsorbed to the carbon nanostructures. Mekki *et al.* [90] successfully obtained a lump free core-shell carbon nanotubes/polyaniline nano-composites by surface modification of CNTs with *P*-aminodiphenylamine which acted as a template for directional polymerization with the aim to obtain an ordered structure (Fig. 5).



**Figure 5.** SEM images of (a) MWCNTs and (b) MWCNTs-DPA/PANI 50%. (c) TEM image of MWCNTs-DPA/PANI 50% showing smooth, protuberance-free aryl-PANI bilayers. Reproduced from ref. [90]. Copyright (2014) Elsevier.

### 5.1.1.3. Thermally-induced modification of carbon nanotubes

Thermally-assisted modification of carbon nanotubes proceeds through one step, commonly known as the free solvent reaction employing *in situ* generated aryldiazonium salts as described by Dyke *et al.* [88]. It is worth to stress that the above reported process is conducted at 60 °C and not at room temperature; for this reason, one can also include it within thermally-assisted processes. This methodology has been widely used and applied to both SWCNTs and MWCNTs. In contrast, Liang *et al.* [91] described, in a distinctive report, a procedure based on ionic liquids for solvent-free modification of CNTs using a new class of stable and conductive ionic liquid-based diazonium salts (Fig. 6). Modification of CNTs has been carried out by both thermal and electrochemical activation of aryldiazonium salts to generate free radicals.



**Figure 6.** Synthetic approach for the ionic liquid-based aryldiazonium and its application for the chemical modification of carbon materials. Reproduced from ref. [91]. Copyright (2006) Wiley.

### 5.1.1.4. Radiation-induced modification of carbon nanotubes

Radiation technology is a growing area in the field of chemical synthesis evidenced by the large number of published papers and reviews in the last few years. One of the promising technologies consists in the microwave-assisted synthesis. It has been widely exploited due to its ability to controlling the reactions as it reduces time, volume of solvent and amounts of reagents.

The multifunctionalization of CNTs with combined aryldiazonium salt chemistry and 1,3 dipolar cycloaddition was the subject of the strategy reported by Brunetti *et al.* [92]. Liu *et al.* [93] described the covalent functionalization of CNTs by aryldiazonium salts using both classical thermal and microwave-assisted reactions. The authors concluded that microwave irradiation can greatly



reduce the steps and shorten the reaction times as the reaction can be accomplished within a few minutes compared to classical methods. The approach is versatile and can be applied to hybrid  $sp^2$  carbon nanomaterials. For instance,  $C_{60}$ @SWCNT peapods are functionalized using *in situ* generated aryldiazonium salts in isoamyl nitrite through a microwave-assisted route for 30 min [71]. In another approach, Pan *et al.* [20] used UV irradiation to modify the surface of CNTs with terpyridinyl phenyls which were covalently grafted onto CNTs surfaces. They also demonstrated that the as-functionalized CNTs were very stable toward electrolytic aqueous solutions and polar organic solvents.

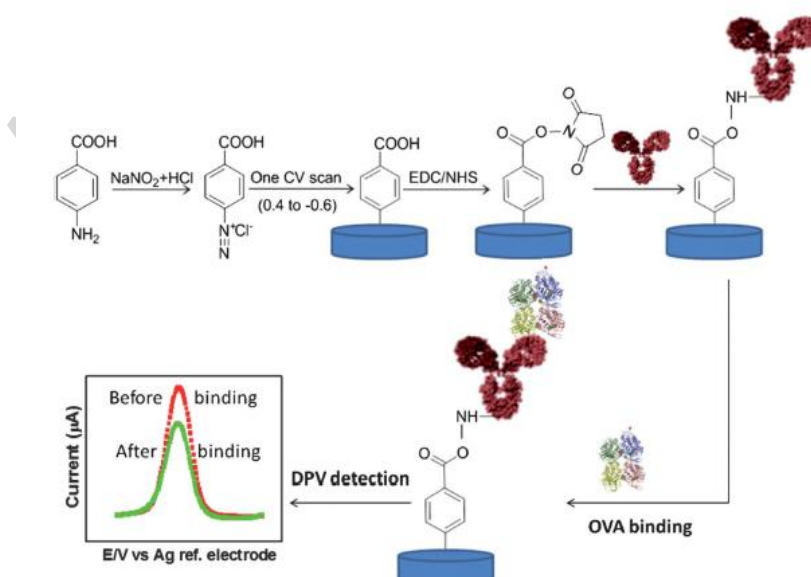
### 5.1.2. Graphene

Graphene is a carbon-based planar atomic crystal. Carbon atoms form a  $\pi$ -conjugated honeycomb lattice. Due to its composition, morphology and structure, graphene possesses interesting electronic, mechanical, thermal and optical properties, making it a promising candidate in a wide range of applications. Several reviews have been published on this allotrope of carbon, describing in details methods of synthesis and functionalization, properties, and potential bio-applications [94,95,96,97,98,99,100,101,102,103,104,105]. Hereafter, the focus will be on the modification of graphene by aryl moieties derived from diazonium salts. These aryl layers could act as stabilizing agents, anchored initiators for ATRP, coupling agents for click chemistry, or as chemical entities for the design of heterostructures or for the tuning of graphene properties.

Functionalization of graphene surfaces using aryldiazonium salt chemistry is well documented. Through an electroless route, it is possible to attach aryl groups bearing four different functionalities ( $-Cl$ ,  $-NO_2$ ,  $-OCH_3$  and  $-Br$ ) to surfactant-wrapped dispersion of chemically converted graphene, prepared by dispersing graphene oxide (GO) in 1 wt % aqueous sodium dodecylbenzene sulfonate (SDBS) surfactant [106]. It is also possible to covalently attach, through a similar process carried out at room temperature, aryl groups to epitaxial graphene (EG), grown on SiC wafers [107]. Reduced graphene oxide was spin coated on Si/SiO<sub>2</sub> and spontaneously grafted with thiophenyl groups from the parent isolated salt to provide non-volatile memory devices [108]. Sinitskii *et al.* [109] reported that the kinetics of aryl chemical functionalization of graphene nanoribbons (GNRs) could be monitored through the recording of changes in the electrical properties of GNRs. Huang *et al.* [110] demonstrated that covalent binding of aryl groups to graphene induced an increase in the electrical conductivity. Sulfonation of pre-reduced graphene oxide with aryldiazonium salt of sulfanilic acid resulted in the formation of sulfonated graphene which was readily dispersed in the pH range 3-10 in water [111]. Englert *et al.* [112] described the activation of bulk graphene using liquid

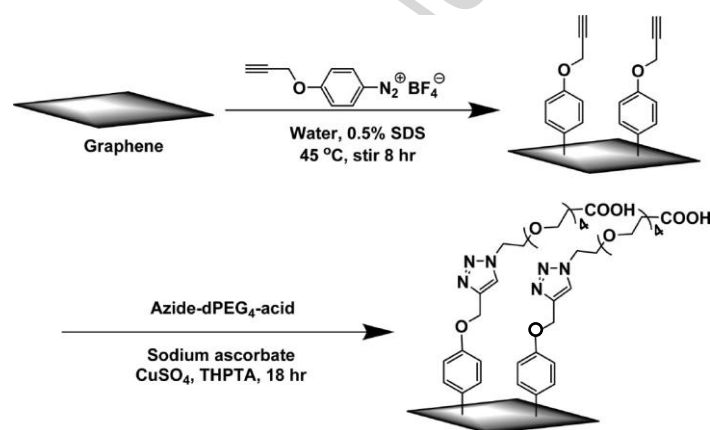
Na/K alloy in dimethyl ether resulting in the intercalation and exfoliation of graphene which was further functionalized with aryls derived from diazonium salts preventing re-aggregation while providing solubility in common organic media.

Electrochemical grafting of aryl groups derived from diazonium salts onto carbon surfaces has proved its efficiency since first reported by Pinson and colleagues [113] and soon extended to a large myriad of surfaces and nano-materials [15]. A few studies, found in the literature, detail the design of sensors starting from the electrochemical grafting of aryldiazonium salts onto graphene sheets [114] or onto electrodes acting hence as anchoring agent to graphene sheets [115] [116], [117], [118]. In both cases, further modification steps are required before obtaining functional sensors. For instance, Eissa *et al.* [114] described, following the first procedure, the design of a label-free voltammetric immunosensor for the detection of the egg allergen ovalbumin starting from graphene-modified screen carbon electrodes to which an *in situ* generated aryldiazonium salt was covalently electro-grafted. These aryl groups were further activated through NHS-EDC procedure allowing the attachment of an antibody. The interaction between the antibody and its antigen causes the current intensity to drop down (Fig. 7) [114]. Haque *et al.* [115] detailed, using the second procedure, the design of an electrochemical immunosensor starting from electro-grafted diazonium salts to an ITO electrode which served as an intermediate for the chemical anchoring of graphene oxide (GO) which were further electrochemically reduced, giving birth to electrochemically reduced graphene oxide (ERGO) and modified using an amphiphilic polymer to which an antibody was tethered. This design served for the ultrasensitive antigen detection.



**Figure 7.** Design and working principle of graphene-based label-free voltammetric immunosensor. Reprinted from ref. [114]. Copyright (2013) The Royal Society of Chemistry.

*In situ* generated diazonium salts have been used to obtain graphene-anchored initiators for the growth of polymer chains using ATRP [119,120]. Diazonium salts and click chemistry could be combined to decorate graphene sheets with polymers. To this end, Cao *et al.* [121] used graphene oxide sheets (GOSs) bearing an alkyne to attach  $N_3$ -terminated polymers for the design of hybrid GOSs-block copolymers via click chemistry. Sun *et al.* [122] used the same procedure to build graphene-polystyrene hybrid material, highly dispersible in a wide range of organic solvents. Following another approach, Jin *et al.* [123] first grafted aryl layers onto graphene. The alkyne-terminated aryls were coupled via click chemistry with a short chain of polyethylene glycol (PEG) as schematically depicted in Figure 8.



**Figure 8.** Schematic illustration of graphene modification with polymers using combined diazonium and click chemistries. Reprinted with permission from ref. [123]. Copyright (2011) American Chemical Society.

Reduced graphene was grafted with aminophenyl groups from *in situ* generated diazonium salts; the as-modified graphene nanosheets (APGNS) were further functionalized by *in situ* oxidative polymerization of pyrrole (PPy) [124]. The resulting PPy-g-APGNS nanocomposites exhibit excellent cycling performance in comparison to the nanocomposites prepared without any diazonium pre-treated graphene nanosheets. The authors of this study claim this fact is due to favourable interfacial Lewis acid-base interactions between the amino groups from APGNS (n donor, Lewis base) and the NH bonds from polypyrrole ( $\sigma^*$ acceptor, Lewis acid); they also propose that polypyrrole could be covalently grafted to the functionalized, aminated graphene nanosheets. PPy-g-APGNS nanocomposites display potential application as antistatic coatings and electrode materials.

To fabricate photo-crosslinkable multilayer films, made of sulfonated graphene and a polystyrene diazonium salt (PSDAS), an electrostatic layer-by-layer (LbL) self-assembly method was

used by Xiong *et al.* [125]. PSDAS was prepared from polystyrene (PS) through nitration, reduction, and diazotization reactions, whereas sulfonated reduced graphene oxide (SRGO) was pre-reduced using the mild reducing agent  $\text{NaBH}_4$  and modified with a diazonium salt prepared from sulfanilic acid. To remove any remaining oxygen, hydrazine was used. The authors brought strong supporting evidence for a UV-assisted reaction between the diazonium from PSDAS and the sulfonate from SRGO:  $\text{PS-N}^+\equiv\text{N} + ^-\text{O-SO}_2\text{-RGO} \rightarrow \text{PS-O-SO}_2\text{-RGO}$ . Multilayer film-coated ITO electrodes were characterized by cyclic voltammetry measurements and found to behave as electrochemical double-layer capacitors (EDLCs). The cross-linked layered material exhibited superior cyclic stability with a 97% capacitance retention even after 10,000 charge-discharge cycles. The cross-linked network structure of the self-assembled films and the high double-layer capacitance of SRGO nanosheets make the multilayer films a promising material in manufacturing supercapacitor electrodes.

