Spontaneous Carbon-Support-Induced Metal Deposition
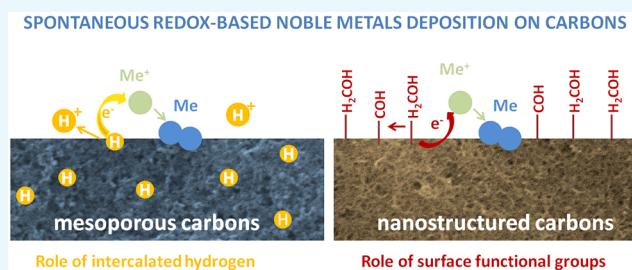
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ABSTRACT: Recent investigations have demonstrated the possibility for spontaneous deposition of noble metal nanoparticles from corresponding metal ion solutions on carbon supports, in the absence of additional reductants in the experimental systems. This process is a result of a direct redox reaction between the solute metal species and the carbon materials and differs from the typical electroless plating, the latter requiring additional reducing agents or catalysts to drive the reduction reaction. Due to the diversity of the used carbon materials including both dispersed nanostructured carbons and supported electrode-like carbon materials and the different approaches to follow the process and characterize the products, these studies are scattered in the scientific literature. The aim of the present review is to put these diverse investigations in a common context and focus on the existing experimental findings, the ways to monitor and control the process, and the general concept. Some aspects that need to be further corroborated are outlined in view of the involvement of the spontaneous redox process as a practical tool for the development of new catalysts.

SPONTANEOUS REDOX-BASED NOBLE METALS DEPOSITION ON CARBONS

mesoporous carbons — Role of intercalated hydrogen

nanostructured carbons — Role of surface functional groups

INTRODUCTION

Various carbon materials including traditional carbon blacks and more recently developed nanostructured carbons, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), nanosheets, nanodots, and graphene, have been employed as promising supports for metal catalysts. The development of carbon-supported noble metal catalysts is often based on the use of complicated synthetic procedures involving a sequence of several experimental steps. There is a need for further progress in the area by simplification of the synthetic procedures, optimization in terms of surface to volume ratio of the catalytic phase, and, in general, minimization of the noble metal content. In the last 20 years, investigations initiated from various viewpoints and with different goals have demonstrated the possibility for spontaneous reduction of noble metal ions on carbon materials in the absence of additional reductants in the experimental system (see Table 1). This process is a result of a direct redox reaction between the solute metal species and the carbon materials and differs from typical electroless deposition that requires additional reducing agents or catalysts to drive the reduction reaction. A series of papers were devoted to the spontaneous metal deposition on highly oriented pyrolytic graphite (HOPG) of Pt,[1−7] Ag,[5] and Au.[5,8] Nanostructured carbons such as single-walled CNTs (SWCNTs), nanodots, and nanosheets were used for spontaneous deposition of Au,[9] Pt,[9,10] Ag,[11,12] Pd,[13,14] Ir, Rh, and Ru.[15] Spontaneous metal reduction was observed also for Ag, Au, and Pd on graphene oxide (GO),[16−20] for Pt on graphene,[21] and for Pd on graphdyine and oxidized graphdyine.[22] Glassy carbon was found to be reactive for the deposition of Pt[23] and porous graphite rods for

spontaneous reduction of Pd.[24] Several screen-printed carbon electrodes, modified with CNTs, SWCNTs, and CNFs, have also been investigated for the spontaneous deposition of Pd.[25]

In general, carbon materials have been used for spontaneous metal deposition either as solid electrode materials or as aqueous dispersions, this difference implying also the distinctive experimental approaches involved to follow the process or characterize the products. Thus, to a significant extent, different scientific communities were involved in these two investigation trends. The divergence in the terms used to name the process (i.e., *spontaneous, open-circuit, electroless, substrate-induced, or substrate-enhanced electroless* deposition) has additionally contributed to some scatter of the knowledge in the research area. Thus, the term *electroless deposition* is often understood only in the narrow sense of electroless plating, the latter being defined as *heterogeneously autocatalyzed conversion of metastable redox pairs formed by dissolved reducing agents and metal complexes.* Nevertheless, the spontaneous reduction of metal ions in the presence of carbon materials does not involve solute-reducing agents; however, it still occurs without external supply of electrons, and thus it is also an electroless deposition process. The aim of the present review is to put all the above-mentioned investigations in a common context and focus on the existing
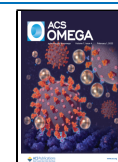
Table 1. Studies on Spontaneous Metal Deposition on Carbon Materials

material	deposited metals	particles size (nm)	type of material	reference
HOPG	Pt	various	cleaved surface	1−7
HOPG	Au, Ag, Pt	9.4 (Au), 31 (Ag), Pt (130−250)	cleaved surface	5
HOPG	Au	depends on pretreatment	cleaved surface	8
SWCNTs	Au, Pt	n.d.	SWNTs on SiO_2	9
CNTs	Pt	5	surface immobilized or dispersion	10
carbon nanodots	Ag	2.88	dispersion	11
carbon nanodots	Pd	15.7	dispersion	13
porous carbon nanosheets	Ag	1.17[a]	dispersion	12
		9.10		
		10.97		
porous carbon nanosheets	Pd	2.00[a]	dispersion	14
		9.85		
		35.40		
		47.81		
porous carbon nanosheets	Ir, Rh, Ru	0.96	dispersion	15
		1.11		
		1.37		
GO (a), r-GO[b] (b)	Ag	6.0 (a), × 10 − 1000 (b)	GO on modified SiOx substrate	16
r-GO	Au	<1−200	r-GO on quartz	17
r-GO	Au	1.8	dispersion	19
GO	Pd	~3.5	dispersion	18
r-GO	Ag−Pd	<1.0	dispersion	20
defective graphene	Pt	~0.8	dispersion	21
graphdiyne, graphdiyne oxide	Pd	~4.0	dispersion	22
		~1.2		
glassy carbon	Pt	32, 150	solid electrode	23
porous graphite	Pd	~100	graphite rod	24
CP[c]-modified porous graphite	Pd	4−12		
carbon, mesoporous carbon, CNT, SWCNT, CNF-modified carbon	Pd	n.d.	commercial screen-printed electrodes	25

