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Review—Hybrid Materials Based on Phthalocyanines and Metal Nanoparticles for Chemiresistive and Electrochemical Sensors: A Mini-Review

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Synergetic combination of the properties of phthalocyanines and metal nanoparticles is known to result in the improvement of various properties of their hybrid materials. This review provides an overview of the application of hybrid materials based on phthalocyanines and metal nanoparticles for the development of chemiresistive and electrochemical sensors, with a focus on methods and approaches for their preparation.

Research on metal nanoparticles (MNP) has received wide interest in the past decade. MNPs are widely used for drug delivery,[1] catalysis,[2] surface-enhanced plasmon resonance,[3] chemical and biological sensing,[4] gas sensing[5] and other areas due to their optical and electrocatalytic properties.

Noble metal nanoparticles, mainly Au, Pd, Rh, are widely used in a number of electrochemical applications, such as electrocatalysis, electrochemical analysis, electrochemical synthesis, due to their inertness and catalytic properties, generally through chemisorption on the surface.[6,7] One more important feature of metal nanoparticles is their high surface area to volume ratio, which is important for sensing applications. A number of techniques, including a chemical reduction method,[8] electrochemical deposition,[9] atomic layer deposition (ALD)[10] and chemical vapor deposition (CVD)[11] have been demonstrated so far to synthesize metal nanoparticles. Chemical reduction method for the preparation of silver and gold nanoparticles has been widely studied and involves the reduction of $AgNO_3$ or $HAuCl_4$ by a reducing agent in the presence of a suitable stabilizer, which protects MNP from aggregation.[12] In a chemical reduction method, particle size depends on the precursor concentration, stabilizer concentration, reaction time, temperature, and some other factors and usually varies in the range from 5 to 30 nm.[13,14] CVD and ALD techniques allow obtaining nanoparticles with the content of metal close to 100% without any surfactants and stabilizers.[15,16]

Metal phthalocyanines (MPc) are organic semiconductors widely used for chemiresistive sensors.[16] Apart from this, their excellent electrocatalytic properties and electron mediator capabilities, together with extensive redox chemistry[17–20] make them very attractive for the application in various types of electrochemical sensors, such as potentiometric ones,[21] amperometric sensors and voltammetric electronic tongues,[22] biosensors.[17] Metal phthalocyanines are known to catalyze the electrooxidation of glucose,[23] nitrite,[24] l-cysteine,[25] dopamine,[26] and many other compounds.[17]

Synergetic combination of the properties of phthalocyanines and metal nanoparticles is known to result in the improvement of various properties of MPc/MNP hybrid materials. There are several reviews devoted on the investigation of effect of nanoparticles on metal phthalocyanine properties in the literature. Among them the review of Nyokong and Antunes in which the authors describe the effect of nanoparticles on photophysical behavior and photodynamic therapy (PDT) activity of metal phthalocyanines.[27] Improvement of antimicrobial activity of phthalocyanine-based composites with metal nanoparticles was described by Mondal and Bera.[28] The synergetic

properties of porphyrinoids and metal nanoparticles nanomaterial conjugated systems allowed to use them for selective drug delivery, theranostic capabilities, and multimodal bioimaging.[29]

This review provides an overview of the applications of hybrid materials based on phthalocyanines and metal nanoparticles for chemiresistive and electrochemical sensors, with the focus on methods for their preparation.

Hybrid Materials for Electrochemical Sensors

Combination of phthalocyanines and nanoparticles possessing electrocatalytic properties can improve the performance of electrochemical sensors. A literature analysis shows the application of various methods for fabrication of composite films based on phthalocyanines and metal nanoparticles and their application to modify electrodes of electrochemical sensors, among them mixing the components,[30,31] electrodeposition,[32,33] layer-by-layer (LbL) deposition[34–37] and Langmuir-Blodgett (LB) technique.[38,39] Some examples of the application of MNP/MPc hybrid materials for the modification of electrodes of electrochemical sensors from the works published over the past 10 year are given in Table I.

Methods such as cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometric (CA) studies are usually used for the investigation of electrochemical behavior of analytes at the modified electrodes.[47]

Often the hybrid materials are obtained by the mechanical mixing of metal phthalocyanines with nanoparticles or their composites with graphite in the presence of polymers or oils to prepare modified electrodes. For example, Abbas et al.[48] compared the efficiency of a graphite paste electrode with that modified with FePc and AuNP, the latter obtained by a citrate-based reduction method.[17] The modified electrode was prepared by mixing FePc with AuNP/graphite composite in the presence of a paraffin oil. The electrode after modification exhibited the enhancement of the anodic redox signal for cysteine. The intensity of this signal depended on the quantity of Au nanoparticles (0.02, 0.055 and 0.11 wt%). The electrode containing 0.055 wt% AuNPs had optimal sensitivity to cysteine with the linear range from 50 to 1000 μM and a limit of detection (LOD) of 0.27 μM.

Atta et al.[31] proposed a similar strategy to improve the sensitivity of biosensors through the modification of carbon paste electrodes (CPE) by metal phthalocyanines and AuNPs. A CPE prepared from the mixture of graphite powder with mineral oil and introduced into an electrode capillary was modified with MPc (M = Co, Ni, Fe, Cu) and immersed in $HAuCl_4$ solution containing KNO_3. A constant potential of -0.4 V was applied for several minutes. Among these

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Table I. Examples of MNP/MPc hybrids used for the modification of electrodes of electrochemical sensors.