Wang *et al.* [126] designed photoactive graphene sheets (GS) via click chemistry between phenylacetylene moieties grafted to graphene and azide-terminated zinc-porphyrin and ruthenium-phenanthroline derivatives to yield zinc-porphyrin-triazole-GS (ZnP-GS) and ruthenium-phenanthroline-triazole-GS (RuP-GS), respectively.

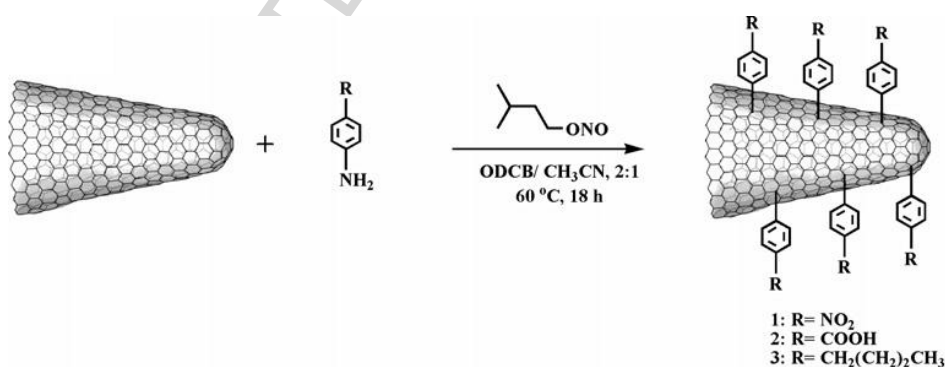
Niyogi *et al.* [127] successfully reorganized the  $\pi$ -bonds in graphene via the covalent attachment of aryl moieties, therefore altering the periodicity of the graphene network. Such change in periodicity resulted in introducing a band gap which is an easy route to tune the electronic properties of graphene. Different aryls derived from diazonium salts could be used to tailor the electrical properties of graphene field-effect transistors [128,129]. Diazonium salt chemistry has proved its efficiency in the improvement of the electrocatalytic properties of carbon-based nanomaterials, including graphene, via the covalent grafting of a porphyrin cobalt complex (Cobalt[tetrakis(*o*-aminophenyl)porphyrin]) (CoTAPP) [130]. The intercalation of aryls derived from diazonium salts between two graphene electrodes has led Seo *et al.* [131] to design a photo-switchable molecular monolayer anchored between highly flexible and transparent graphene electrodes.

Degupta *et al.* [132] attached a thiol-terminated diazonium salt onto reduced graphene oxide (RGO) sheet surface in order to anchor CdSe quantum dots (QDs) resulting in RGO-QDs hybrid structures with enhanced optical properties. Modification of GO using 2-aminoanthracene derived from a diazonium salt has led Lu *et al.* [133] to fabricate graphene composite with a blue emission. It is also possible to use GO modified with a diazonium salt as a platform for drug delivery [134]. The reaction of diazonium salt of sulfanilic acid with  $\text{Fe}_3\text{O}_4$ -GO resulted in the design of sulfonated

magnetic graphene oxide composite (SMGO) which proved its efficiency in the removal of Cu(II) ions from aqueous solution [135]. The improvement of the mechanical and thermal properties of resins is achieved through the incorporation of aryl functionalized graphene and graphene oxide [136].

### 5.1.3. Nanohorns and nano-onions

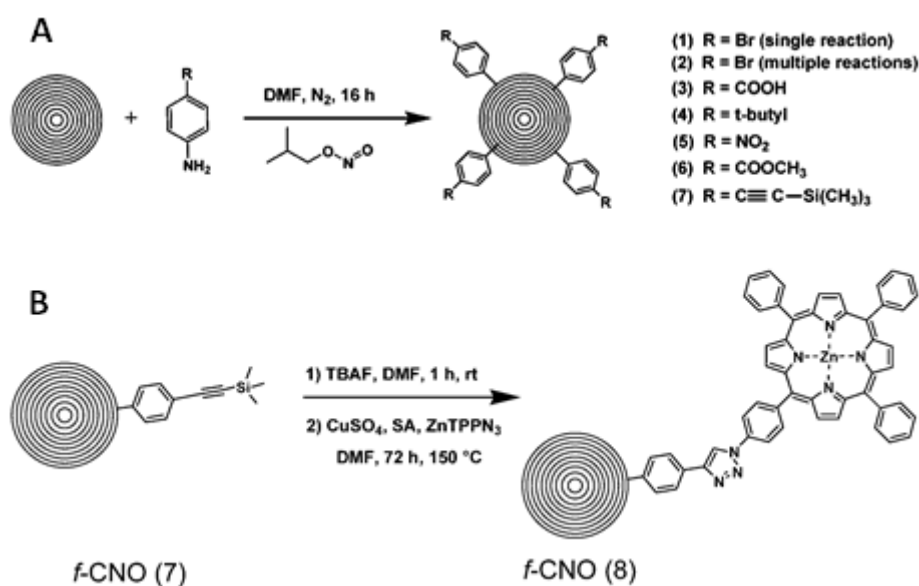
Carbon nanohorns (CNHs) are elongated carbon nanostructures which are mainly used in biomedical applications [137], fuel cells [138] and gas storage [139]. Nano-onions are multilayer fullerenes and constitute ideal nanomaterials for lubrication due to their remarkable tribological properties [140]. Nano-onions are potentially useful in fuel cells [141] and supercapacitors [142]. However, to fulfill these goals the surface of these nanomaterials, often, must be derivatized. Towards this end, diazonium surface chemistry has been tested with success when applied to  $C_{sp^2}$  materials. Given the obvious downside of the “isolated diazonium salts” strategy and the tedious purification steps, nanohorns and nano-onions have rather been modified by *in situ* generated diazonium salts. Pagona *et al.* [78] modified CNHs by various diazonium salts (Fig. 9) in order to achieve their solubilization in organic solvents and water.



**Figure 9.** Functionalization of carbon nanohorns with *in situ* generated aryl diazonium salts. Reprinted from ref. [78]. Copyright (2008) Elsevier.

Guerra *et al.* [137] grafted a polyamidoamine dendrimer on nanohorns from an amino moiety functionalized by *in situ* grafting of a Boc-protected *p*-aminomethylaniline. The condensation of methyl acrylate gave nanohorns functionalized with an ester moiety then finally the dendrimer was grafted by amidation. This material served as a nano-carrier for DNA into the cells while the dendrimer enhanced CNH solubility in biological media and acted as a DNA reservoir.

As far as nano-onions are concerned, Flavin *et al.* [143] used the *in situ* strategy to graft porphyrin to carbon nano-onions using *P*-((trimethylsilyl)ethynyl)benzenamine. The nano-onions attached to *P*-((trimethylsilyl)ethynyl)phenyl groups were deprotected and let to react with zinc monoazaporphyrin resulting in Huisgen's 1,3-dipolar cycloaddition (Fig. 10). In this approach, the authors demonstrated the possibility of grafting some simple molecules to achieve more complex heterostructures from nano-onions and porphyrin.



**Figure 10.** Functionalization of CNOs by *in situ* generated diazonium bearing different terminal groups (A) followed by deprotection of alkynyl moiety of *f*-CNO (7) and subsequent coupling with zinc monoazaporphyrin using click chemistry resulting in *f*-CNO (8) synthesis (B). Adapted from ref. [143]. Copyright (2010) American Chemical Society.

#### 5.1.4. Carbon black, carbon spheres and carbon-coated metallic particles

The modification of carbon black (CB) powders can be carried out by their spontaneous reaction with diazonium salts in aqueous solution. The work was initially disclosed and patented by Cabot corporation [144] which described the modification of various types of carbon powders with a large variety of organic moieties. However, comprehensive physicochemical characterization was lacking. Toupin and Bélanger [48] filled the gap by providing information related to the structure and thermal stability of functionalized Vulcan powders by one-pot synthesis with *p*-nitrophenyl, *p*-azobenzene and phenyl shells from the *in situ* generated aryl diazonium cations in aqueous solution. Another approach pertaining to the modification of CNTs and glassy carbon spheres was conducted via electrochemical methods which involved the reduction of diazonium salts to form

attached layers on substrate surface [145]. The latter was used to covalently anchor a bulk modified surface renewable carbon composite which was successfully applied in the determination of trace levels of lead and cadmium ions from sewage water battery effluent.

One of the surface modification methods ranked under “green” protocols is the so-called “ball milling.” It is assumed that the solvent usage is almost nil therefore facilitating the generation of active site centers on the materials. Ball milling induces the decomposition of diazonium salts under the influence of frictional forces generated by the collision between the reactant surfaces resulting in increasing internal energy temperature. Hence, Pandurangappa *et al.* [72] showed the efficiency of surface modification of glassy carbon spheres with *p*-nitrobenzenediazonium tetrafluoroborate using ball mill grinding. Note, however, they emphasized that high temperature generated from the ball mill grinding may transform the diazonium salts to explosive reagents. Although efficient, ball milling approach must be conducted with extreme care.

*In situ* generated diazonium salts served to modify carbon blacks in order to obtain carboxylic acid-grafted particles (CB-COOH). A timely, elegant and environmental application of these modified carbon blacks is their use as dispersants for marine oil spills [146]. The diazonium-modified CBs were more hydrophilic, could disperse in simulated sea water and in the same time adsorb benzene, a model hydrocarbon representing the more soluble and toxic low-molecular weight aromatic fraction of petroleum. Interestingly, the CB-COOH particles were demonstrated to be non-toxic at all concentrations to brine shrimp *Artemia franciscana*, taken as a model marine microcrustacean, compared to the annealed or as produced CBs which had adverse effects.