[a]The different values correspond to different deposition times. [b]r-GO: reduced GO. [c]CP: conducting polymer.

experimental findings, the general concept, and the ways to monitor and control the process and, finally, to outline some aspects that need to be further clarified in order to involve the spontaneous redox-based metal deposition as a practical tool for the development of new catalysts.

■ EXPERIMENTAL FINDINGS

Compact Carbon Materials. The first experimental evidence for spontaneous metal deposition was obtained for Pt on a freshly cleaved HOPG surface.[1] It was shown that the Pt particles are concentrated at the top of the step edges of the basal planes. It was suggested that the thermodynamic driving force for platinum deposition originates from the reaction of incompletely oxidized functionalities (such as aldehydes, alcohols, and ketones) existing at defects on the graphite surface (Figure 1).[1] In support of this assumption, it was shown that electrochemical preoxidation of the graphite surface in sulfuric acid[1] or in the platinum plating solution[4] reduces significantly the amount of spontaneously deposited metal. Nevertheless, the large amounts of metal obtained in further experiments seemingly exceeded the possible amount of surface functional groups.[2,3] Thus, additional sources of electrons consumed for platinum complex ion reduction have been considered. Shen et al.[2] suggested that, together with the incompletely oxidized surface functional groups and other defects of the delaminated graphite layers, hydrogen originating from hydrogen-terminated carbon atoms on the HOPG surface is involved as a reductant for
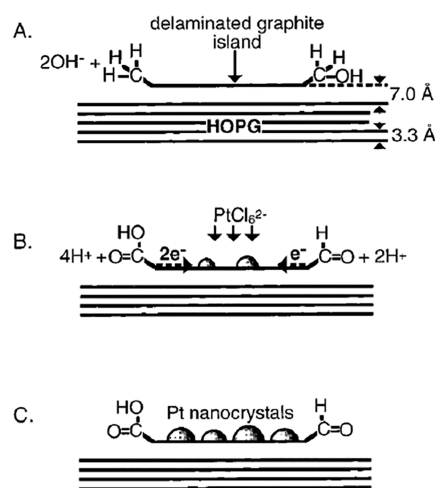

Figure 1. Schematic presentation of the surface oxygen-containing groups supported reduction of $PtCl_6^{2-}$ ions at delaminated graphite islands of HOPG: A, B, and C show the consecutive steps of the formation of the Pt nanocrystals. Reprinted with permission from ref 1. Copyright 1998 American Chemical Society.