| Nanoparticles/Phthalocyanine	Electrode	Preparation of a hybrid materials	Analyte	Linear range, μM	LOD, μM	References
AuNP/FePc	GPE	Mixing FePc with AuNP/graphite composite in a paraffin oil	Cysteine	50–1000	0.27	30
AuNP/MPc (M = Co, Ni, Fe, Cu)	CPE	Mixing MPc with AuNP and graphite in a mineral oil	Morphine	0.4–900	0.00548·	31
AuNP/CoPc	CPE	Electrodeposition of AuNP on CPE covered with CoPc	Dobuta-mine	6.0–200·	8.4	40
PdNP/CoTAPc	GCE	CoTAPc electropolymerization, PdNP electrodeposition	Hydrazine	—	1.3	32
(PAH/FePc/AgNP)$_n$	ITO	LbL	Dopamine	2–97	0.86	35
(AuNPs-PAH/NiTsPc)$_5$	Au	LbL	Tartrazine	0–3 4–9	0.055 0.122	36
AuNP/NiTsPc	ITO	Electrodeposition of AuNP, LbL of poly(ethylene imine) and NiTsPc solutions	Propyl-paraben	2–20	8.01×10^{-2}	37
AuNP functionalized with (11-mercaptoundecyl) tetra(ethylene glycol)/LuPc$_2$	ITO	LB	Hydro-quinone	5–150	0.1–1	39
AuNP modified with 3-mercaptopropionic acid/FePc(NH$_2$)$_4$	GCE	Covalent functionalization of electrodeposited AuNP with FePc(NH$_2$)$_4$	NO$_2^-$	1.9–2040	0.21	41
AuNP/NiPc(NH$_2$)$_4$	Au	Covalent functionalization of electrodeposited AuNP with NiPc(NH$_2$)$_4$	Hydrazine	10–100	$5 \cdot 10^{-2}$	42
AuNP^{tOcBr}-S-ZnPc^{RS}, Fig. 3c	ITO	Covalent functionalization of AuNP^{tOcBr}	Catechol	—	0.13	43
AuNP/TaPcR$_8$ (Figs. 3i, 3a) AuNPs/TaPcR$_8$ (Figs. 3i, 3b)	Au	Noncovalent functionalization of AuNP with TaPc	Bisphenol A	—	$4.78 \cdot 10^{-4}$ $2.76 \cdot 10^{-4}$	44
RhNP/CoPc(NH$_2$)$_4$	GCE	Covalent functionalization of RhNP with CoPc(NH$_2$)$_4$	Cytochro-me c	0.1–3	$3.33 \cdot 10^{-2}$	45
PdNP/CoPc	GCE	Methanol-mediated weakly-capping growth approach	NO$_2^-$	0.2–50 500–5000	0.1	46
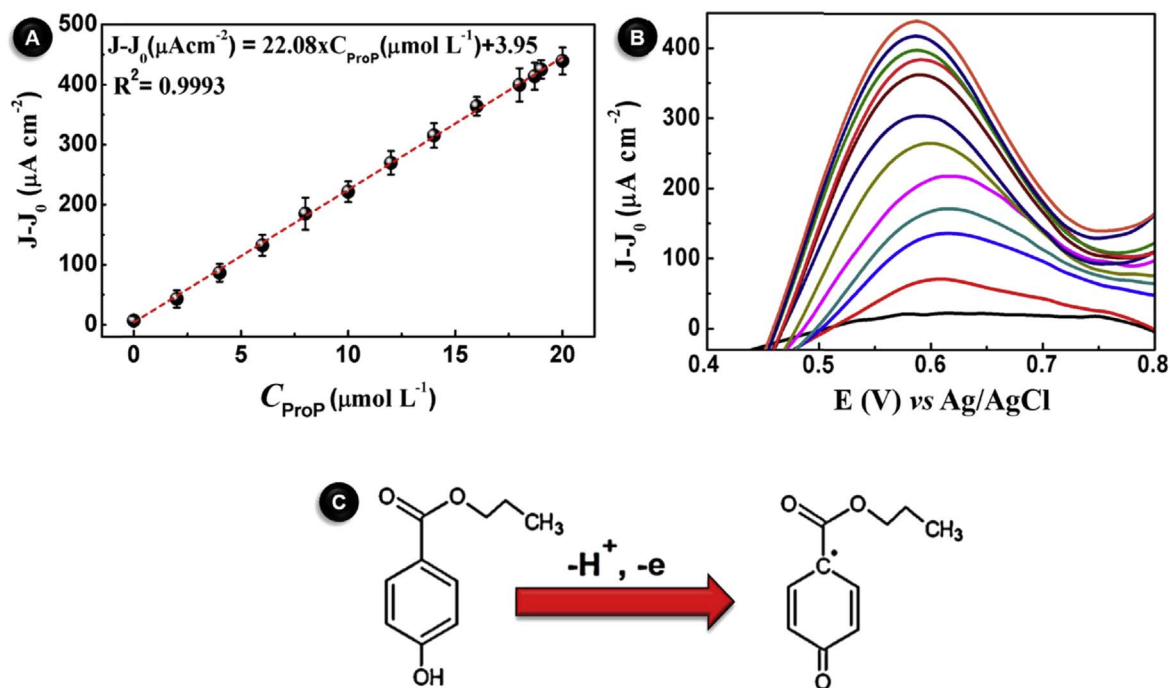
Figure 1. (A) Linear regression for analytical curve; (B) Differential pulse voltammogram for 0.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 18.5, 19.0 and 20.0 μmol l^{-1} of ProP in PBS pH 7; (C) Oxidation reaction of ProP to generate quinone. Reproduced from Ref. 37 with kind permission from Elsevier S.A.

MPcs the electrode modified with CoPc demonstrated the highest current response and the best electroactivity towards morphine oxidation compared to the other modified electrodes. The linear range and LOD were shown to be $4.0 \cdot 10^{-7} - 9.0 \cdot 10^{-4}$ mol l^{-1} and $5.48 \cdot 10^{-9}$ mol l^{-1}, respectively.

In another work of the same group[40] a suspension of cobalt phthalocyanine was dropped on the surface of a bare carbon paste electrode for its modification. The electrode was dried in oven, then immersed in 6 mmol l^{-1} HAuCl$_4$ solution containing 0.1 mol l^{-1} KNO$_3$, and a constant potential of -0.4 V was applied for 4 min The modified electrode was used for the determination of dobutamine (DB) in water solutions and human urine samples. The prepared sensor had a LOD of 0.84×10^{-7} mol l^{-1} in the linear dynamic range from $6.0 \cdot 10^{-6}$ mol l^{-1} to $2.0 \cdot 10^{-4}$ mol l^{-1}.

Other important techniques used for the modification of electrodes of electrochemical sensors are electrodeposition and electropolymerization. Maringa and Nyokong combined Pd nanoparticles and cobalt tetraaminophthalocyanine (CoTAPc) to improve the oxidation potential for the detection of hydrazine and to increase its detection limit.[32] For this purpose, they used electropolymerization (50 cycles) to modify a glass carbon electrode (GCE) with CoTAPc. Then palladium nanoparticles were electrodeposited on the top of poly-CoTAPc by cyclic voltammetry in a deaerated solution containing 1 mM PdCl$_2$ (0.1 M HCl). The electrodes demonstrated a LOD of hydrazine of 1.3 μM which is more than 7 times higher compared to the electrode covered with poly-CoTAPc without PdNPs.