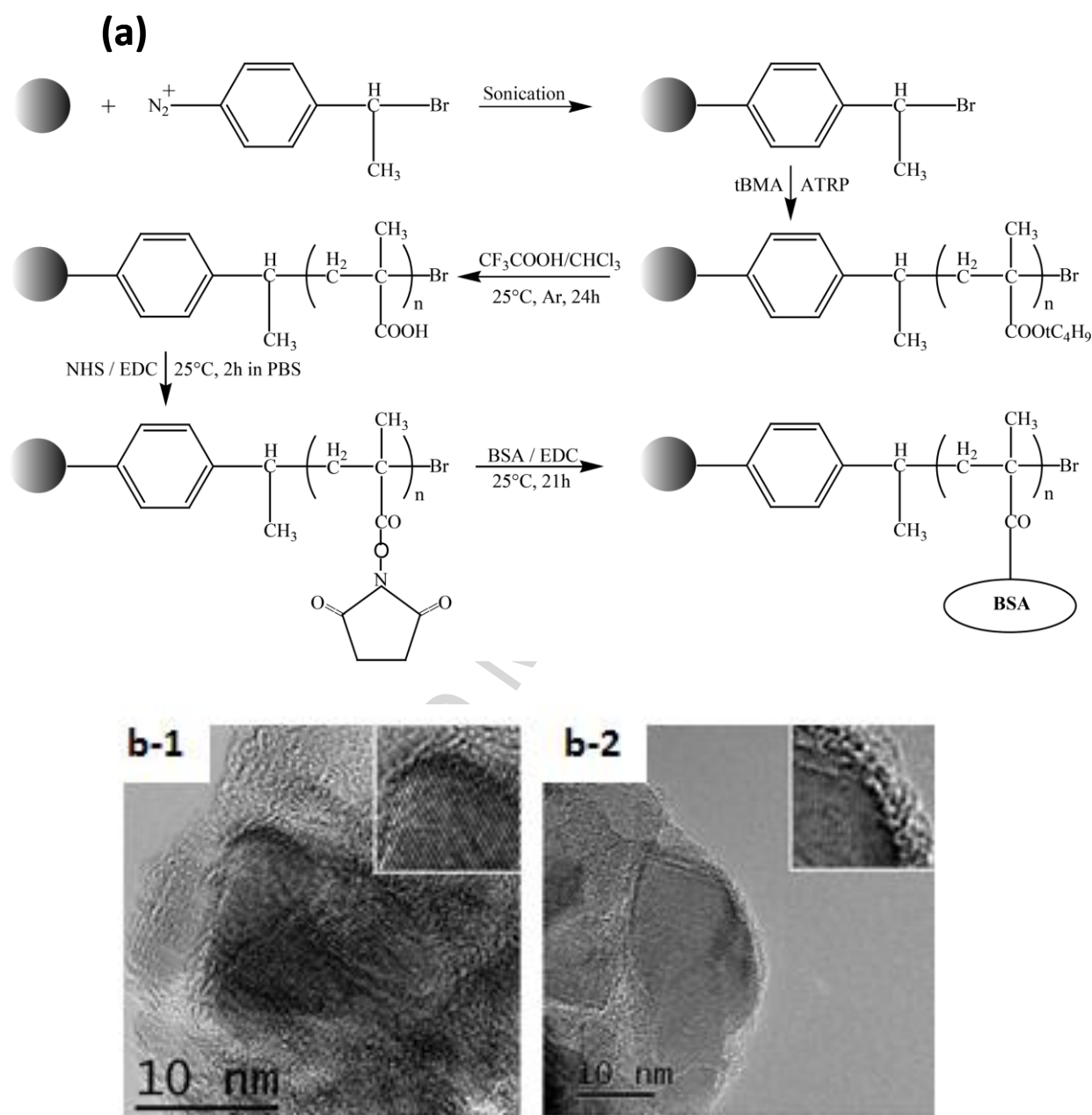
Carbon-coated magnetic nanoparticles have received much attention recently. For example, iron, cobalt and nickel are employed for ferrofluids, catalysis and bio-imaging purposes. Their encapsulation by carbon prevents their oxidation and agglomeration [147]. Metal (Fe, Co, Ni, Ag) and carbide (Fe<sub>3</sub>C) nanoparticles were subjected to diazonium surface modification in aqueous solutions with or without surfactants [148,149] with reasonable grafting densities. Clearly, the carbon shell has enough reducing power towards the diazonium compound to yield aryl radicals that readily bind to the core/shell hybrid particles.

## 5.2. Nanodiamonds

Diazonium modification of nanodiamonds takes its source from the work by Carlisle’s group when they electrochemically grafted aryl layers from diazonium salts to ultra nanocrystalline

diamond films (UNCD) and controlled the hydrophilic/hydrophobic characters of surfaces [150]. However, electrochemistry is difficult to be amenable to the surface modification of suspended nanodiamonds. To overcome this impediment, an ultrasound-assisted grafting of nitrophenyls from the diazonium precursor was envisaged in this regard [66]. Grafting could be conducted in water or acidic aqueous medium; both XPS and IR were used to monitor the increase in the attachment of nitrophenyls *versus* time or initial concentration of the nitrobenzenediazonium tetrafluoroborate. Dahoumane *et al.* [67] extended the work to the fabrication of NDs modified by aryl layers bearing initiators of ATRP for the efficient growth of poly(tert-butyl methacrylate), PtBMA, which were further hydrolyzed into poly(methacrylic acid) chains (PMAA). These chains were post-functionalized by bovine serum albumin (BSA) via the NHS/EDC coupling procedure. The whole process, depicted in Figure 11, proved efficient in constructing bioactive nanodiamonds. First, NDs were modified by aryl layers (step 1) under very mild conditions in water at RT and under sonication. These layers act as surface-attached initiators of ATRP for the efficient growth of PtBMA (step 2). The hydrolysis of PtBMA chains (step 3) formed PMAA which can be readily activated following the NHS-EDC procedure (step 4) for the covalent attachment of bovine serum albumin, taken as a model protein (step 5). This methodology proved its efficiency and versatility in the design of bioactive nanodiamonds.





**Figure 11.** Upper Panel (a): General scheme for the design of protein functionalized hairy NDs (gray sphere): (Step 1) electroless grafting of aryls derived from a diazonium salt; (step 2) surface initiated ATRP (SI-ATRP) of tBMA leading to the growth of PtBMA chains; (step 3) generation of PMAA chains by hydrolysis of PtBMA chains; and (steps 4 & 5) activation of PMAA and covalent tethering of BSA. Lower Panel: (b) Lattice TEM imaging clichés of bare fNDs (b-1) and of fND-PtBMA nanocomposite (b-2). Inset in (b-1), higher magnification image shows clearly that individual fND lattice planes are not affected from the core to the very edge of the grain. Inset in (b-2) depicts a non-crystalline low Z edge polymeric layer, consistent with a 1-2 nm shell of PtBMA. Reproduced from ref. [67]. Copyright (2009) American Chemical Society.

Instead of ultrasonic-assisted aryl grafting, it was demonstrated that electroless modification of NDs could be achieved on hydrogenated NDs [151] rather than pristine O-NDs but the extent of modification, as probed by XPS, was the same as the one reported by Mangeney *et al.* [66]. Nevertheless, electrochemical grafting process on hydrogenated polycrystalline boron-doped diamond (BDD) films proved to be an essential step prior to the electrochemical reductive modification of BDD surface by aryl layers for surface-initiated radical photopolymerization of HEMA [152].

Liang *et al.* [153] tackled the de-agglomeration of nanodiamonds via a process coined “bead-assisted sonication of diamond” (BASD). Even when the original material is not dispersible in the reaction solvent, increasing the functionalization of agglomerates improves their stability. A simple condensation reaction leading to arylation with diazonium salts was performed on detonation nanodiamond (D-ND) agglomerates to achieve surface functionalization on primary NPs. Diazonium salts react with C=C bonds produced at high temperature or a BASD pre-treatment as portrayed in Figure 12.



**Figure 12.** Surface functionalization of nanodiamonds. Arylation of nanodiamonds using diazonium salts. They react with C=C or -OH groups after surface modification at high temperature or a BASD pre-treatment. Adapted from [153]. Copyright (2009) American Chemical Society.

### 5.3. Metallic and semi-conductor nanoparticles

Regarding metallic and semi-conductor nanoparticles, much work has been devoted to the modification of gold nanoparticles. We focus on these nanoparticles in this section and briefly summarize the findings on other metallic and semi-conductor nanostructures.

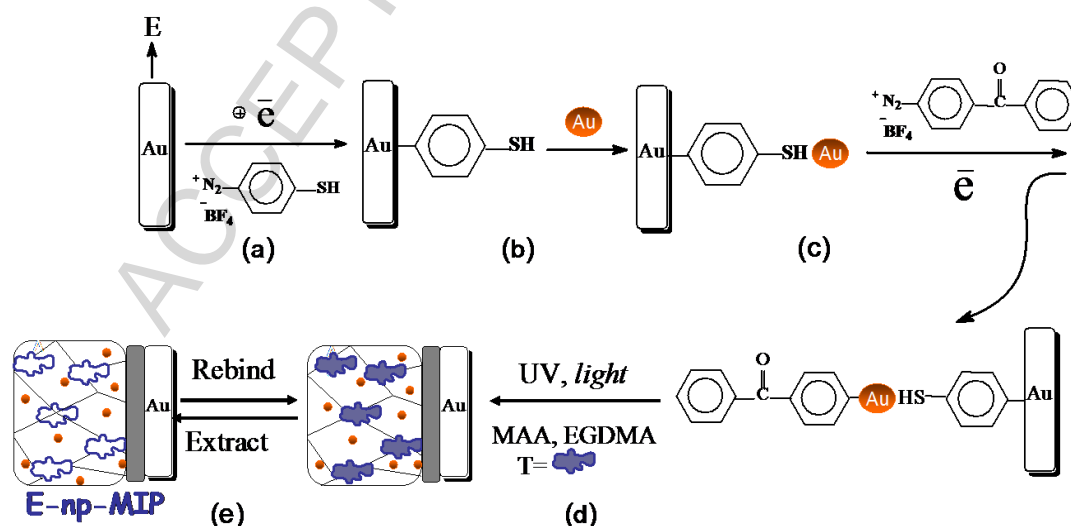
#### 5.3.1. Gold and other metallic nanoparticles

Gold nanoparticles grafted by aryls derived from diazonium salts can be prepared by: (i) electrochemistry [23], (ii) chemical reduction of diazonium salts in the presence of gold nanoparticles

[54], (iii) phase-transfer of tetrachloroaurate(III) to a diazonium salt solution [56], (iv) reduction of both auric and isolated diazonium salts in aqueous medium [154], and (v) direct synthesis of benzenediazonium salt bearing tetrachloroaurate(III) [155]. Other metals have also been capped with aryl layers from diazonium salts, namely platinum [56], titanium [156], palladium [157], iron [158] and vanadium [159].

### 5.3.1.1. Electrochemistry

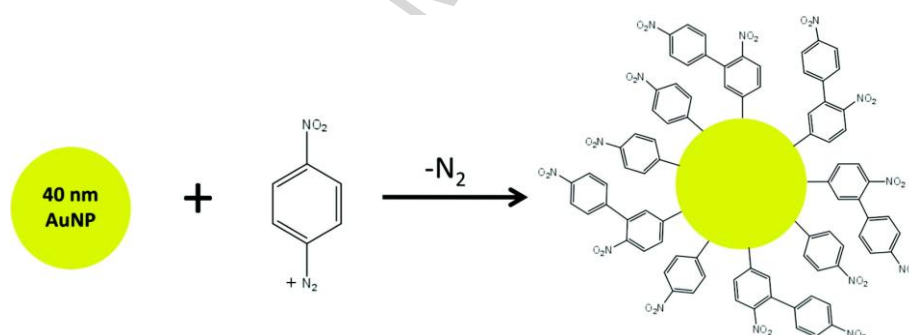
Gam-Derouich *et al.* [23] immobilized citrate-stabilized gold NPs on thiophenyl-functionalized gold plates. The immobilized nanoparticles, in turn, were modified with *p*-benzoylbenzenediazonium salt to provide *p*-benzoyl phenyls which acted as tethered photosensitizer for the UV-graft radical copolymerization of methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) in the presence of dimethylaniline as a hydrogen donor and dopamine as the template (Fig. 13). Via this route, it was possible to design ultra-sensitive molecularly imprinted polymer (MIP) layers for the specific and selective recognition of dopamine, achieving a limit of detection (LOD) of  $0.35 \text{ nmol.L}^{-1}$  measured by square-wave voltammetry. This LOD is almost three times lower than that achieved without embedded gold NPs.



**Figure 13.** Schematic representation of the preparation of MIP grafted with embedded nanoparticles on Au electrode (E-np-MIP). Reproduced from ref. [23]. Copyright (2011) Elsevier.

### 5.3.1.2. Chemical reduction of diazonium salts in the presence of gold NPs

Diazonium salts can be spontaneously reduced on gold NPs (Au NPs) as described by McDermott *et al.* [54]. They simply mixed citrate-capped 40 nm-sized gold NPs and a nitrobenzenediazonium salt in acetonitrile to obtain aryl-modified Au NPs (Fig. 14). The structure and bonding of the film were probed with surface-enhanced Raman scattering spectroscopy (SERS). It was found using extinction spectroscopy and SERS that a nitrobenzene film formed on gold NPs from the corresponding diazonium salt. Comparison of the SERS results with those computed from density functional theory (DFT) models revealed a band characteristic of Au-C stretching frequency. The observation of this stretching is a direct evidence of covalent bonding. A similar band was observed in high-resolution electron energy loss spectra (EELS) of nitrobenzene on planar gold. The bonding of these types of films by covalent bonding on gold is consistent with their observed enhanced stability. The authors concluded on the interest in using diazonium-derived films on gold and other metals in applications where high stability and/or strong adsorbate-substrate coupling is needed.