the metal ionic species. The authors of a further investigation on the spontaneous Pt deposition on HOPG[3] suggested that the reduction of metal ions involves *free electrons of the carbon matrix*.
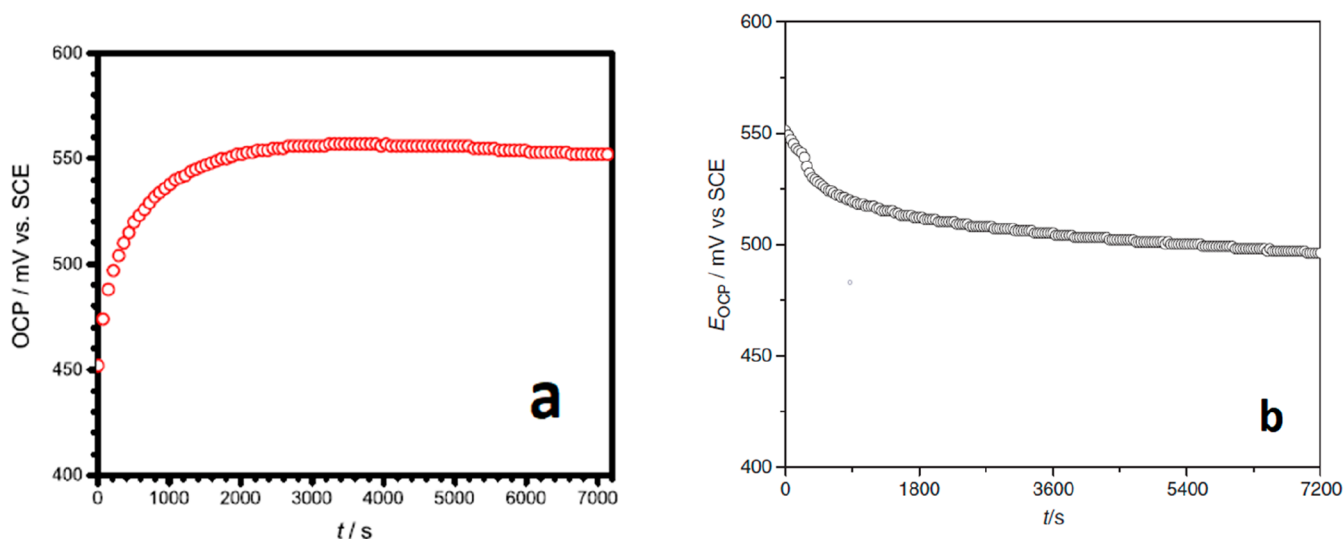
Figure 2. OCP transients obtained in 1 mM H_2PtCl_6 + 0.05 M H_2SO_4 solution during spontaneous deposition of Pt on (a) glassy carbon. Reprinted with permission from ref 23. Copyright 2018 Springer Nature Customer Service Centre GmbH: Springer. (b) HOPG. Reprinted with permission from ref 6. Copyright Clearance Center: John Wiley & Sons Ltd. Copyright 2015.
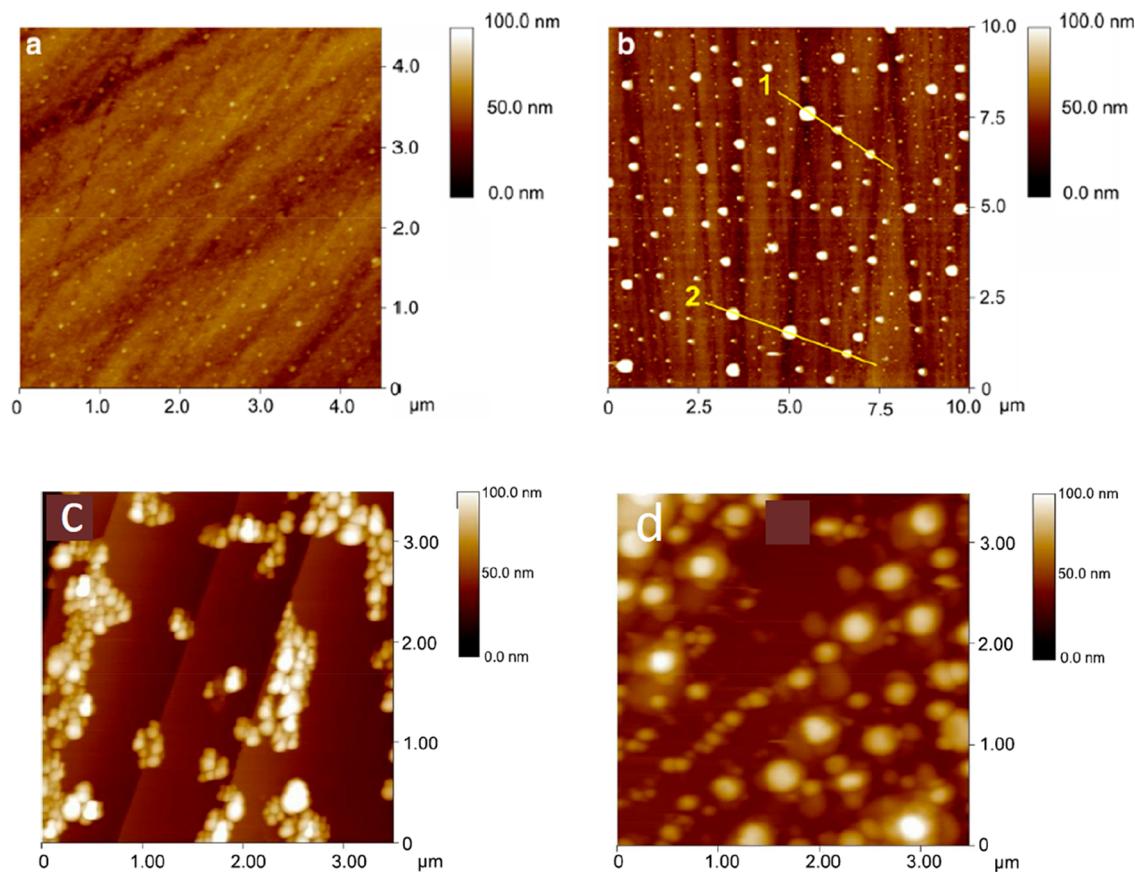

Figure 3. AFM images of Pt deposits on (a,b) glassy carbon (Reprinted by permission from ref 23. Springer Nature Customer Service Centre GmbH: Springer. Copyright 2018) and (c, d) HOPG (Reprinted by permission from ref 6. Copyright Clearance Center: John Wiley & Sons Ltd. Copyright 2015). The deposition times are (a) 200 s, (b) 2 h, (c) 2 h, and (d) 3 h.