Electrocatalytical properties of Pt nanoparticles were used to improve electrocatalytic activity of a composite of multiwalled carbon nanotube with copper phthalocyanine in the process of oxygen reduction.[49] Pt metal nanoparticles were deposited electrochemically onto GCE preliminarily coated with CuPc or CuPc-CNT composite using electrochemical reduction of K$_2$PtCl$_6$ in 0.1 M HCl solution. The CNT increased the electroactive surface area in this system, while Pt nanoparticles and CuPc played the role of an electrocatalyst for the reduction of oxygen. Gold nanoparticles (AuNPs) were deposited on the glassy carbon electrode via electroreduction of HAuCl$_4$ solution in NaNO$_3$.[50] Then poly-tetrasulfonated nickel phthalocyanine (NiTSPc) films were obtained by

electrodeposition on top of the electrodeposited AuNPs to prevent the leakage of the components from the electrode. Similarly, polymerization of cobalt tetraamino phthalocyanine was performed on top of glassy carbon electrode covered with electrodeposited AuNPs.[33] AuNPs in the modified electrodes improved the electron transfer kinetics in the processes of nitrite oxidation resulting in the higher current.

One more promising method for the preparation of hybrid structures is layer by layer (LbL) electrostatic assembly. In this method, the multilayered structures are fabricated by alternately assembling of negatively and positively charged compounds. Alencar et al.[34] used LbL method to prepare mixed films of AuNPs and tetrasulfonated nickel phthalocyanine that show an improved electrocatalytic activity towards H$_2$O$_2$. AuNPs stabilized with poly(allylamine hydrochloride) (PAH) was employed as cationic electrolyte while tetrasulfonated nickel phthalocyanine was an anionic one. An indium-tin-oxide (ITO) electrode covered with the multilayer film containing alternating layers demonstrated a catalytic effect toward H$_2$O$_2$ oxidation with increased peak currents for the electrochemical processes associated with the phthalocyanine ring and nickel at 0.52 and 0.81 V (vs SCE), respectively. At the same time, in the case of the PAH/NiTsPc films, which did not contain AuNPs, only the first redox process was observed.

A similar method was also used to introduce silver nanoparticles (AgNP) in LbL films based on poly(allylamine hydrochloride) (PAH) and unsubstituted iron phthalocyanine in order to increase sensitivity to dopamine.[35] The multilayer LbL films (PAH/FePc/AgNP)$_n$ were prepared by immersing the substrate for three minutes alternately into PAH solution in water, FePc solution in chloroform and Ag colloidal solution obtained by a citrate-based reduction method.[30] After deposition of each layer, the films were washed with ultrapure water and dried in air. The electrodes modified in this way were shown to demonstrate electrocatalytic properties in detecting, the neurotransmitter, dopamine in aqueous solutions. The linear dependence of the peak current on dopamine concentration was observed in the range between $2.0 \ 10^{-6}$ M and $9.7 \ 10^{-5}$ M, while the calculated LOD was $0.86 \ 10^{-6}$ M.

De Lima et al.[36] reported the application of Au-(AuNPs-PAH/NiTsPc)$_5$ architecture prepared by the LbL technique for the

detection of tartrazine in juice samples through DPV. The Layer-by-Layer deposition was achieved by interaction between a positively charged layer of gold nanoparticles stabilized with PAH and a negatively charged NiTSPc. The sensor exhibited the calculated LODs of 0.055 μmol l^{-1} for the first linear range (0–3 μmol l^{-1}) and 0.122 μmol l^{-1} for the second one (4–9 μmol l^{-1}).

The same group of authors used composites on the basis of nickel (II) phthalocyanine tetrasulfonate and gold nanoparticle for the preparation of electrochemical sensor for the detection of propylparaben (ProP) in cosmetics.[37] Gold nanoparticles were first deposited onto an ITO substrate by an electrodeposition method. Then the substrate was immersed in the poly(ethylene imine) cationic solution, washed in ultrapure water and immersed in the NiTsPc anionic solution. This procedure was repeated three times. The LOD of propylparaben in cosmetics, obtained by differential pulse voltammetry, was 8.01×10^{-8} mol l^{-1}, while the linear range was from 2.0 to 20.0×10^{-6} mol l^{-1} (Fig. 1). The use of gold nanoparticles caused an increase of the ability to charge transfer between the modified electrode and cosmetic sample containing propylparaben.

Besides layer by layer electrostatic assembly, the deposition of Langmuir-Blodgett (LB) multicomponent films looks to be a very attractive method for the preparation of active layers of electrochemical sensors. Medina-Plaza et al.[39] used the Langmuir–Blodgett technique for co-deposition of two electrocatalytic materials, *viz.* AuNPs functionalized with (11-mercaptoundecyl)tetra(ethylene glycol) and lutetium bisphthalocyanine (LuPc$_2$). They suggested an original technique in which water soluble AuNPs were inserted in floating LuPc$_2$ films and amphiphilic matrix (*viz.* dimethyldioctadecylammonium bromide). The prepared films were used for the modification of ITO electrodes. It was shown that the modified electrodes exhibited electrocatalytic properties in the process of hydroquinone oxidation, which were evidenced by a decrease in the

oxidation potential of hydroquinone from 0.8 V (on a bare electrode) to 0.45 V. The sensors demonstrated a linear range from 5 to 150 μM and LOD from 10^{-6} to 10^{-7} M with dependence on the ratio of components in LB films. The synergistic effect was due to the interaction of two electrocatalytic materials and large surface area of nanostructured films.

Phthalocyanines themselves can also play the role of stabilizing agents in the preparation of metal nanoparticles or interact with the functional groups of organic molecules stabilizing MNPs. Phthalocyanines can be covalently linked to the molecules stabilizing nanoparticles or can interact with them via Van der Waals forces. For example, Saeed et al.[41] used iron phthalocyanine modified AuNPs for the creation of sensors for electrocatalytic determination of nitrite in phosphate-buffered saline (PBS) by cyclic voltammetry and DPV methods. For this purpose, gold nanoparticles were electrodeposited onto GCE with the following self-assembly of 3-mercaptopropionic acid (MPA) (Fig. 2). Then the terminal carboxylic groups of the thiol linker were activated by immersing the MPA/AuNPs/GCE in the solution of N-(3-dimethylamino-propyl)-N'-ethylcarbodiimide hydro-chloride in ethanol. The covalent immobilization of iron(III) monoamino-phthalocyanine was performed by immersing the electrode in its solution in DMF. The modified electrode was used for the detection of nitrite in real water samples. It demonstrated a selective sensor response to NO$_2^-$ with a linear range of 1.9 μM–2 μM and LOD of 0.21 μM.