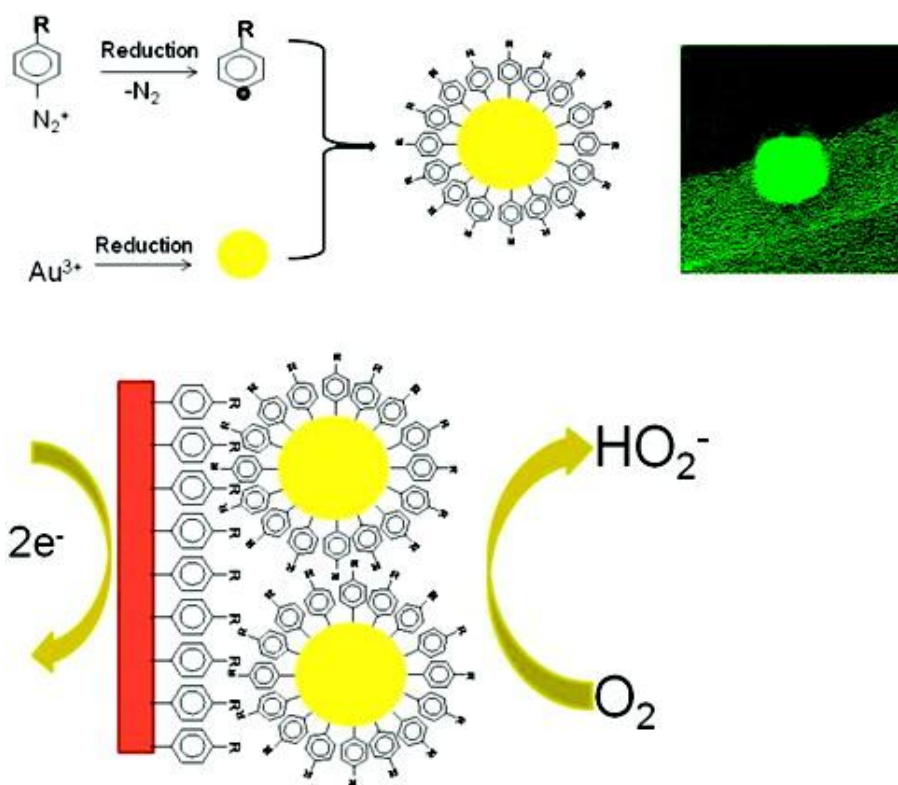
**Figure 14.** Reaction scheme for the spontaneous adsorption of dNB on 40 nm AuNPs illustrating the proposed film structure on the surface of the nanoparticles. Reproduced from ref. [54]. Copyright (2011) American Chemical Society.

The simplicity of the reaction between gold nanoparticles and isolated diazonium salts opened new avenues in sensor science and technology. For example, CTAB-stabilized gold nanorods (length:  $35 \pm 3$  nm, breadth:  $15 \pm 3$  nm) were reacted with 2-(phenoxy)-ethyldiethylcarbamadithionate diazonium chloride ( $\text{ClN}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{-CH}_2\text{-DEDTC}$ , DEDTC: *N,N*-diethyldithiocarbamate) to make a macro-iniferter for the the UV-graft co-polymerization of methacrylic acid and bisacrylamide in the presence of folic acid. Water soluble, core/shell gold nanorod/MIP were obtained and used for plasmonic sensing of the template molecule folic acid with a limit of detection of  $0.1 \mu\text{mol L}^{-1}$  [160].

In a similar procedure, Kesavan and John prepared aminotriazole grafted gold nanoparticles by spontaneous reaction between gold NPs and aminotriazole diazonium cations prior to their deposition on glassy carbon electrodes for the electroanalysis of theophylline and uric acid [161]. In another study by the same group, they attached aminophenyl groups to gold NPs prior to their self-assembly onto GC or ITO electrode surfaces [162]. However, instead of using isolated aryl diazonium salts, they were generated in the presence of gold NPs. The modified electrode showed improved electrocatalytic activity over bare GC towards the oxidation of dopamine [162] or purine derivative [163]. Interestingly, the authors claimed 6-month stability of the aminophenyl-capped gold NPs obtained via *in situ* generated diazonium salts over the method using isolated diazonium salts. A systematic comparative study is thus worth to be conducted to confirm the results pertaining to the stability of the aryl diazonium-modified gold NPs.

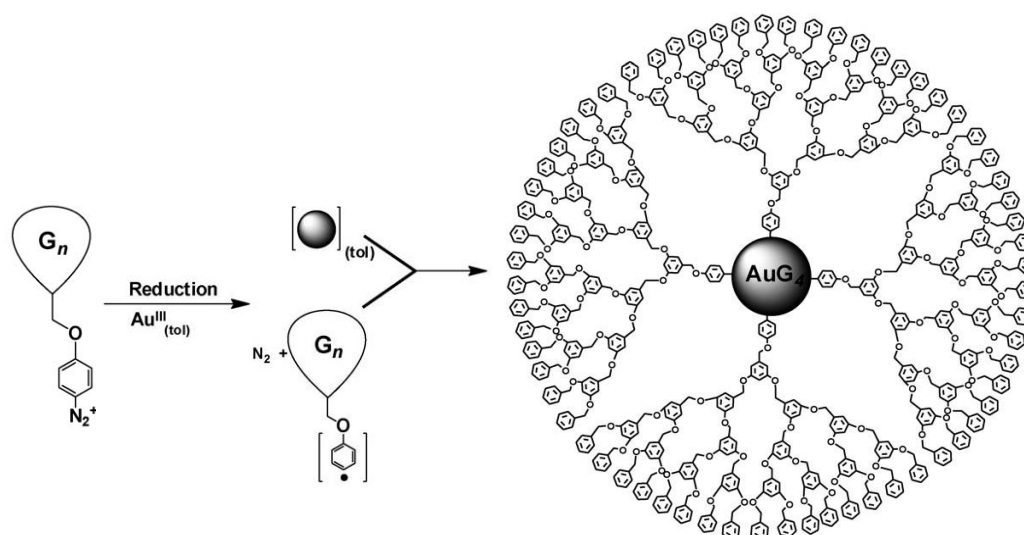
#### 5.3.1.3. Phase transfer of diazonium cation to $[\text{AuCl}_4]^-$ phase

In this method, reported by Mirkhalaf *et al.* [56], gold nanoparticles were synthesized in a two-phase system by transferring  $\text{AuCl}_4^-$  into a toluene phase using the diazonium cation as the phase transfer agent. The diazonium  $\text{AuCl}_4^-$  salt was formed and subsequently reduced by treating the toluene phase with 0.1 M  $\text{NaBH}_4$  aqueous solution [56]. The method is versatile and can be adapted to diazonium modification and stabilization of Pt NPs [56]. Mirkhalaf and Schiffrin [164] have also grafted aryls bearing long decyl chains to gold NPs. The decyl-capped Au NPs were adsorbed on glassy carbon electrodes grafted with decylphenyl from diazonium tetrafluoroborate precursor (Fig. 15). The interaction of decyls from Au NPs with those attached to the electrode surface permitted to obtain gold nanoparticles monolayers and this electrode system proved efficient in the reduction of oxygen, a process of relevance to fuel cells.



**Figure 15.** Synthetic route to decylphenyl-capped gold NPs and their adsorption on decylphenyl-modified glassy carbon electrode for the reduction of oxygen. The top right side of the figure shows capped gold NPs (size: 7 ± 2 nm). Reprinted from ref. [164]. Copyright (2010) American Chemical Society.

In a series of papers, Ghosh *et al.* synthesized a 2-4 nm sized decylphenyl (DP) and biphenyl (BP) monolayer-protected Pd NPs [157], 2-4 nm sized Ru-biphenyl, series of Ru-alkylphenyl NPs (alkyl = C4, C6, C8, C10, C12) [165], and 1-3 nm sized Ti-biphenyl NPs [156] according to the approach first described by Mirkhalaf *et al.* [56]. Pb-BP, Ti-BP and modified Ru NPs exhibited metal-like behavior. A team from India has taken advantage of the phase transfer approach to construct metallic nanoparticles cored dendrimers [166]. The general preparation pathway is displayed in Figure 16.

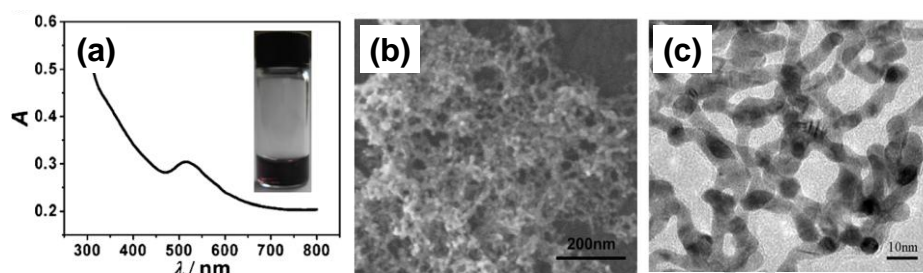


**Figure 16.** Synthesis of NCDs from the simultaneous reduction of Au(III) and the diazodendron. The wedge represents Fréchet-type dendrons of different generations ( $G_n = G_1$  to  $G_4$ ). The final NCD represents generation four ( $G_4$ ) dendron-functionalized gold nanoparticles. Adapted from ref. [166]. Copyright (2010) Wiley.

The same authors recently proposed a similar strategy for constructing Pd-cored  $G_1$  dendrimers (Pd- $G_1$ ) as a selective catalyst for the reduction of C=C and C≡C at room temperature and mild hydrogen pressure [167]. The Pd- $G_1$  was found also to be a good catalyst in Suzuki, Stille and Hiyama coupling reactions [168]. The catalyst exhibited good recovery and recyclability in Suzuki coupling reactions.

#### 5.3.1.4. Reduction of diazonium salts in the presence of gold salt and $\text{NaBH}_4$

Instead of the phase transfer method reported by Mirkhalaf *et al.* (*vide supra*), it is possible to generate gold nanostructures in an aqueous phase. To this end, the reaction of  $\text{HAuCl}_4$ ,  $\text{NaBH}_4$  and the diazonium salt prepared from *p*-aminobenzoic acid resulted in the formation of gold nanocorals (Au-NCs) [154]. These are composed of nanowires of a diameter of 5.3 nm (Fig. 17). When assembled on a glassy carbon electrode, Au-NCs trigger intense electrochemiluminescence of the luminol/ $\text{H}_2\text{O}_2$  system at a potential of  $-0.13$  V. The effect was exploited in sensing  $\text{H}_2\text{O}_2$  with a detection limit of 30 nM.



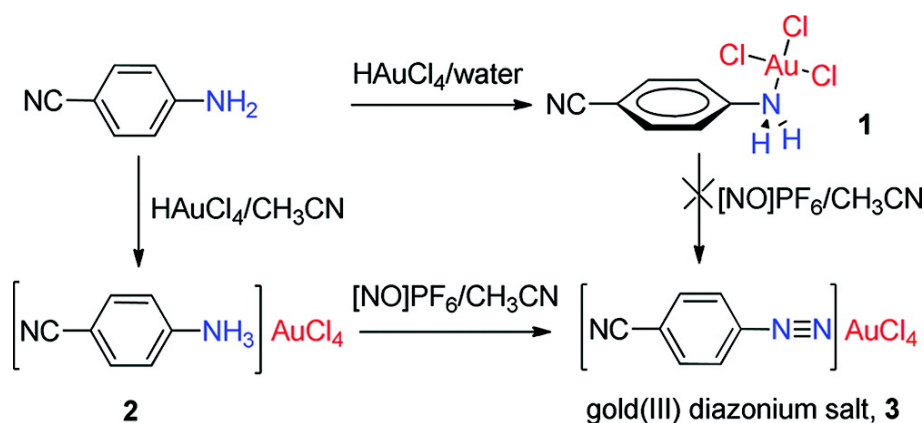
**Figure 17.** Characterization of gold nanocorals: (a) UV-Vis spectrum of Au-NCs solution showing absorbance at 520 nm, (b) SEM image, and (c) TEM image giving a diameter of 5.3 nm. Reproduced from ref. [154]. Copyright (2013) Springer.