A comparative study on spontaneous deposition of Pt, Au, and Ag on HOPG[5] has demonstrated that nanowires can be obtained with the three metals along the step edges of the basal graphite planes but with different shapes and morphologies. DFT-based calculations of nanowire formation on bare and functionalized step edges have partially confirmed the idea of the incompletely oxidized surface functionalities as a supply of electrons. The theoretical analysis has also shown that the electronic redistribution among the atoms participating in the bonds between the metallic nanowire and the step edges shows a
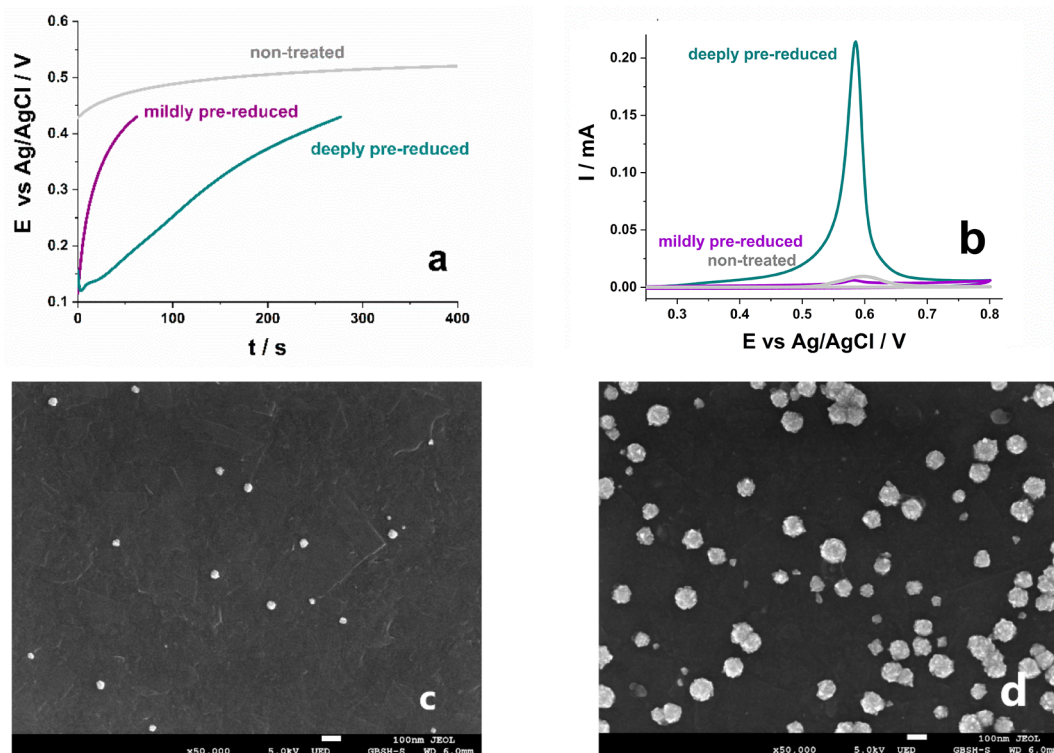
Figure 4. Spontaneous deposition of Pd on porous graphite: (a) OCP transients obtained in 2 mM $PdSO_4$ + 0.5 M H_2SO_4 solution; (b) corresponding anodic dissolution curves of Pd obtained after different pretreatments; (c,d) SEM of Pd particles obtained after mild ($E = -0.16$ V vs Ag/AgCl) (c) and deep ($E = -0.94$ vs Ag/AgCl) (d) reductive pretreatments in a solution of $LiClO_4$ (own results).

complicated pattern and that different orbitals are expected to participate in the interatomic bonds. Furthermore, detailed studies on Au deposition after acidic pretreatment in four different acids (HCl, HNO_3, aqua regia, and H_2SO_4) were performed by combining XPS analysis and AFM observations.[8] A correlation between the nature of the functional groups produced at the surface and the nature of the gold that is deposited was observed. Thus, OH groups generated predominantly by the weaker acids (HCl and HNO_3) tended to result in the deposition of Au^0 species, whereas further oxidation, provoked by a stronger acid (e.g., aqua regia), led to the formation of carbonyl- and ether-type groups. The exposure to the aqueous gold-complex-ion-containing solution resulted in this case mainly in Au^{3+} deposition.

Apart from HOPG, it was demonstrated that Si/SiOx-supported GO and reduced GO (r-GO) can be used to obtain Ag^{16} and Au^{17} particles by spontaneous reduction of the corresponding ions. The comparative study of Ag ion reduction on GO and r-GO has revealed a much higher density of Ag NPs with smaller sizes formed on the GO surface compared to the lower-density and bigger Ag particles formed on r-GO (see Table 1). It was suggested that carboxylic acid, hydroxyl, or epoxide groups on the GO surface serve as nucleation sites for metal particle deposition on GO. In contrast, r-GO was found to be characterized with fewer surface functional groups and thus fewer nucleation sites but on the other hand with a largely restored π-conjugated network that provided more electrons to reduce Ag ions and form larger Ag particles.[16]

More recently, it was shown that glassy carbon can also drive spontaneous deposition of Pt (Figures 2a and 3a).[23] Rather large platinum structures were detected at the electrode surface after a

long time (2 h) treatment in hexachloroplatinic solution (Figure 3a).

A comparative study[24] on the spontaneous deposition of Pd on porous graphite rods, in the absence and presence of a conducting polymer coating, has revealed the important role of the porous graphite substrate and its pretreatment for the amount of deposited metal. The graphite electrodes were pretreated by electrochemical reduction at constant potential in supporting electrolyte.[24] The potential used for the pretreatment procedure affected markedly the amount of deposited Pd with more negative potential treatment resulting in a larger amount of spontaneously deposited metal (Figure 4). The presence of a prereduced conducting polymer layer, coating the graphite surface, played in this case the role of an additional source of electrons. Nevertheless, it was demonstrated that the quantity of deposited Pd depends primarily on the graphite substrate, whereas the polymer coating played the role of a membrane that affected mainly the metal particle size and distribution. The mass of Pd found on the graphite substrate alone after strong reduction at a rather negative potential amounted to $12-19$ $\mu g/cm^2$. If considering this as a metal amount distributed as a thin layer over the geometrical area of the graphite electrode, this would result in a Pd layer with a thickness of $1-1.6$ μm. This is certainly a very large amount that could be hardly attributed to the involvement of surface functional groups alone.