Jeevagan et al.[42] synthesized non-peripheral amine substituted nickel(II) phthalocyanine capped gold nanoparticles and immobilized them on gold electrode modified with 1,6-hexanedithiol (HDT) (Fig. 3a). The lone pair of electrons present in the nitrogen atom of the amine groups in phthalocyanine ring stabilized gold nanoparticles by electrostatic repulsion. The modified electrode exhibited excellent electrocatalytic activity towards oxidation of hydrazine
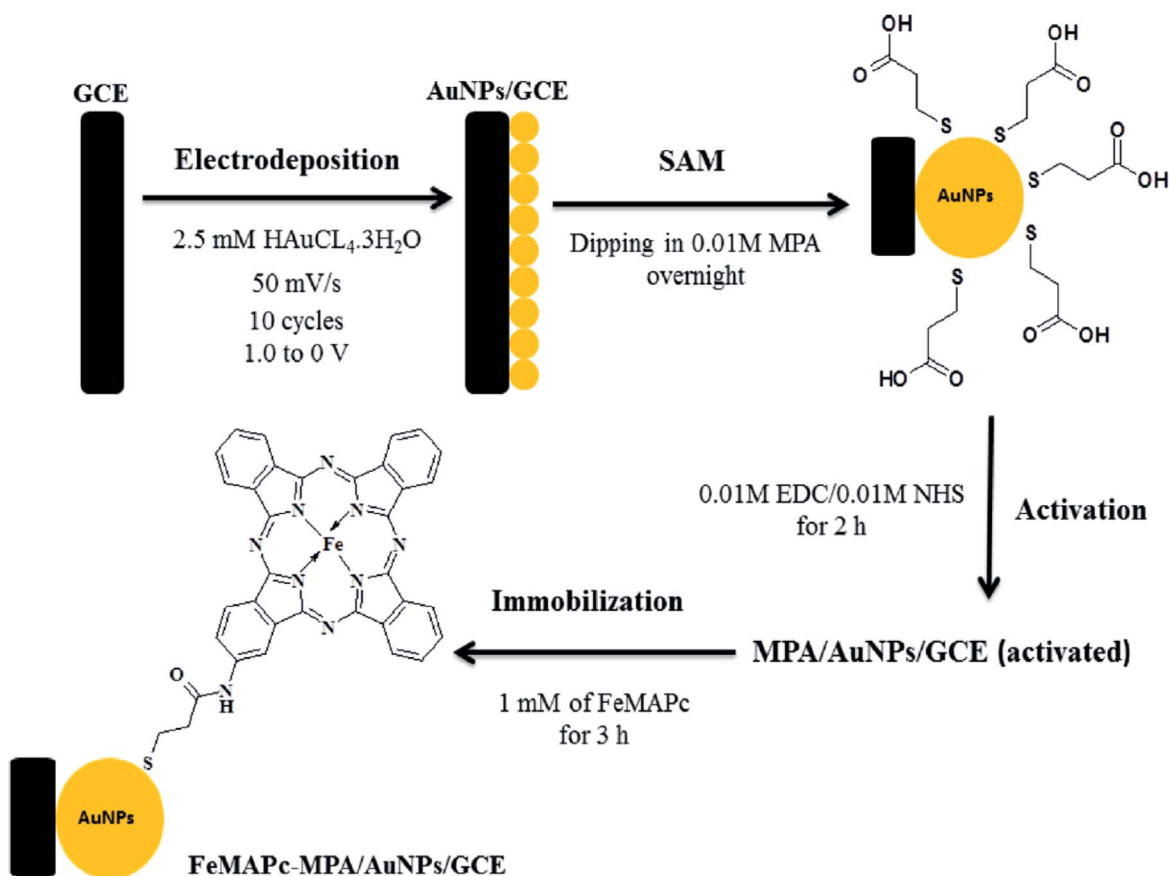

Figure 2. Schematic illustration of the glass carbon electrode modification with a FePc derivative. Reproduced from Ref. 41 with kind permission from WILEY VCH VERLAG GMBH & CO.
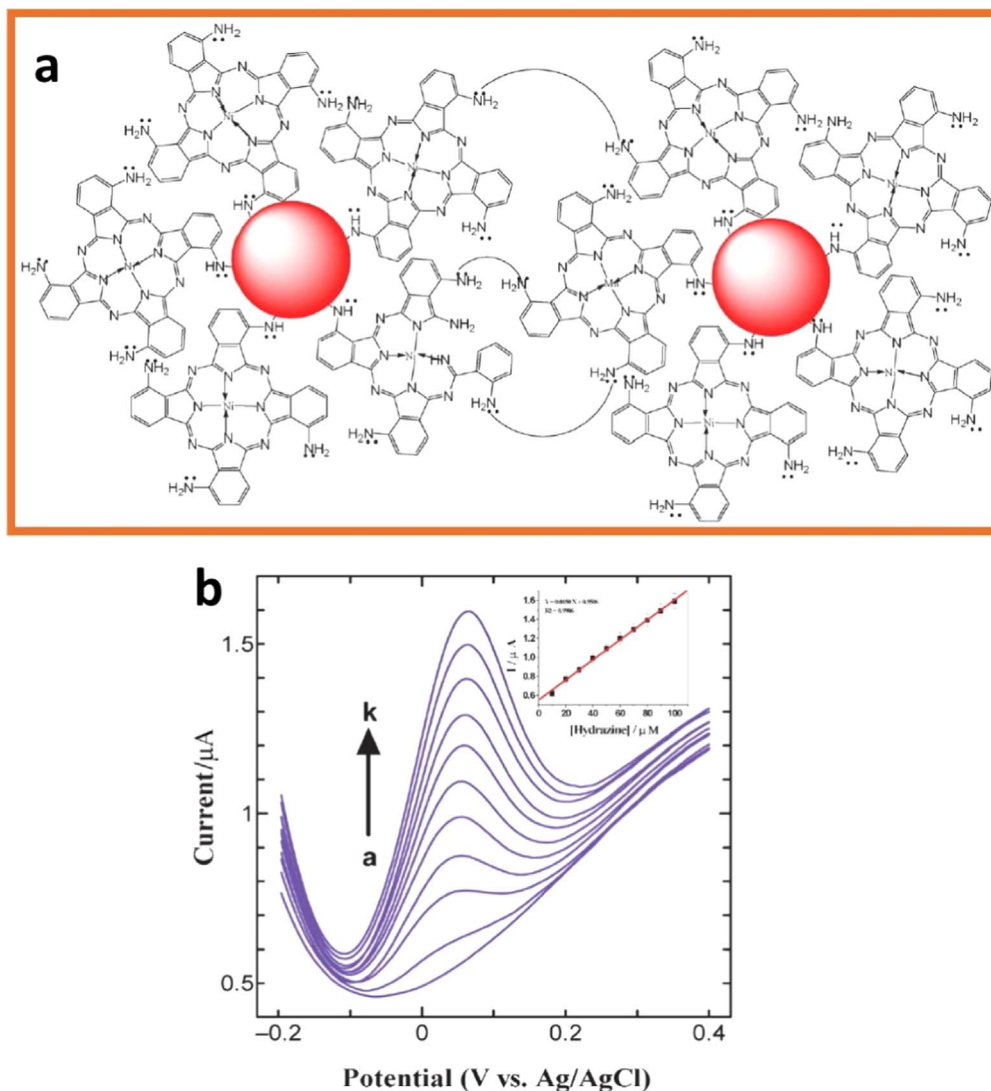
Figure 3. (a) Schematic representation of stabilization of AuNPs by a non-peripheral amine substituted nickel(II) phthalocyanine. (b) DPVs obtained for 10 mM of hydrazine at the Au/HDT/NiPc-AuNPs modified electrode in 0.2 M PB solution (pH 7.2). Inset: plot of current vs concentration of hydrazine. Reproduced from Ref. 42 with kind permission of Royal Society of Chemistry.