The same procedure holds for the construction of aryl-capped platinum nanostructures [169]. 2-2.5 nm sized aryl-modified Pt NPs were produced in water/THF by the simultaneous reduction of aryldiazonium salts and  $\text{H}_2\text{PtCl}_4$  using freshly prepared  $\text{NaBH}_4$ . The increasing trend of the oxygen reduction reaction (ORR) catalytic performance of the  $\text{Pt-C}_6\text{H}_4\text{-R}$  nanoparticles was as follows:  $\text{R} = -\text{CH}_3$ ,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{OCF}_3$ , and  $-\text{CF}_3$ , and was interpreted in terms of Hammett substituent constant ( $\sigma$ ), meaning a higher ORR for a higher  $\sigma$ . In a similar procedure, the same group produced butylphenyl-capped Pt NPs ( $2.93 \pm 0.49$  nm) for the electrocatalytic oxidation of formic acid [170]. Interestingly, aryl layers grafted to Pt NPs effectively blocked the CO poisoning which results from spontaneously dissociative adsorption of formic acid on the catalyst.

#### 5.3.1.5. Formation of aryl-modified Au NPs by reduction of diazonium tetrachloroaurate(III) salts

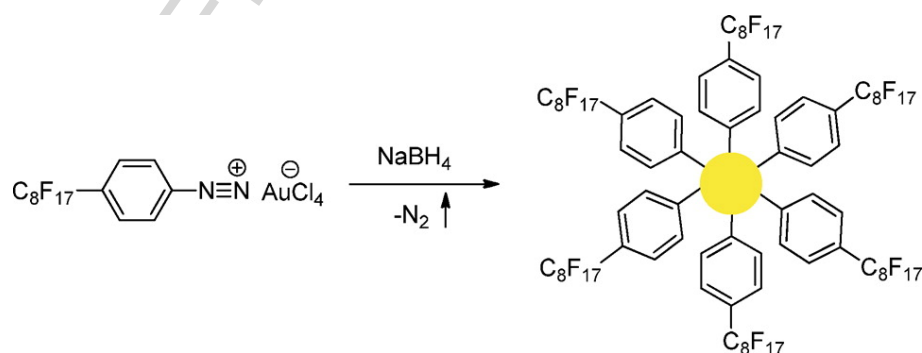
Overton and Mohamed [45] have been recently able, for the first time, to synthesize stable diazonium tetrachloroaurate(III) complexes  $[\text{R-4-C}_6\text{H}_4\text{N}\equiv\text{N}]\text{AuCl}_4$  ( $\text{R} = \text{CN}$ ,  $\text{C}_8\text{F}_{17}$ ,  $\text{Br}$ ,  $\text{NO}_2$ ,  $\text{F}$ ,  $\text{C}_6\text{H}_{13}$ ) in a high yield (Fig. 18). Protonation of  $\text{CN-4-C}_6\text{H}_4\text{NH}_2$  with  $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$  in water resulted in **1**, however protonation in acetonitrile formed the anilinium tetrachloroaurate(III) salt  $[\text{CN-4-C}_6\text{H}_4\text{NH}_3]\text{AuCl}_4$ , **2**, which was easily oxidized by  $[\text{NO}]\text{PF}_6$  to form the yellow diazonium tetrachloroaurate(III) salt  $[\text{CN-4-C}_6\text{H}_4\text{N}\equiv\text{N}]\text{AuCl}_4$ , **3**, in 92% yield.





**Figure 18.** Synthesis of diazonium tetrachloroaurate(III) complexes. Reprinted from ref. [45]. Copyright (2012) American Chemical Society.

A single-phase synthesis of organometallic gold nanoparticles was reported in a recent communication [155]. Sodium borohydride ( $\text{NaBH}_4$ ) reduction of  $[\text{C}_8\text{F}_{17}\text{-4-C}_6\text{H}_4\text{N}_2]\text{AuCl}_4$  produced ruby red gold-carbon nanoparticles (Fig. 19). The fluorinated ligand acts as a stabilizer and phase-transfer agent and circumvents the use of the phase-transfer catalyst tetraoctylammonium bromide (TOAB). The nanoparticles did not gradually lose their colloidal stability in acetonitrile when exposed to air for a long period of time. The nanoparticles are robust and able to withstand prolonged sonication in ethanol and acetonitrile and indefinite exposure to ambient conditions in the solid state. The organic shell is resistant to elimination and oxidative coupling.



**Figure 19.** Synthesis of gold-carbon nanoparticles from benzenediazonium tetrachloroaurate(III)  $[\text{C}_8\text{F}_{17}\text{-4-C}_6\text{H}_4\text{N}_2]\text{AuCl}_4$ . Reproduced with permission from ref. [155]. Copyright (2014) American Chemical Society.

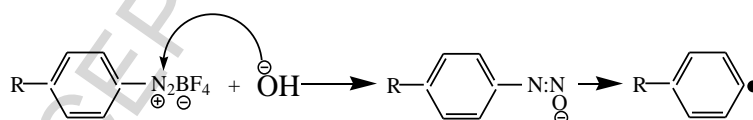
### 5.3.2. Semi-conductor nanoparticles

*p*-Carboxybenzenediazonium modified Si nanoparticles [171] were used in energy storage purposes. The *p*-carboxyphenyl-modified Si anodes in Li ion batteries exhibited reversible capacities of 1173 and 527 mA h g<sup>-1</sup> at the 1<sup>st</sup> and 50<sup>th</sup> cycles, much higher than those of bare Si electrodes of only 56 and 62 mA h g<sup>-1</sup>, respectively. InAs quantum dot-decorated GaAs substrates were functionalized with air-stable aminobenzenediazonium, nitrobenzenediazonium, and biphenyldiazonium salts to provide advanced, hybrid biocompatible organic molecule-optical and electronic semiconductor devices [172]. These systems are chemically stable and able to withstand heat treatment up to 100 °C without significant alteration in their photoluminescence properties due to the robust In-C, As-C, and Ga-C covalent bonds.

## 5.4. Metal oxide nanoparticles

### 5.4.1. Modification of silica, alumina and Fe<sub>3</sub>O<sub>4</sub> through diazoate chemistry

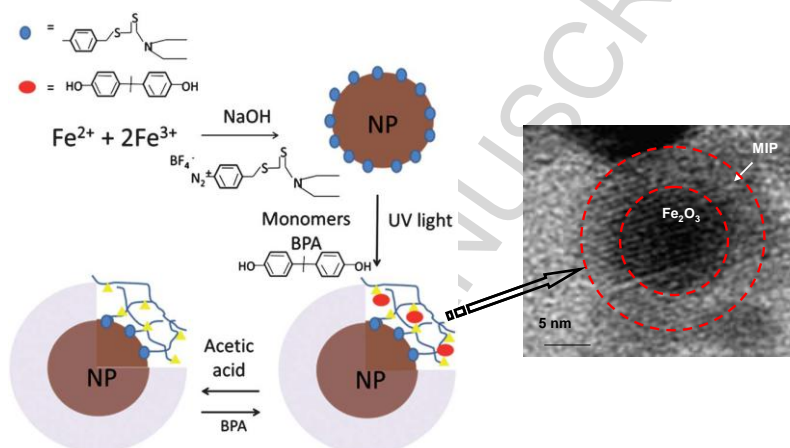
It is well known from organic chemistry textbooks [173] that, in alkaline aqueous solutions, diazonium salts turn into diazoates which subsequently cleave into radicals (Fig. 20).



**Figure 20.** Transformation of a diazonium salt into diazoate in alkaline medium.

Diazoate formation was exploited by Pinson *et al.* [174] to spontaneously modify iron and gold surfaces by aryl layers. As far as nanoparticles are concerned, water soluble magnetic Fe<sub>3</sub>O<sub>4</sub> NPs capped with aryls were prepared via the synthesis of magnetic particles in alkaline media from one equivalent Fe(II) and two equivalents Fe(III) in the presence of diazonium salts [175]. The iron salts produced Fe<sub>3</sub>O<sub>4</sub> NPs the size of which was controlled by the elapsed time from the beginning of NP formation. Introducing the diazonium salts into alkaline medium gave diazoates which themselves provided radicals that reacted with the NPs by adsorbing onto their surface therefore stopping their growth. The “diazoate” approach was applied to pre-formed magnetic NPs resulting in their surface functionalization by aryl layers. By employing a diazonium salt bearing a dithiocarbamate, a type of radical photopolymerization initiator, it was possible to obtain core-shell magnetic Fe<sub>3</sub>O<sub>4</sub>/MIP

nanocomposite directed toward bisphenol A (BPA) removal as schematically displayed in Fig. 21 [176]. After specific and selective recognition of BPA, the particles could be recovered with a simple magnet to concentrate the BPA. In another publication, and through iniferter (iniferter: *initiator-transfer-terminator*) approach, Griffete *et al.* [177] prepared core-shell  $\text{Fe}_3\text{O}_4/\text{PMAA}^a$ ; the NPs are magnetic, pH-responsive and could be recovered by a magnet. They sediment at pH 5.5 but disperse well in water at pH 8 upon conversion of COOH groups to carboxylates.



**Figure 21.** General protocol for constructing biomimetic magnetic MIP-capped nanoparticles for the specific and selective removal of bisphenol A. Adapted from ref. [176]. Copyright (2012) The Royal Chemical Society.

The same protocol can be applied to silica NPs in order to obtain pH-responsive, inorganic core/organic shell silica/aryl-PMAA hybrid materials [178]. The organic shell is about 10-20 nm thick as characterized by TEM. Although the whole process is straightforward and provides interesting applications, still there is no clear mechanism that could account for the attachment of aryl radicals from diazoates to silica NPs. Indeed diazoates might be repulsed by the negatively charged silica nanoparticles in alkaline medium. This crucial point is for sure worth deeper investigation.

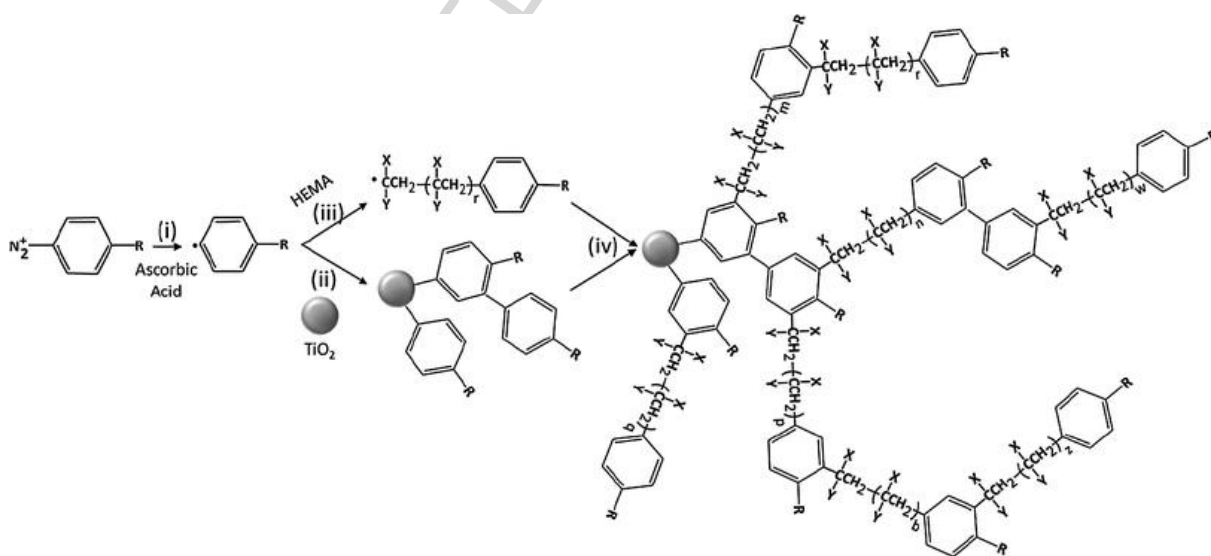
Recently,  $\text{Al}/\text{Al}_2\text{O}_3$  particles were reacted with diazotized dithiocarbamate to provide a macroinitiator for the iniferter polymerization of methacrylic acid [53]. The method provides  $\text{Al}@\text{Al}_2\text{O}_3@\text{PMAA}$  core/double shell nanoparticles with a PMAA overlayer thickness in the 1.6-4.3 nm range. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) suggested a main grafting of PMAA to the alumina shell through Al-O-C bonding. In addition, the aryl layer was claimed to prevent the underlying aluminium from oxidation.