Finally, five different carbon-based screen-printed electrodes (SPEs) were also studied for spontaneous Pd deposition.[25] The amount of deposited Pd was smaller than on the graphite rod electrode and depended both on the availability of nano-structured carbon (e.g., CNTs) on the otherwise compact
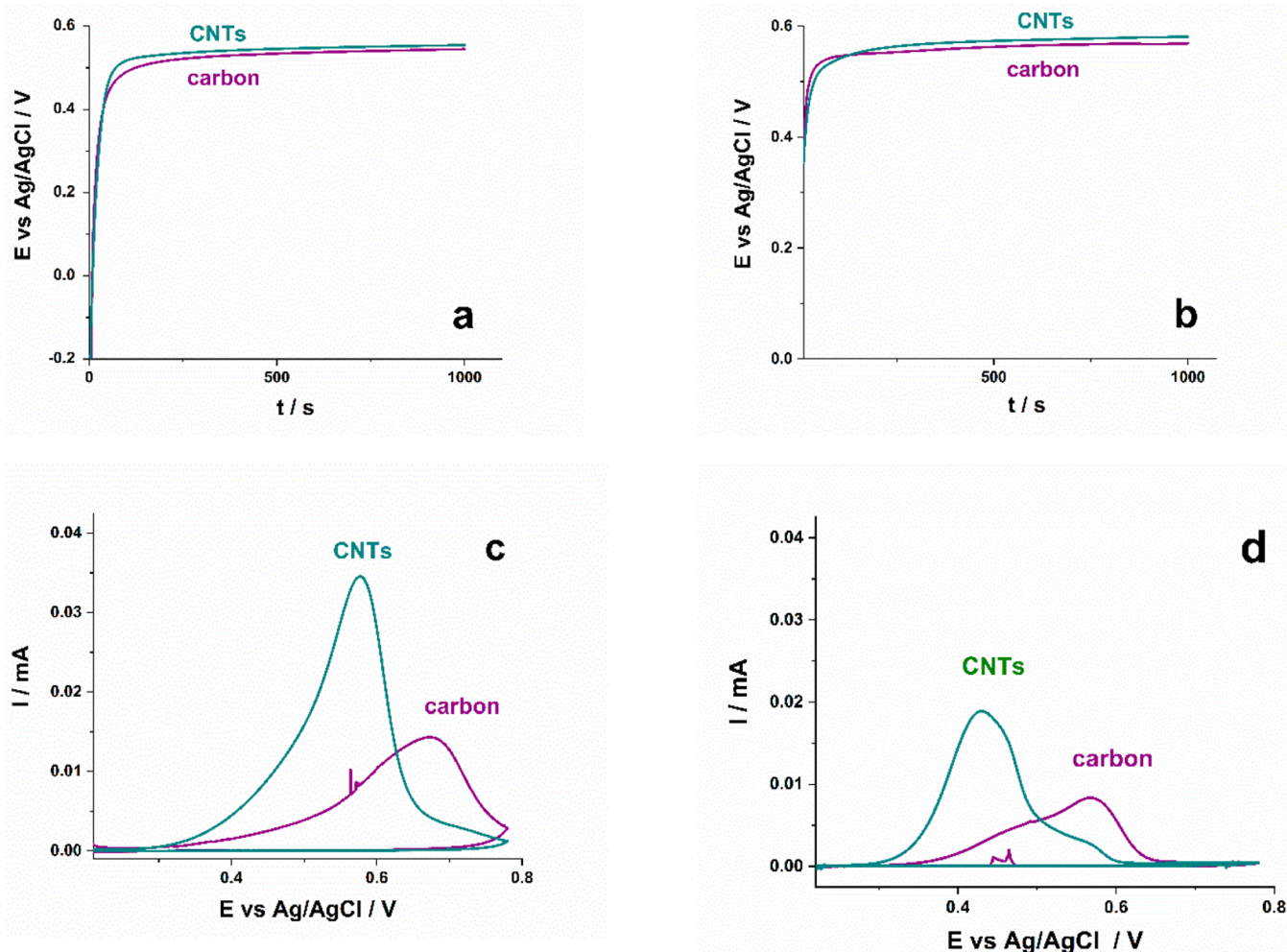
Figure 5. Spontaneous deposition of Pd on two types of SPEs, carbon and CNTs-modified carbon: (a,b) OCP transients obtained in 2 mM $PdSO_4$ + 0.5 M H_2SO_4 solution; (c,d) corresponding anodic dissolution curves obtained after reductive pretreatment in $LiClO_4$ solution (at $E = -0.94$ V vs Ag/AgCl) (a,c) and in H_2SO_4 solution (at -0.16 V vs Ag/AgCl) (b, d). Adapted with permission from ref 25; own results.

carbon SPE and on the medium (acidic or neutral) used for the prereductive step (Figure 5).

Aqueous Dispersions of Carbon Materials. The first demonstration of the possibility for spontaneous reduction of gold and platinum tetrachloride ions on the sidewalls of SiO_2-supported SWCNTs was shown by Choi et al.[9] It was followed by several investigations that have used aqueous dispersions of different nanostructured carbons such as multiwalled carbon nanotubes,[10] nanodots,[11,13] and nanosheets[12,14,15] for the deposition of Pt,[10] Pd,[13,14] Ag,[11,12] and Ir, Rh, or Ru.[15] It was demonstrated that the functionalization of the CNTs in a mixture consisting of H_2SO_4/HNO_3 or H_2SO_4/H_2O_2 can produce oxygen-containing functional groups such as −COOH, OH, etc., which make the CNTs hydrophilic and make it possible for an efficient reduction of Pt^{4+} ions.[10] It was proposed that the oxygen-containing functional groups also play a role in anchoring the Pt particles on the walls of the CNTs. FTIR spectra have indicated that the −COOH groups of the functionalized CNTs play a reducing role in Pt deposition. FTIR investigations before and after Ag deposition on carbon nanodots[11] gave evidence for the disappearance of the stretching vibration of − C═O bonds on the Ag/carbon nanodot samples, suggesting the C═O bond breaking during the formation of Ag nanoparticles. In several cases,[12,14,15] XPS studies were used to

evaluate the amount of the surface −C−OH and −CHO groups before and after metal deposition. It was suggested that the abundant oxygen-based surface groups on the porous carbon surface enable its strong reductivity for metal ions even with a low redox potential such as Ru^{3+}.[15]