resulting in the enhancement of its oxidation current in comparison with non-modified electrode. Figure 3b shows the DPVs obtained for hydrazine in the concentration range of 10–100 mM at the electrode modified with the prepared hybrid in 0.2 M PBS. The linear dependence of DPV current on hydrazine concentration was observed in the range from 10–100 μM, while the calculated LOD was $5 \cdot 10^{-8}$ M.

Ruiz-Carmuega et al.[43] reported about development of voltametric sensors based on hybrid materials of gold nanoparticles capped with tetraoctylammonium bromide (AuNP^{tOc}, Fig. 4a) and a sulfur-substituted zinc phthalocyanine (ZnPc^{RS}, Fig. 4b). The covalent adduct (AuNP^{tOcBr}-S-ZnPc^{RS}, Fig. 4c) linked through thioether bonds was prepared as described by Blas-Ferrando et al.[51] The sensor response of the ITO electrode modified with this covalent adduct towards catechol was compared with those modified with the mixture of AuNP^{tOcBr}/ZnPc^{RS} and with sulfur-substituted zinc bisphthalocyanine: (ZnPc^{R}-S-ZnPc^{R}, Fig. 4d). It was shown that the electrocatalytic properties and the kinetics of the electrochemical reaction depended on the type of interaction between both components in the hybrids: electrodes modified with the covalent adduct exhibited an increase in the intensity of the oxidation peak. A LOD of catechol was $9 \cdot 10^{-7}$ mol l^{-1} for the electrode modified with the mixture AuNP^{tOcBr}/ZnPc^{RS}, while with

value decreased to $1.3 \cdot 10^{-7}$ mol l^{-1} in the case of the electrode modified with the covalent adduct AuNP^{tOcBr}-S-ZnPc^{RS}.

To improve the charge transfer behavior the citrate stabilised AuNPs was combined with tantalum phthalocyanines (TaPc)[44] (Fig. 5). The authors suggested that the TaPc complexes were simply adsorbed onto the AuNPs after sonication of the mixture of their solutions. Combination of these two extraordinary catalytic units led to the enhancement of catalytic activity in the processes of electrocatalytic oxidation of bisphenol A. Gold electrodes modified with these composites by drop and dry method demonstrated the limits of detection for complexes a and b (Fig. 5) were $4.78 \cdot 10^{-10}$ and $2.76 \cdot 10^{-10}$ mol l^{-1}, respectively.