<sup>a</sup> PMAA: poly(methacrylic acid). The authors prepared a crosslinked PMAA shell using ethylene glycol dimethacrylate as a crosslinker.

The “diazoate approach” has recently been explored in view of constructing ~21 nm-sized, nitrophenyl capped zero valent iron nanoparticles [158]. However, no proof for metal-carbon bond was demonstrated.

#### 5.4.2. TiO<sub>2</sub>

Mesnager *et al.* [58] modified TiO<sub>2</sub> nanoparticles using nitrobenzenediazonium salt in the presence of the reducing agent ascorbic acid and the monomer 2-hydroxyethyl methacrylate (HEMA). This is an interesting route as the reduction of the diazonium salt by ascorbic acid yields phenyl radicals which can (i) initiate polymerization of HEMA and (ii) establish covalent link with TiO<sub>2</sub> surface. The attached aryl onto the surface can react with the growing radical oligomers therefore leading to a grafted polymer shell around TiO<sub>2</sub>. As shown in Fig. 22, a copolymer of HEMA and aryl units is expected to be grafted and not homo-PHEMA chains. Thermogravimetric analysis (TGA) indicated as low as 4% weight mass loading of the organic coating, nevertheless, sufficient for the grafted HEMA repeat units to be probed by IR and high resolution XPS C1s peak.

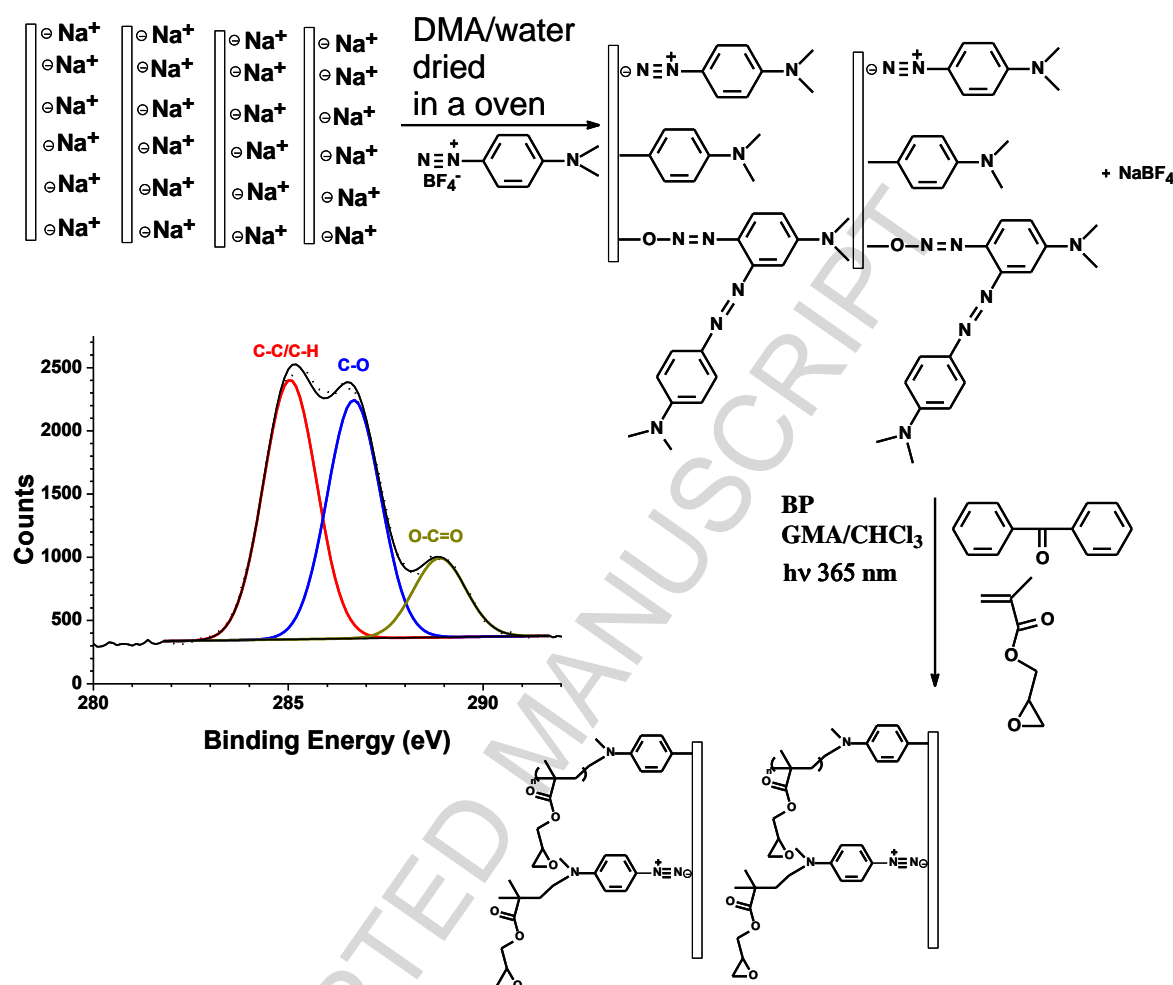


**Figure 22.** Mechanism of methacrylate polymer grafting onto TiO<sub>2</sub> nanoparticles by DIAP route. Reproduced from ref. [58]. Copyright (2011) Springer.

## 5.5. Clays

Modification of clays using diazonium salts has rarely been investigated. Two distinct strategies were reported in this regard: (i) modification of clay catalysts as the first step in the preparation of azo dyes and (ii) construction of clays-polymer nanocomposites. Via the first approach, Dabbagh *et al.* [179] conducted the diazotization and the diazo coupling reactions of sodium sulfanilate dihydrate and *p*-diazonium benzene sulfonyl azide with aromatic phenols over an eco-friendly clay catalyst. The method is interesting as it completely avoids the use of acids, alkalis and toxic solvents in the diazotization and diazo coupling reactions.

In the second approach, Salmi *et al.* [34] proposed to intercalate the clay by exchanging sodium with the diazonium cation. XPS shows the absence of  $\text{BF}_4^-$  counter-anion and strong decrease in the sodium cation content. The existence of an IR band assigned to  $\text{N}\equiv\text{N}$  stretching frequency indicates that the cation exchange occurred. With *N,N*-dimethylaminobenzenediazonium cation intercalated within the layered silicate, it was possible to initiate radical photopolymerization of glycidyl methacrylate (GMA) in the presence of benzophenone photosensitizer. The process resulted in highly intercalated clay/PGMA nanocomposites with an onset of exfoliation. The complete process and the possible mechanisms of the formation of clay-PGMA nanocomposites are displayed in Fig. 23. One can also see the high resolution  $\text{C}1\text{s}$  region from the nanocomposite fitted with three components centered at 285, 286.5 and 289 eV, in the  $\sim 3/3/1$  atomic ratio, assigned to  $\text{C-C/C-H}$ ,  $\text{C-O}$  and  $\text{O-C=O}$  chemical environments, respectively. The high resolution peak is quasi-identical to that of a pure PGMA.



**Figure 23.** Possible DMA diazonium cation-clay interaction followed by *in situ* photopolymerization of glycidyl methacrylate. Attachment of PGMA chains to the aryl layer is shown only for simplicity, generic monomolecular modification of one Si-O group from the clay. Adapted from ref. [34]. Copyright (2013) American Chemical Society.

The intercalation of clays by diazonium compounds was further explored by Jlassi *et al.* [180] to exchange sodium by diazotized diphenylamine (DPA) in order to prepare exfoliated clay/PANi nanocomposites. The intercalation of diazonium cations increased the interlamellar spacing and facilitated the *in situ* oxidative polymerization of aniline which resulted in exfoliation of the clay. Nanocomposites prepared with diazonium-modified clay exhibited a conductivity of  $2 \times 10^{-3}$  S/cm, 5 orders of magnitude higher than the corresponding nanocomposites prepared with no diazonium pretreatment of the clay.

## 6. Attachment of nanoparticles to diazotized surfaces and diazotized nanoparticles to surfaces

Attachment of nanoparticles to surfaces can be performed using diazonium salts in two routes: (i) attachment of nanoparticles to diazotized surfaces and (ii) attachment of diazotized nanoparticles to surfaces.

### 6.1. Immobilization of particles on diazotized surfaces

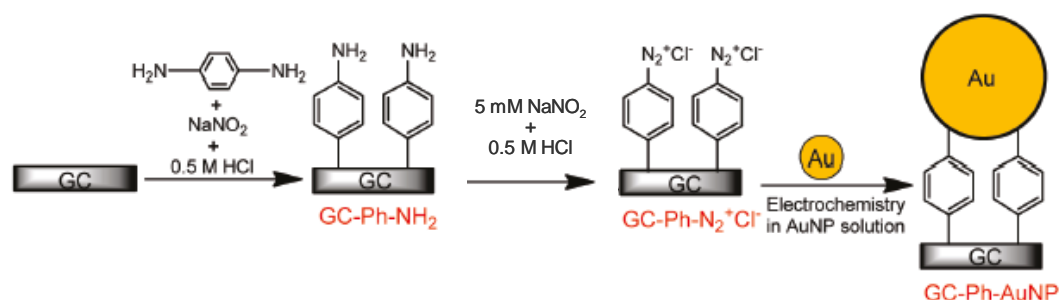
This is actually an old approach that was proposed several decades ago in view of attaching proteins and enzymes to stationary phases in affinity chromatography [181]. Considering that proteins have colloidal properties and most of them are globular, one can rank them as “soft” particles and, in this sense, these strategies definitely fall within the scope of this review. The process has been revisited with “hard” particles using various routes. Generally speaking, if up to now we have considered aryl diazonium salts as “molecular” species for modifying surfaces, in this section we report on surfaces bearing diazonium salts reaction with particles. One can thus coin such diazotized surfaces as “macro-diazonium salts.”

In summary, concerning enzymes, the strategy consists of functionalizing the surface of silica [182] or cellulose [183] by *p*-aminobenzoyl layers which can be further diazotized using  $\text{NaNO}_2/\text{HCl}$ . The diazotized silica or cellulose reacts with tyrosine or histidine residues from an enzyme to provide surface-grafted enzymes with interfacial azo bonds.

Gold surface has been modified by *in situ* generated diazonium salt from 1,4-phenylenediamine dihydrochloride. The surface-free amino group was further reacted to provide diazotized gold surface which readily reacted with bovine serum albumin (BSA) [184]. The BSA-decorated gold plates were reacted with AFM tips which were previously modified with various diazonium salts. The authors provided detailed information on the interaction of proteins with various chemical functionalities to adjust the hydrophobicity/hydrophilicity and charge. Specifically, the authors studied unfolding intermediates during the protein stretching.