Dispersed GO^{18-20} and recently defective graphene[21] were also used for spontaneous deposition of metals (Table 1). Ultrafine Pd nanoparticles monodispersed on GO surfaces were successfully prepared by the redox reaction between $PdCl_4^{2-}$ and GO.[18] Spontaneous deposition of Au was demonstrated on r-GO.[19] By means of zeta potential measurements, it was found that the as-synthesized r-GO sheets are highly negatively charged and thus have high absorption capacity toward positively charged Au(III) ions (after partial replacement of the Cl^- ligands). Upon exposure to the tetrachloroaureate solution, the zeta potential changed to more positive values. Furthermore, based on XPS studies, it was suggested that most Au(III) ions were coordinated by the heteroatoms at the defects on the r-GO sheets, especially the N heteroatoms, which acted as the initial nucleation sites for Au clusters.[19] It was stated that the obtained Au/r-GO material is a covalent hybrid based on the coordination or chemical effect between the heteroatoms, for example, N, O, and Au clusters. Simultaneous redox reactions between $AgNO_3$, K_2PdCl_4, and GO led to bimetallic Pd−Ag

NPs supported on GO.[20] (A post treatment transformed the GO support in r-GO.) By means of XPS it was established that the relative intensity of the C—O and C=O peaks in Pd—Ag/GO is smaller than those in GO. It was assumed that the oxygen-containing functional groups were partly removed in the reaction, which left defects on the surface of the GO, providing binding sites for Pd—Ag NPs.

A recent investigation on Pt deposition on defective graphene[21] has shown for the first time concomitant formation of Pt nanoparticles (avg. size of 1.8 nm) and Pt atomic clusters (avg. size of 0.8 nm). The stabilization of atomic clusters was associated with the defects in the graphene material, whereas the formation of Pt NPs was observed in more concentrated $PtCl_4$ solutions when the number of defects within the defective graphene matrix is insufficient to reduce and stabilize the massive number of Pt ions supplied. It was suggested that the excess Pt ions were reduced within the defect-free regions on the carbon basal plane, and they freely aggregated into NPs.[21]

Thus, there is plenty of experimental evidence for the spontaneous noble metal deposition on various carbon supports, but the practically relevant questions are how to monitor the process and how to control the amount of deposited metal.

■ HOW TO MONITOR THE METAL DEPOSITION PROCESS

Open-Circuit Potential (OCP) Transients. In general, *in situ* measurements of OCP transients show the initial energetic state of an electrode/electrolyte system and its drift in the course of a spontaneous redox process. Although compact (non-dispersed) solid carbon materials provide easily the opportunity for OCP measurements, such kinds of studies were presented only in a few cases. Quaino et al.[3] have provided an OCP measurement obtained in the course of Pt deposition on HOPG. The rather high OCP values varied for the different HOPG electrodes between 0.8 and 0.9 V vs RHE and corresponded to low overpotentials for Pt deposition, favoring nucleation of metallic structures at the step edges. The importance of anodic pretreatment of the HOPG electrode on the Pt deposition was clearly demonstrated by OCP measurements of treated and untreated HOPG samples.[4] OCP transients were published also for Pt deposition on HOPG and on glassy carbon (Figure 2).[6,23] Interestingly, the OCP transient on HOPG decreased with time (Figure 2b) with varying (from electrode to electrode) values that were attributed to the different grades of HOPG surface oxidation.[6] On glassy carbon, however, the OCP values increased in the course of the deposition (Figure 2a) and in all experiments remained slightly above those reported for the standard potentials of the $PtCl_6^{2-}$/Pt and $PtCl_4^{2-}$/Pt couples.[23]

OCP transients registered in the course of spontaneous deposition of Pd on porous graphite rods have confirmed the crucial importance of the pretreatment of the graphite surface (Figure 4a).[24] A rather flat slightly increasing OCP curve was observed for pristine, nontreated samples, whereas reductive pretreatments resulted in a marked increase in OCP, starting from rather low values. OCP transients were extensively studied also in the course of spontaneous Pd deposition on carbon-based SPEs[25] subjected to reductive pretreatment in two different solutions (Figure 5a,b). In both solutions, the OCP transients have shown a rapid rise to steady-state values which remained below the Pd/Pd^{2+} equilibrium potential in the corresponding solution. However, the type of prereductive procedure affected significantly the initial OCP potential and thus the amount of deposited metal (Figure 5c,d). On the other hand, at a given reductive pretreatment, the OCPs of carbon and CNT-modified carbon showed identical behavior, but nevertheless the amount of deposited Pd markedly differed. Finally, the comparison between the two types of materials, porous graphite (Figure 4) and thin-film carbon and CNT-modified carbon SPEs (Figure 5a,c), both subjected to the same pretreatment procedure, clearly shows the importance of the nature of the used carbon substrates for the spontaneous metal deposition process.