Apart from AuNPs rhodium nanoparticles are also used for the modification of electrodes of electrochemical sensors. Lokesh et al.[45] prepared rhodium nanoparticles in which aminosubstituted phthalocyanine was used as a stabilizing agent. Covalent interaction between nitrogen atoms of the amine groups with rhodium was confirmed by spectral methods. Glassy carbon electrodes modified with the prepared colloidal rhodium nanoparticles exhibited a sensor response to cytochrome c, measured by a differential pulse voltammetric method, with the linear relationship between the oxidation peak currents and cytochrome c concentration in the range from 100 nM to 3 μM and calculated LOD of 33.3 nM. Rodium
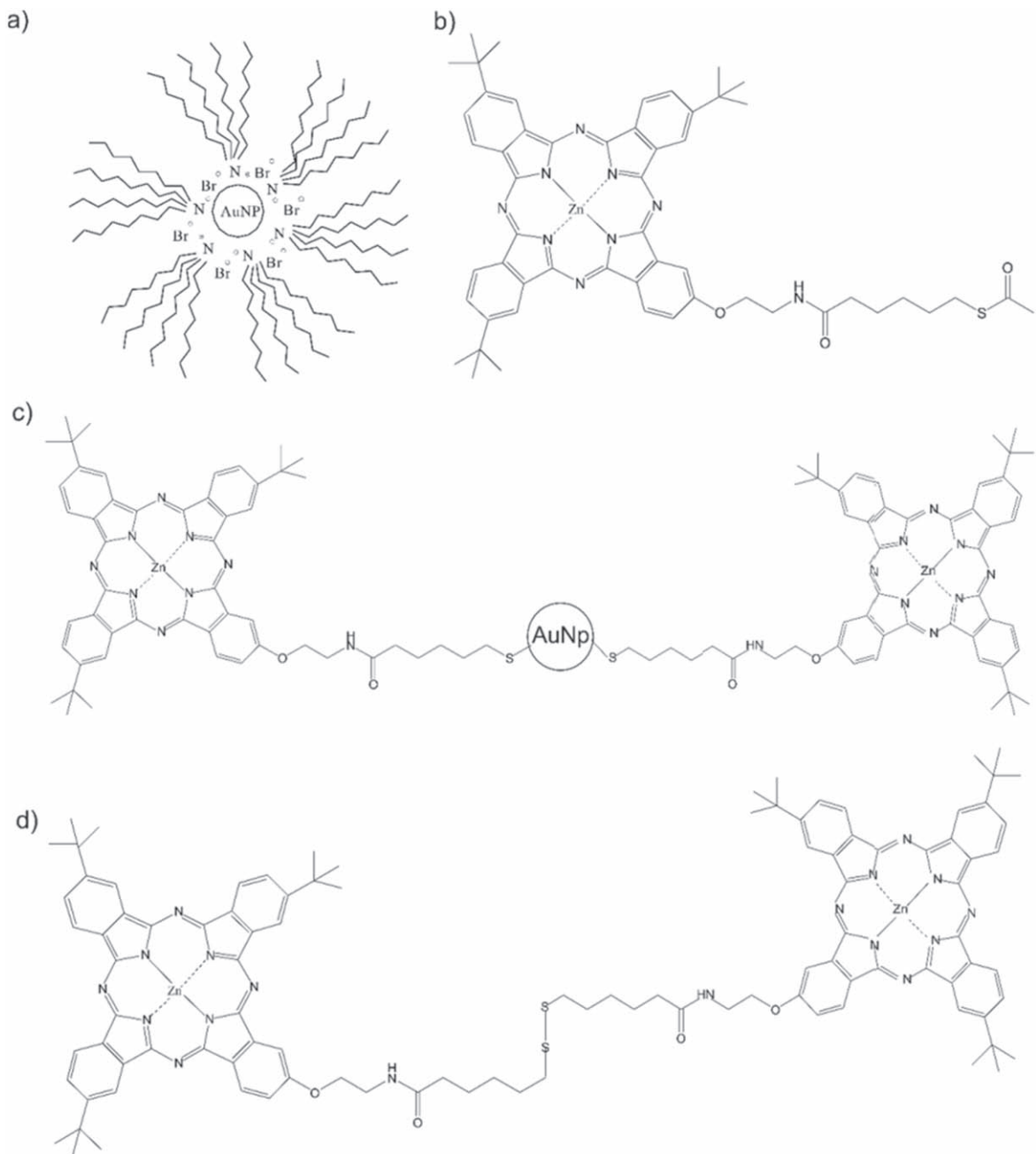
Figure 4. Scheme of the electrocatalytic materials. (a) Tetraoctylammonium bromide-capped gold nanoparticles (AuNP^{tOcBr}), (b) sulfur-substituted zinc phthalocyanine (ZnPc^{RS}), (c) covalent adduct (AuNP^{tOcBr}-S-ZnPc^{RS}), (d) dimeric sulfur-substituted zinc bisphthalocyanine: (ZnPc^R-S-ZnPc^R). Reproduced from Ref. 43 with kind permission from MDPI.

nanoparticles were shown to play an important role in the electron transfer between cytochrome c and the electrode.

In another work[46] Pd nanoparticles were used for the preparation of composites for electrodes modification. Song et al.[46] suggested a methanol-mediated weakly-capping growth approach in which anhydrous methanol was used as a mild reductant for the preparation of PdNP/CoPc nanocomposites (Fig. 6) In this process, palladium acetate adsorbed on cobalt phthalocyanine was reduced in situ. The electrocatalytic activity of PdNP/CoPc deposited on GCE was evaluated toward the oxidation of nitrite in water solutions and sausage filtrates. The sensor based on Pd/CoPc composite displayed a linear range of 0–5.0 mmol l^{-1}, fast response time and good selectivity in the presence of various cations, e.g. Na$^+$, K$^+$, Mg^{2+}, Zn^{2+}, NH$_4^+$, CO$_3^{2-}$, SO$_4^{2-}$, Cl$^-$, NO$_3^{3-}$, H$_2$PO$_4^{4-}$.

Hybrid Materials for Chemiresistive Sensors

Composite materials on the basis of phthalocyanines and metal nanoparticles can also be used as sensing layers of chemiresistive sensors; however the works on this subject are not so numerous as in the case of electrochemical sensors.

Films of metal phthalocyanines are widely used in chemiresistive sensors towards various gases and volatile organic vapors.[16,18,52] Phthalocyanine layers exhibit high sensor response, good reversibility, low response and recovery time, however they have quite low conductivity in comparison with metal oxide semiconductors and carbon nanomaterials. For this reason, the study of sensor properties requires expensive highly sensitive electrometers, which makes it difficult to manufacture miniature sensor devices based on phthalocyanine films. Small additions of conducting carbon nanotubes or
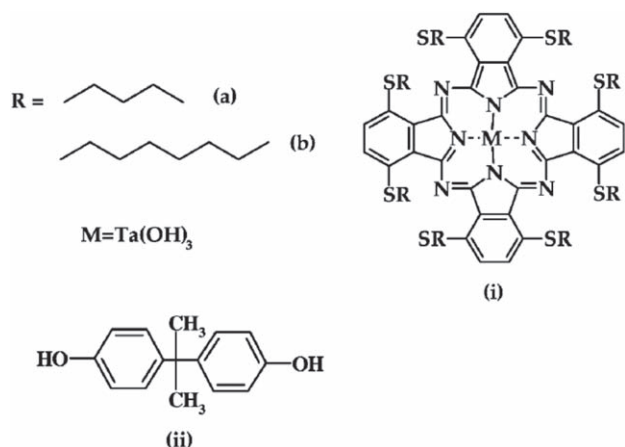
Figure 5. Structural formulas of tantalum phthalocyanines (i) and bisphenol A (ii).

metal nanoparticles in the preparation of phthalocyanine films can overcome this obstacle. Addition of metal nanoparticles to phthalocyanines causes an increase of conductivity of their films. For example, Khurana et al.[53] prepared the hybrid films by drop casting of the mixture solution of CuPc and AuNP stabilize with oleylamine in toluene. The measurement of I(V) dependence of the films showed that the current measured at 8 V increased from 4 nA for a pure CuPc film to about 38 nA for the hybrid film obtained from the solution of CuPc containing 300 μl AuNP. Inclusion of hexadecylamine capped gold nanoparticles into the matrix of liquid crystalline copper phthalocyanine bearing long alkyl substituents also led to the increase of the room temperature conductivity of the films by about two orders of magnitudes.[54]