As far as “hard” inorganic particles are concerned, Gooding and co-workers [185] grafted aminophenyl layers to glassy carbon surfaces and the functional amino groups were further converted to diazonium cations. The potential of the diazotized GC electrode was swept cathodically, therefore providing radicals which readily reacted with gold NPs leading to their strong attachment

(Fig. 24). 97.1% of the Au NPs withstood sonication thus stressing the interest in the approach in decorating diazotized surfaces with Au NPs.



**Figure 24.** Attachment of Au NPs to diazotized glassy carbon electrode. Adapted from ref. [185]. Copyright (2011) American Chemical Society.

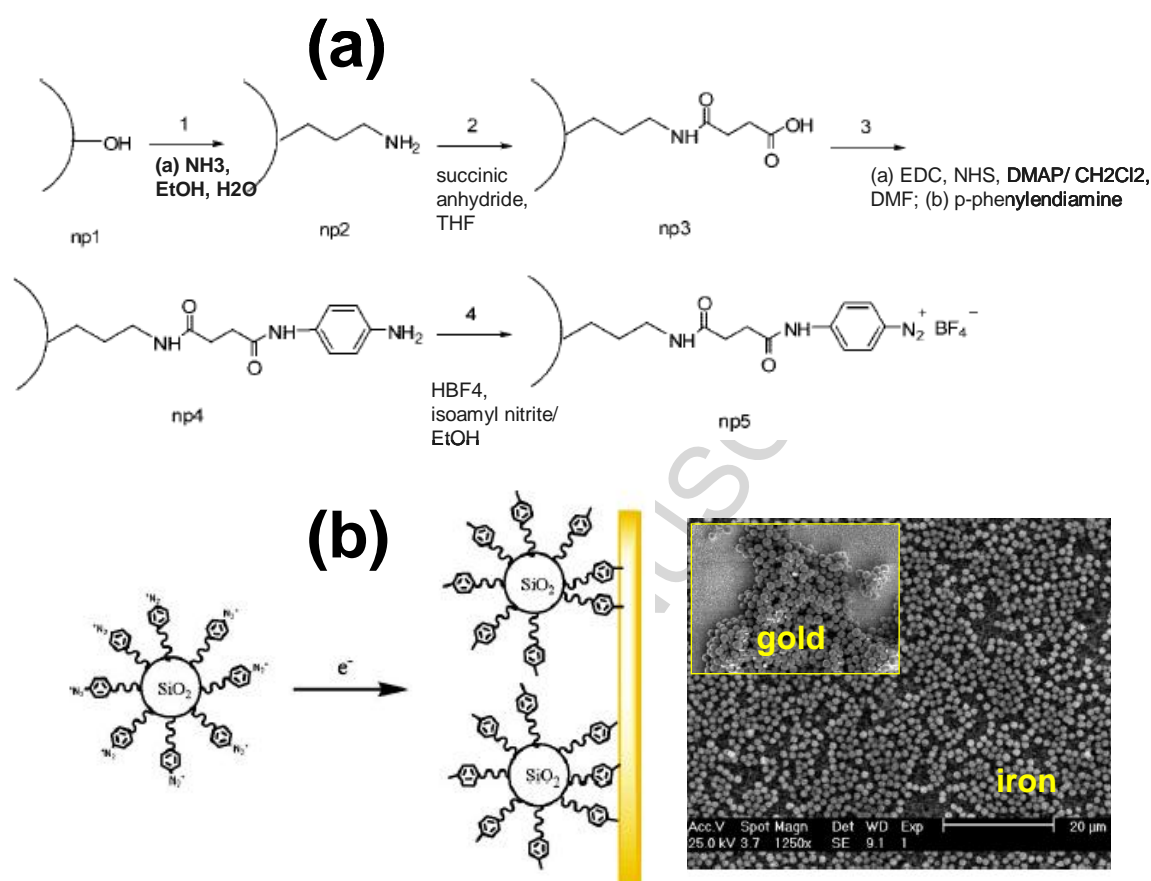
Sun and Ma [186] followed a similar approach to design highly stable electrochemical immunosensor for carcinoembryonic antigen (CEA). Aminophenyl groups bound to GC surface were diazotized and reacted with gold NPs. Anti-CEA was directly adsorbed on the surface of Au NPs. The detection limit of the immunosensor was found to be as low as  $3 \text{ fg.mL}^{-1}$  at signal to noise ratio of 3. Interestingly, one can take advantage of this strategy to build layered materials through interfacial chemistry of diazotized materials as reported above in section 5.1.2. for LBL prepared PSDAS-graphene nanocomposites [125].

Besides proteins and nanoparticles, carbon nanotubes were also attached to diazotized macroscopic surfaces following a strategy resembling that shown in Figure 24 [187]. The reaction of CNTs with diazonium groups bound to the surface is spontaneous and results in covalent attachment of CNTs. Viel *et al.* [187a] termed the diazotized platforms as “self-adhesive surfaces”.

## 6.2. Attachment of diazotized particles

The method rests on the functionalization of particles by an aminophenyl layer which is then converted to diazonium cation. For example, Williams *et al.* [188] diazotized silica NPs therefore providing “macro-diazonium salts.” Upon electrochemical reduction, they attached silica NPs to both iron and gold electrode surfaces with distinct assembly morphologies. The complete process is displayed in Figure 25.

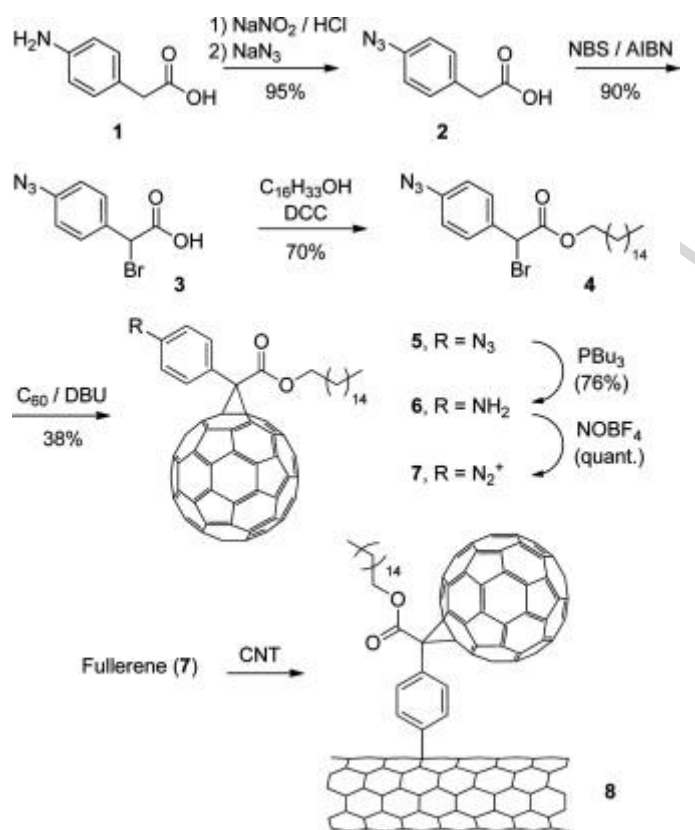




**Figure 25.** Method of diazotization of silica NPs and their electrochemical reduction at the surface of iron and gold electrodes. Adapted from ref. [188]. Copyright (2008) American Chemical Society.

A similar procedure was conducted by Liu *et al.* [189] who electrochemically attached diazotized gold NPs to a GC electrode. The resulting nanoparticle-decorated electrodes served for the design of an electrochemical immunosensor for the detection of botulinum neurotoxin type A. It is to note that, in this sensing system, the immobilized gold NPs played the role of both electronic bridges and signal amplifiers.

Given the propensity of diazonium salts to spontaneously reduce on carbon surfaces, one can take advantage of this strategy to design C<sub>60</sub>-decorated SWCNTs [190]. The nanohybrids were prepared in *o*-dichlorobenzene by the reaction of diazotized C<sub>60</sub>, acting as a macro-diazonium cation, with SWCNTs, as schematically shown in Figure 26. These nanohybrids were found to have superior nonlinear optical limiting properties compared to SWCNTs and C<sub>60</sub> taken separately or their mixtures.



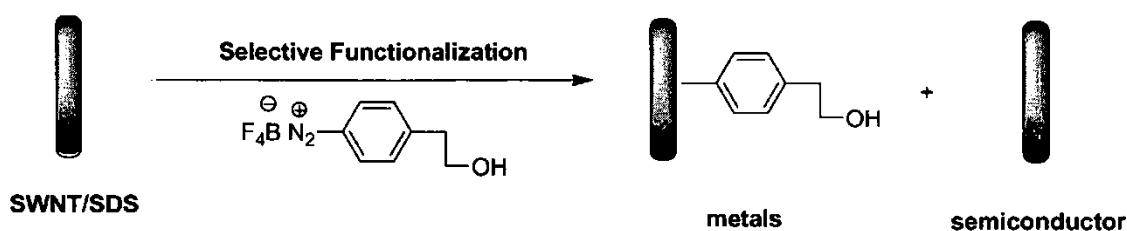
**Figure 26.** Synthesis of SWCNT- $C_{60}$  nanohybrids using diazotized  $C_{60}$ . Reproduced from ref. [190]. Copyright (2014) Elsevier.

## 7. Patents and industrial applications

### 7.1. Carbon nanotubes

Tour *et al.* [191] described methods of carbon nanotubes derivatization via *in situ* generation of diazonium salts leading to a degree of functionalization of one out of every 20 to 30 carbon atoms per single nanotube. Suitable chemical groups led to modified carbon nanotubes that are chemically compatible with polymer matrices therefore permitting the design of composite materials. Improving the grafting density on CNTs was achieved without using a solvent in isoamyl nitrite at 60 °C in the presence of an aromatic amine [192].

Distinguishing metallic from semiconductor SWCNTs is important for electronics purposes. Diazonium modification of SWCNTs is a key step in this regard as metallic SWCNTs over-react with diazonium salts compared to their semiconducting counterparts (Fig. 27) [193].



**Figure 27.** Selective functionalization of metallic over semiconductor SWCNTs using diazonium. Adapted from ref. [193].

The same research group modified SWCNTs with bromobenzenediazonium compound which provides a macro-initiator for the *in situ* anionic polymerization [194]. The resulting polymer-carbon nanotubes improved the dispersion ability in polymer matrices. The inventors claimed that the resultant CNT-grafted polymers can be blended with pre-formed polymers to establish compatibility and enhance dispersion of nanotubes, otherwise hard to disperse, in matrices resulting in significantly improved material properties. Such nano-objects were also proposed for drug delivery and as scaffolds for tissue engineering.

## 7.2. Carbon black

Carbon black (CB) is of a paramount importance as filler particularly for the rubber industry and the production of inkjet inks. For these reasons, carbon black has received much interest in view of modification of its surface by aryl diazonium salts. For example, Cabot company and others have described the design of modified carbon blacks with ionic groups for inkjet inks [195,196], aqueous inks and coatings [197], non-aqueous inks and coatings [198,199], esterification catalysts [200] and fuel cells [201]. Diazonium modification of carbon blacks and pigments ensures control over their surface energy, dispersion and printing resolution. For more details on carbon blacks for inkjet inks, the reader is referred to refs [202,203].

The dispersion of carbon blacks can be improved using grafted polymer chains. CB particles were first modified by *in situ* generated diazonium salt of *p*-aminobenzoic acid [204]. The CB-COOH particles were converted, using bromoisobutyrate, to CB-Br macroinitiator for the ATRP of *n*-butyl acrylate (*n*-BA) which resulted in PnBA-modified CB, dispersible in THF. Owing to the living character of ATRP, the composite particles CB-PnBA bearing terminal C-Br served to initiate the growth of a

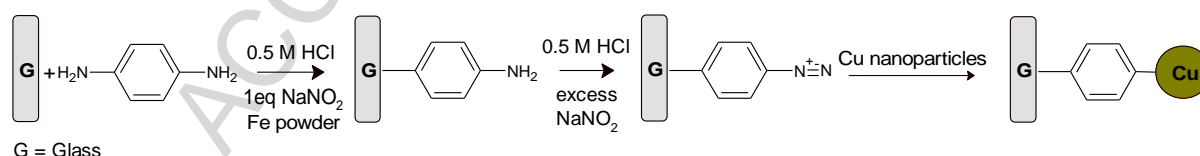
second polymer block, namely poly(ter-butylmethacrylate). The final CB-PnBA-block-PtBMA was also found to be dispersible in THF.