Zeta Potential Measurements. In analogy to OCP, zeta potential measurements in the course of the spontaneous metal deposition could give valuable information on the surface charge of the dispersed carbon particles. As already mentioned this was demonstrated in the study of Au deposition on r-GO sheets.[19] The initial surface charge state of the carbon particles should play a crucial role for the initiation and progress of the metal deposition process.

Amount of Deposited Metal. One of the most important and practically relevant aspects of the so far discussed spontaneous redox process is how to monitor and thereafter how to control the amount of the deposited metal. This quantity was so far rarely evaluated, although in many cases metal/carbon materials obtained through spontaneous metal deposition were further studied for different catalytic reactions. However, a reasonable comparison of the catalytic performance is possible only based on mass activities which require us to know the amount of the deposited metal. For compact (nondispersed) carbon substrates, the electrochemical approach based on anodic dissolution in appropriate acidic electrolytes may solve the problem for metals such as Ag and Pd (see, e.g., Figures 4b and 5c,d) and in specific solutions also for Au. The total amount of deposited metal in the case of a redox process on carbon dispersions can be evaluated spectrophotometrically after calcination of the reaction product[10] or by determining the metal ion concentration in the filtrate after the completion of the spontaneous deposition.[14]

Concerning the way to influence the metallic content, it was shown that the amount of deposited metal increases with increasing concentration of the metallic ions in the solution.[19,21] This may be considered as an expected result, as according to the Nernst equation the equilibrium potential of the metal/metal ion couple shifts to more positive values with increasing metal ion concentration. A more interesting point is the role of the immersion time on the deposited metal amount as observed for the deposition of Pt on HOPG (Figure 3a)[6] and glassy carbon (Figure 3b)[23] and of Ag and Pd in dispersed carbon nanosheets (Table 1).[12,14] Specifically, the sizes of Pd NPs increased nonlinearly with increasing reaction time, but there were also indications for the availability of more metallic particles.[14] The observed nonlinearity in the growth size could be ascribed to Ostwald ripening[14] in the early stages and presumably to the exhausting of the available supply of electrons in the latter ones, but no definite conclusions could have been drawn without data for the time dependence of the particle numbers and the total amount of deposited metal.

■ GENERAL CONCEPT

The possibility for spontaneous noble metal deposition on carbon materials is usually considered from a physical point of view by comparing the work function (WF) of carbons with the standard equilibrium potentials of the noble metal/metal ion couples (Figure 6). Because carbons may have WF values that correspond to more negative potentials than the standard
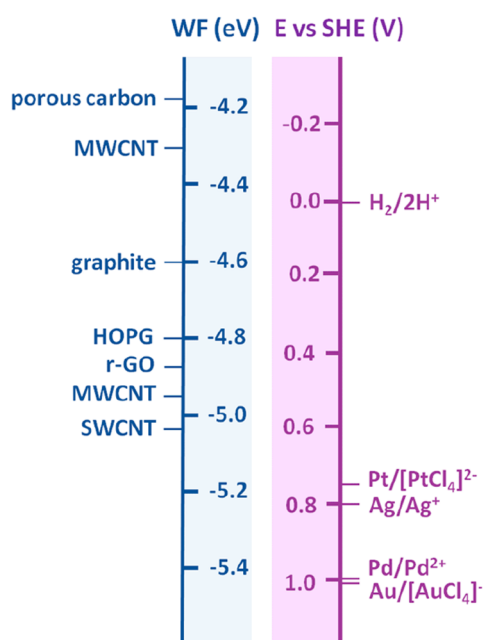
WF (eV) E vs SHE (V)

Figure 6. WF and standard electrode potentials (E vs standard hydrogen electrode, SHE) of carbon materials and noble metal/metal ion couples.

equilibrium potentials of several noble metal/metal ion couples, a spontaneous process of carbon oxidation (and loss of electrons) coupled to metal ion reduction (and gain of electrons) is expected to occur. This is analogous to the spontaneous redox process occurring in a galvanic couple consisting of two metals with largely differing values of the standard equilibrium potential.

Data for the WF of several carbon materials are summarized in Table 2 and show a large scatter of values. The WF is a key

Table 2. Data for the Work Function (WF) of Different Carbon Materials

material	WF (eV)	reference
graphdiyne	4.11	22
porous carbon nanosheets	4.17	15
porous carbon	4.19	12
graphdiyne oxide	4.23	22
graphite	4.6–4.7	26
HOPG	4.8	27
MWCNT	4.95	27
SWCNT	5.05	27
r-GO	4.88	17

parameter that depends on the collective interaction of the surface functional groups and the type and amount of defects in the carbon structure. Therefore, as suggested in most of the investigations described above, the surface chemistry plays a major role for the initiation of the spontaneous redox process. Studies on spontaneous noble metal deposition mention various sources for the coupled surface oxidation reaction, e.g., step-edge functional groups of HOPG,[1,7] incompletely oxidized functionalities of HOPG,[5] oxygen-based surface functional groups in porous carbon,[12,15] and defects in intentionally produced defective graphene.[21]

Apart from surface functional groups, there is still another, yet underestimated, factor that may play an important role in the

spontaneous metal deposition process. Numerous investigations have demonstrated the possibility to use different carbon materials, i.e., high surface graphite, CNFs, CNTs, and MWCNTS, for hydrogen storage. It was suggested that adsorbed atomic hydrogen may intercalate in the carbon electrode or recombine at the surface to molecular hydrogen and diffuse further into the electrode or form gas bubbles at the surface of the electrode. It was found that the amount of reversibly stored hydrogen in graphite samples may range from 0.04 to 0.46 mass %, depending on the type of graphite and the specific surface area of the carbon sample. In general, intercalated atomic hydrogen available in the carbon structure can be easily involved in spontaneous metal ion reduction due to the large difference in the standard electrode potentials of the H/H^+ couple and the noble metal standard potentials (Figure 6). This opportunity was so far intentionally used only in the studies on Pd deposition on prereduced graphite and carbon SPEs.[24,25] Nevertheless, also in other studies depending on the starting material and possible pretreatments, the role of adsorbed hydrogen could not have been excluded.