Application of composite materials on the basis of semiconductors and metal nanoparticles possessing catalytic properties (e.g. Pt, Pd, Au) is known to result in the improvement of their sensor performance due to the so-called spillover effect. This effect is attributed to the activation of gas molecules on a metal catalytic particle with its subsequent diffusion into the semiconductor film.[55]
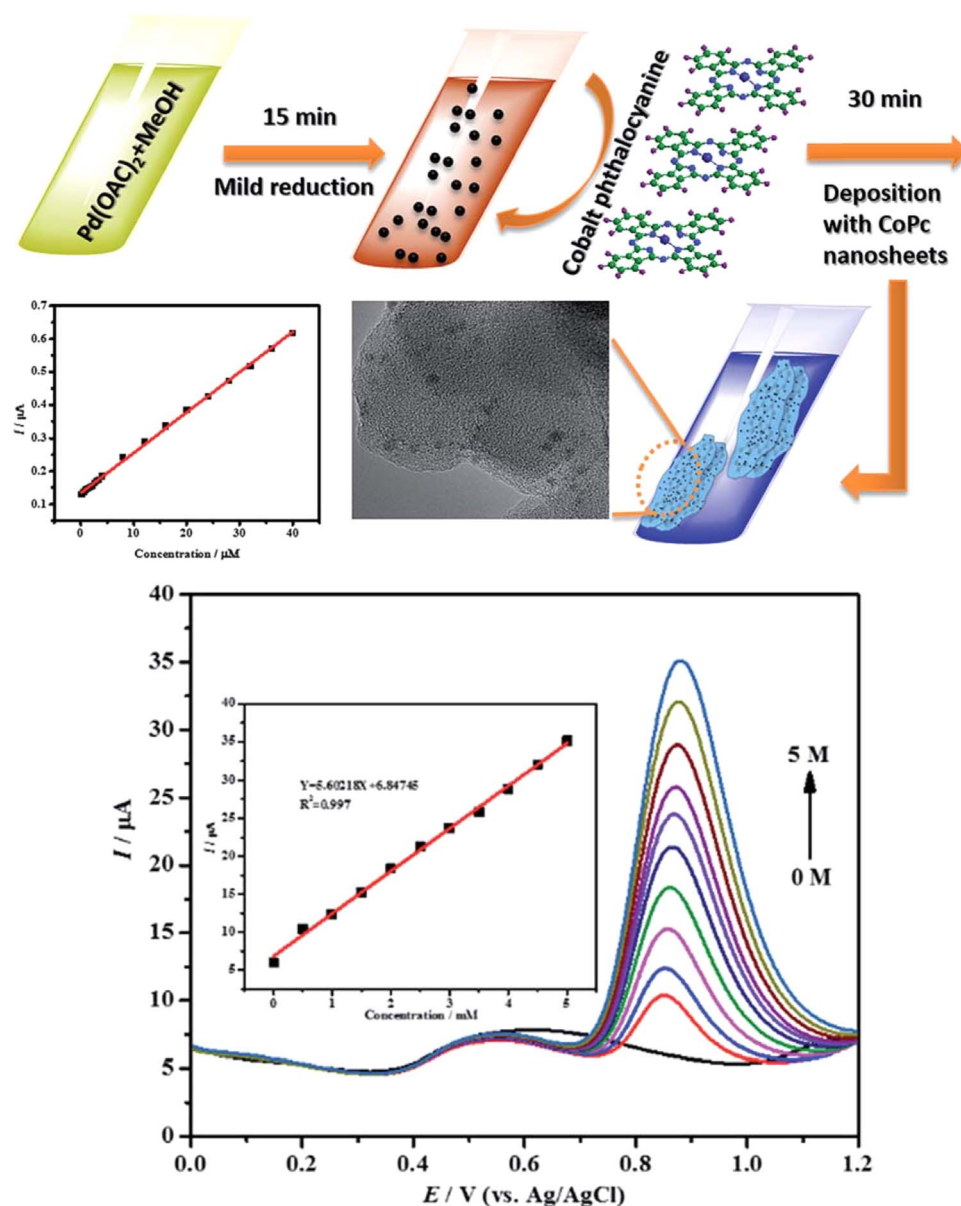

Figure 6. (a)—Schematic representation for the preparation of the Pd/CoPc nanocomposite. (b)—DPVs of the Pd/CoPc nanocomposite modified GCE in a pH 6.0, 0.2 M PBS containing various concentrations of nitrite. Inset: plot of peak current vs nitrite concentrations. Reproduced from Ref. 46 with kind permission of Royal Society of Chemistry.
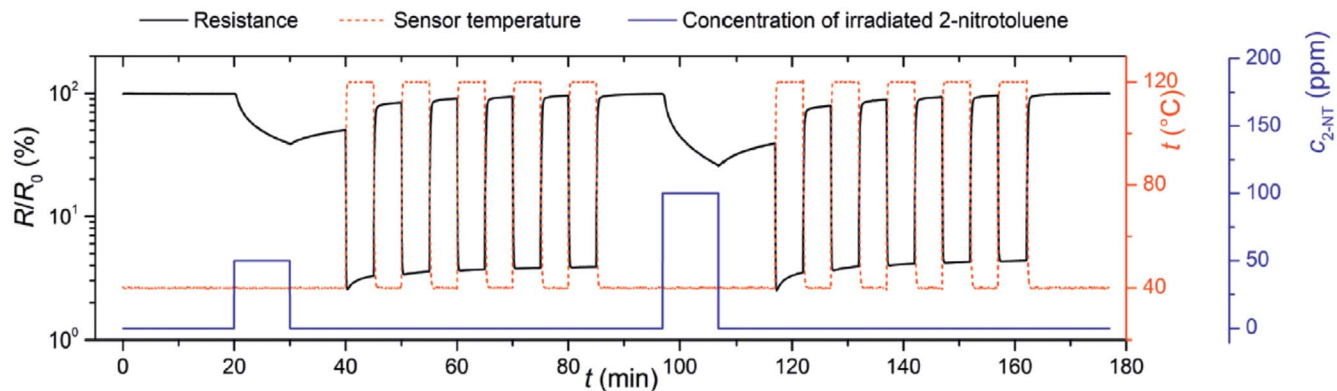
Figure 7. Regeneration of Pd(1 nm)/AgPc(250 nm) sensor after measurement of 50 and 100 ppm of activated 2-nitrotoluene vapors. Regeneration steps at 120 °C provide full recovery of original baseline level. Reproduced from Ref. 58 with kind permission of Elsevier S.A.