Recently, there has been a growing demand for carbon blacks with low polyaromatic hydrocarbons (PAH) content - from less than 1 ppm to 75 ppm max, as PAHs have the potential to cause adverse health effects. These can be prepared using diazonium salts of the primary amines  $H_2N-Ar-S_k-Ar'-NH_2$  or  $H_2N-Ar-S_k-Ar''^b$  ( $k = 1$  to  $8$ ) [205].

Another Swiss company, TurboBeads, produces carbon-coated cobalt (Co@C) and other nanoparticles bearing surface aryl groups. The beads Co@C have a diameter of less than 50 nm and a grafting density of the aryl groups  $-C_6H_4-CH_2-COOH$  higher than 0.1 mmol/g [158,206]. These diazonium-modified beads have several biomedical applications, such as blood purification, immunoassays, protease detection and magnetic enzymes, and catalytic applications [206].

### 7.3. Immobilized copper nanoparticles

Copper NPs can be assembled onto diazotized surfaces as described above in Section 6.2. Toward this end, a glass plate can be modified by the reduction of the monodiazonium salt of *p*-phenylenediamine resulting in attached aminophenyl layers which, in turn, can be diazotized. The so-diazotized surface reacts readily with graphene layers, CNTs, copper NPs and organic compounds such dendrimers [207]. Fig. 28 displays the patented strategy for immobilizing copper NPs.



**Figure 28.** Binding of copper NPs to a diazotized glass surface. Adapted from ref. [207].

<sup>b</sup> Ar and Ar' are independently substituted or unsubstituted arylene or heteroarylene groups, Ar'' is an aryl or heteroaryl group.

## 8. Conclusions and future prospects

Modern surface chemistry of aryl diazonium salts started with electrochemical studies and focused mainly on glassy and other carbon electrodes. However, it soon became clear that it could be extended to  $sp^2$  carbon micro- and nano-materials followed by many other types of supports, namely metallic, semi-conductor and metal oxide nanoparticles, diamond, clays and polymers. In this review, we focused on functionalization of nanomaterials using aryldiazonium salts to draw the attention of materials scientists to the widespread applications of diazonium-modified nanomaterials in various domains related to catalysis, energy, environmental science and nanomedicine engineering. Table 2 reports handpicked, timely applications described in the present review and the corresponding aryldiazonium-modified nanomaterials involved in the developed devices or systems. Clearly, Table 2 shows that there are unlimited combinations of nanomaterials and diazonium salts to address specific applications, and the versatile interface chemistry of diazonium salts has better days ahead.

If the surface chemistry of aryldiazonium salts has progressed at an outstanding pace, the rationale explanation lies in its remarkable simplicity and applicability to many types of materials such as carbon, diamond, metals, oxides, semi-conductors, clays and even organic polymers. This is by far superior to any known surface modifiers and coupling agents employed in the general domains of materials science, surface science and adhesion. Such simplicity has led to the industrial development of aryldiazonium-modified micro- and nano-materials.

Materials scientists can tackle surface modification with either isolated or *in situ* generated aryldiazonium salts. Isolated aryldiazonium salts are interesting because of their spontaneous reaction with  $sp^2$  carbon nanomaterials as well as with gold and other metals. For this reason, we believe that specialty aryldiazonium salts aimed for specific application will continue to be synthesized and isolated. However, long term stability has been a major concern. To address this critical point, the group of one of the authors of this review Ahmed Mohamed designed “gold diazonium” salts with a remarkable stability [45,46,155]. Other authors have confirmed the stability of aryldiazonium tosylate salts [149] on the top of their interesting water solubility.

Instead of using isolated salts, one can achieve high grafting densities of aryl layers using *in situ* generated salts, particularly when they react with CNTs [47]. One additional advantage of this approach was claimed concerning the colloidal stability of aryl-capped gold NPs [162]. Authors of this

study reported at least 6-month colloidal stability of aryl-capped gold NPs synthesized in the presence of *in situ* generated rather than isolated diazonium salts.

**Table 2.** Selected applications of nanomaterials modified by aryldiazonium salts and the corresponding systems or devices.

Application	Nanomaterial	Diazonium functional group	System / Device	Refs.
Adsorbents of hazardous compounds	SMGO	SO <sub>3</sub> H	SMGO-SO <sub>3</sub> H for copper removal	135
	Fe <sub>3</sub> O <sub>4</sub>	CH <sub>2</sub> -DEDTC	MIP-capped magnetic NPs for selective removal of bisphenol A (PBA).	176
Antistatic coating	rGNS	NH <sub>2</sub>	rGNS/PPy	124
Bioactive nanodiamond	Nanodiamond (50 nm)	-CH(CH <sub>3</sub> )Br	ND-PMAA-BSA bioconjugate	67
Catalysis	MWCNTs	C≡C-H	MWCNT/polymer-immobilized Pd NPs for Suzuki coupling	61
	Pd NPs	dendron	Pd-cored G1 dendrimer for the reduction of C=C and C≡C; and Suzuki, Stille and Hiyama reactions	167, 168
	Pt NPs	CH <sub>3</sub> , F, Cl, OCF <sub>3</sub> , and CF <sub>3</sub>	Pt-C <sub>6</sub> H <sub>4</sub> -R for the catalysis of oxygen reduction reaction	169
Dispersant for marine oil spills	Carbon black	COOH	CB-COOH	146
Electrocatalysis	Gold NPs	C <sub>10</sub> H <sub>21</sub>	Diazonium-modified GCE coated with decylphenyl-capped Au NPs for O <sub>2</sub> reduction	164
Electrochemical sensor	SWCNTs	N <sub>3</sub>	GCE coated with SWCNT-clicked Fe phthalocyanine	80
	Gold NPs	-C <sub>6</sub> H <sub>4</sub> -CO-C <sub>6</sub> H <sub>5</sub>	MIP sensing layer with embedded Au NPs	23
Immunosensor	GSPE (graphene)	COOH	GCE-GSPE-antibody	114
	Au NPs	N <sub>2</sub> <sup>+</sup>	GCE-Au NPs designed by electroreduction of diazotized Au NPs on GCE for immunosensing neurotoxins	189
Plasmonic sensor	Gold nanorods	O-CH <sub>2</sub> -CH <sub>2</sub> -DEDTC,	Au NR-MIP for selective optical detection of folic acid	160
Energy storage	Si NPs	COOH	Si-COOH anode in lithium-ion batteries	171
Fillers	MMT clay	N(CH <sub>3</sub> ) <sub>2</sub>	Exfoliated clay/PGMA nanocomposite filler	34
	Bentonite clay	HN-C <sub>6</sub> H <sub>5</sub>	Exfoliated, conductive clay/PANI nanocomposite filler	180
	SWCNTs	Br	SWCNT-PS nanofiller for PS matrix	194
Inkjet inks	CB	COONa, SO <sub>3</sub> Na	Water dispersible CB-COONa and CB-SO <sub>3</sub> Na for inkjet inks	195,203
Memory device	rGO	SH	Gold NP coated thiophenyl-modified rGO layer	110
Nano-biocarrier	CNH	CH <sub>2</sub> -NH <sub>2</sub>	CNH-dendrimer biocarrier	137
Supercapacitors	SRGO	SO <sub>3</sub> H	Crosslinked polystyrene-graft-SRGO multilayers on ITO.	125
Theranostic Nanomedicine	Co@C and other metal NP@C	CH <sub>2</sub> -COOH	Co@C-CH <sub>2</sub> -COOH for immunoassay, magnetic enzyme, etc.	206

CB: carbon black; CNH: carbon nanohorn; DEDTC: *N,N*-diethyldithiocarbamate; GCE: glassy carbon electrode; GSPE: graphene-modified screen carbon electrodes; rGO: reduced graphene oxide; ITO: indium-tin-oxide electrode; MIP: molecularly imprinted polymer; PPy: polypyrrole; SRGO: sulfonated reduced graphene oxide.

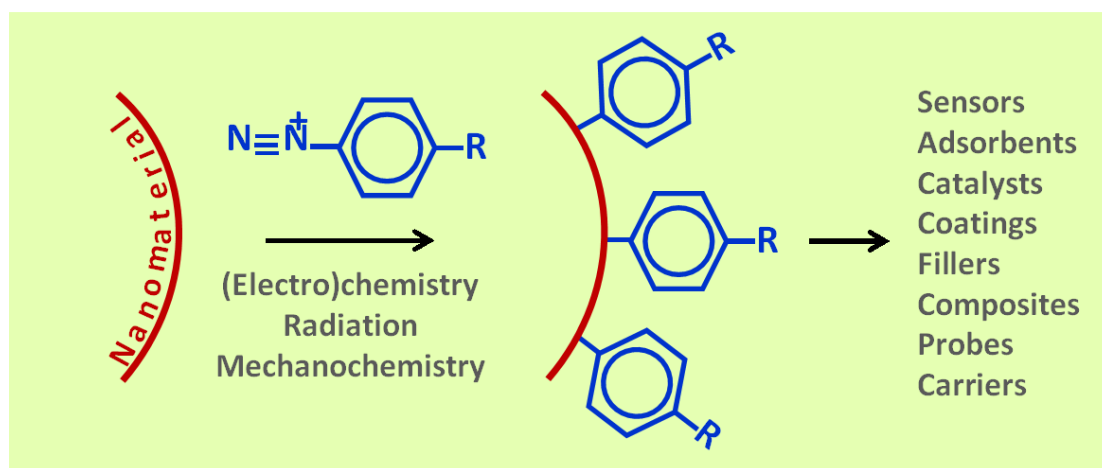
Clearly, much has been achieved with diazonium interface chemistry; however if trials and errors are crucial and depend on the imagination of the researchers and the challenges they face, it is

of paramount importance to understand the mechanisms by which diazonium salts react with surfaces. The task is tricky as diazonium cations react practically with all types of surfaces through specific and considerably investigated mechanisms.

From the above, we foresee diazonium-modification of nanomaterials will continue to attract researchers and will be renewed constantly as testified by the recent and challenging applications such as theranostics, memory devices, self-adhesive surfaces and particles, and fillers for nanocomposites, to name but a few. Given the outstanding achievements of the “diazonium community” in various domains, we introduce the terminology of “diazonics” which we define as the science and technology of aryldiazonium salt-based materials.

### **Acknowledgements**

A. A. Mohamed is grateful to the University of Sharjah (Sharjah, UAE) for the financial support. A. Mekki is thankful to the Ecole Militaire Polytechnique (Algiers, Algeria) for the 6-month travel support at Paris Diderot University, France. M.M. Chehimi is indebted to LABEX MMCD (Multi-Scale Modelling & Experimentation of Materials for Sustainable Construction) for the financial support.



Graphical abstract



***Functionalization of nanomaterials with aryldiazonium salts***

By: Ahmed A. MOHAMED, Zakaria SALMI, Si Amar DAHOUMANE, Ahmed MEKKI, Benjamin CARBONNIER, Mohamed M. CHEHIMI.

Submitted to Advances in Colloid and Interface Science

**Highlights**

- ♦ Versatility of aryldiazonium salt surface chemistry
- ♦ Functionalization of a wide range of nanomaterials by aryl layers
- ♦ Attached aryl layers serve as coupling agents for post-modification
- ♦ Diazonium-modified nanomaterials concern several domain science and technology domains.
- ♦ Diazonium-modified micro- and nanomaterials are developed industrially

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