Finally, the equilibrium at the carbon support/metal particle/ solution interface, established as a result of the spontaneous carbon-support-induced redox process, depends also on the characteristics of the metal ions containing solution. The standard electrode potentials (e.g., those shown in Figure 6) correspond to 1 mol dm^{-3} activity of the metal ions. The metal ion concentration and the type of the metal ion ligand shell determine the energetic state of the metal ions (i.e., the electrode potential values) and thus will affect also the final equilibrium state. Furthermore, the solution acidity may influence both the surface chemical state of the carbon support and the type of the metal ion complexes. Thus, the characteristics of the solution "side" should also be considered as an instrument for influencing the spontaneous metal ion reduction on carbon supports.

■ CONCLUSIONS

The presented studies on spontaneous metal deposition on various carbon supports clearly demonstrate the possibility to obtain catalytic materials with a highly distributed metallic phase comprising, in the prevailing number of cases, metal particles with sizes in the subnanometer to several nanometers range (Table 1). Despite the general understanding that this spontaneous redox process is driven by the difference in the energy levels of the free electronic states of the carbon support and the metal ions available in solution, there are still open questions to be answered. The role of available oxygen-containing surface functional groups, other structural defects in the carbon structure (e.g., nitrogen heteroatoms), or intercalated atoms (such as hydrogen) needs to be clarified and investigated in more detail for every particular metal/carbon support system. This aspect is particularly important also from the viewpoint of catalytic applications because defects can not only serve as the anchoring sites to stabilize metal clusters but also help to tune the electronic and/or geometric structures of the defect-based coordination sites, thus facilitating specific electrochemical reactions.[28]

The initial surface chemical state of the carbon materials can be easily influenced by chemical or electrochemical pretreatment procedures, and therefore it needs to be strictly controlled in order to understand the role of oxygen-containing surface functionalities in the metal deposition process. A further important aspect of the spontaneous metal ion reduction on carbon supports relates to the presence of intercalated atomic

hydrogen that together with the surface-oxidizable function-alities may play the role of reductant. It is known that hydrogen is always found in carbon blacks since it is one of the main constituents of the hydrocarbon precursors. Studies on a number of carbon blacks have shown that the WF values of these materials correlate with the concentration and functional-ity of the surface functional groups and especially with the surface concentration of hydrogen.[29] In this respect it would be useful to study the possibility of spontaneous metal deposition also on carbon blacks and to combine studies on the hydrogen sorption capacity of various carbon supports with spontaneous metal deposition studies. Thus, new insights and opportunities could be opened.

The understanding on the way to control the surface chemistry and/or bulk content of the carbon supports may be of utmost importance for the involvement of the spontaneous redox process in the development of more sophisticated materials. Thus, the opportunity to renew the initial surface state or to recover the amount of intercalated atoms in the carbon supports by repeated surface treatment or intercalation procedures (after one step metal deposition) may open the way for the codeposition of more than one metal and thus the opportunity to develop multimetal carbon-supported nano-catalytic systems.

Furthermore, the kinetics of the spontaneous metal deposition is scarcely studied and far from being understood. Detailed investigations on the evolution in time of the particle numbers, size, and overall metal amount are needed in order to understand the mechanisms of nucleation and growth of the metallic phase. OCP transients show in some cases mild but in other cases significant OCP changes that correspond to low and, respectively, high and abruptly decreasing overpotentials for the metal phase formation. This creates rather different conditions for the two stages, nucleation and growth, in the metal deposition process.

Finally, carbon materials should be considered in most cases as semiconductors, whereas metal nanoparticles (with sizes within a few nanometers) have discrete energy levels due to quantum confinement. The energy equilibria used to illustrate the thermodynamic probability for the process (Figure 6) correspond to bulk materials. Bearing in mind that in several cases there is a nanosize confinement not only for the metal particles but also for the carbon supports (nanosheets, nanodots, CNTs, SWCNTs etc.) the bulk energy diagrams are probably not well suited to illustrate the interfacial band structure at the nanoparticle/nanocarbon interface. These aspects should be studied and clarified by combining experimental and simulation modeling approaches.

In general, there is plenty of room for further investigations based on the modern tools for materials characterization and contemporary modeling techniques that in combination could bring us forward in the understanding of this spontaneous, nature-driven process. A more profound insight in the control of the process will provide better opportunities for the develop-ment of mono- and, possibly, multimetal carbon-supported nanocatalysts.

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Notes
The author declares no competing financial interest.

Biography

Vessela Tsakova, DSc, is currently a Professor of Electrochemistry and Head of the Department of Phase Formation, Crystal and Amorphous Materials at the Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria. She received her PhD in physical chemistry with studies on the initial stages of electrochemical nucleation and growth. Her research interests cover a broad field and include the electrochemistry of conducting polymers, the synthesis and character-ization of electroactive composite materials, and electroanalytical and electrocatalytic applications. She also has extensive expertise in the field of electrochemical phase formation and electrocrystallization phenom-ena.

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