There are a number of works on composite materials of semiconducting metal oxides with metal nanoparticles[56,57] while papers on application of composites on the basis of phthalocyanines with metal nanoparticles are sporadic.

Tomeček et al.[58] demonstrated metal/silver phthalocyanine chemiresistors for the detection of taggants in explosives (2-nitrotoluene and 2,3-dimethyl-2,3-dinitrobutane) and NO_2 as a product of their photodecomposition. For the determination of taggants they were activated by fourth harmonic frequency of Nd: YAG laser ($\lambda = 266$ nm). Silver phthalocyanine layers were deposited by Organic Molecular Evaporation (OME) in vacuum. Then the films were covered with a controlled amount of noble metals (Pd, Ag, Au) by magnetron sputtering technology. The authors showed that the response time of M/AgPc active layers of chemiresistive sensors 1 ppm of NO_2 noticeably decreased in comparison with layers of AgPc. Moreover Pd(1 nm)/AgPc sensors exhibited the chemiresistive sensor response and excellent recovery after detection of photoactivated 2-nitrotoluene (Fig. 7).

Klyamer et al.[15] prepared bilayered structures on the basis of unsubstituted vanadyl phthalocyanine and palladium nanoparticles for hydrogen detection. VOPc films on the substrate with inter-digitated electrodes were prepared by physical vapor deposition. Then Pd nanoparticles were deposited by a pulse-CVD method with the different pulse cycles number from 20 to 40, using palladium hexafluoroacetylacetonate as a precursor. The surface microstructure of a VOPc film covered with Pd nanoparticles (20 cycles of pulse-CVD) is presented in Fig. 8a. It was shown that the sensor response of bilayer structures on the basis of VOPc films and PdNPs deposited during 40 pulse-CVD cycles increased by 4–5 times in comparison with VOPc films (Fig. 8b) At the same time, their LOD of hydrogen decreased to 10 ppm (cf. 30 ppm for VOPc films). The authors suggested that similarly to sensors based on metal oxide

layers modified with PdNPs, the increase of the sensor response in the case of MPc/Pd heterostructures was due to the increased surface area and "spill-over" effect.[59]

Conclusions and Remarks

Among numerous organic semiconductors, metal phthalocyanines are of particular interest because of their high thermal and chemical stability combined with their unique electronic properties. Apart from single-component phthalocyanine films, this article describes the use of MPc films decorated with metal nanoparticles for sensing applications. According to the literature analysis, various methods are used to obtain hybrid materials based on phthalocyanines and metal nanoparticles and to modify the electrodes of electrochemical sensors, among them mixing of components, electrodeposition, layer-by-layer deposition and Langmuir-Blodgett technique. These methods have their own advantages and limitations and are determined by the properties of phthalocyanines and the structure of nanoparticles, as well as the purpose of the study. The mechanical mixing components is an easy-to-perform method that allows adjusting the ratio of components, but there is no chemical interaction between the components of the mixture, which can lead to leakage of one of the components. In addition, this method often requires the use of binding components (polymers, oil), which can lead to poor charge transfer. In the case of Au/MPc hybrids obtained by covalent functionalization, the interaction between two electroactive components is much stronger. Layer-by-layer deposition and Langmuir-Blodgett techniques lead to the formation of homogeneous thin films on the electrode surface with sufficiently strong interaction between the binding components, but the set of phthalocyanines that can be used in these methods is quite limited. In contrast to the "wet" methods, electrodeposition, CVD and ALD
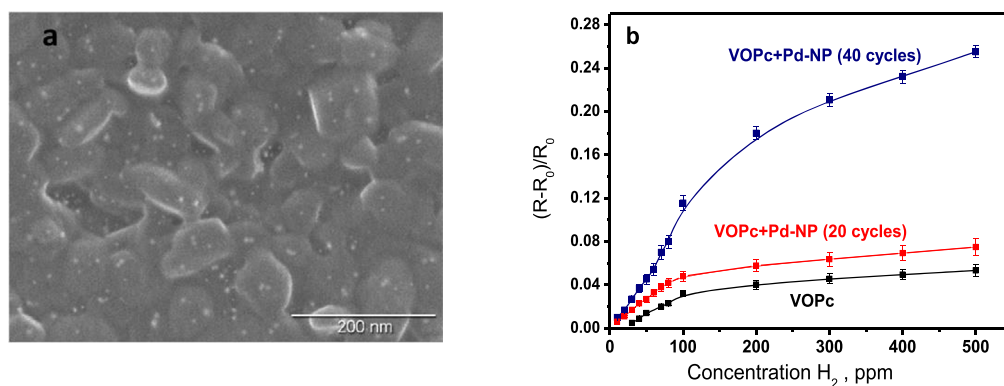

Figure 8. (a)—Surface morphology of VOPc film covered with Pd nanoparticles (20 cycles). (b)—Dependence of the sensor response of a VOPc film and a VOPc film covered with Pd nanoparticles during 20 and 40 cycles of pulse-CVD on hydrogen concentration. Redrawn from Ref. 15.

techniques allow obtaining nanoparticles with a metal content close to 100% without any surfactants and stabilizers, but CVD and ALD techniques require complex vacuum equipment and a relatively high temperature of MNP deposition. Electrodeposition offers some advantages including ease of controlling the coating thickness using experimental parameters, lower operating temperature and relatively low cost.

Application of metal nanoparticles with catalytic properties leads to an increase in the sensitivity and selectivity of sensing layers because of the activation of gas molecules on a metal catalytic particle and their diffusion into a gas-sensitive semiconductor layer. These types of hybrid organic/inorganic nanomaterials are found to responsible for widening the scope and perspectives in phthalocyanine chemistry, as well as their electrochemical applications. Metal-phthalocyanine hybrid structures with large surface areas and ultrahigh porosity are believed to be ideal sensing materials because chemical sensors rely highly on surface reactions. In addition, these structures can be used as a membrane to utilize their unique gas adsorption and separation characteristics.

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