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Hyper-Cross-Linked Polymer Loaded with PtRu-MoS_2 for Ammonia Detection

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Here we report the performance in ammonia detection of polystyrene-based hyper-cross-linked polymer (HCLP) synthesized with a new synthetic route. The resin loaded with PtRu nano-alloy covered by MoS_2 nanosheets, prepared according to a "wet chemistry" approach, was broadly characterized: TEM images and XRD spectra showed the formation of nanoparticles with a few nanometers size partially covered by MoS_2 layers. The sample was tested as an electrochemical sensor for the detection of small traces of NH_3 in aqueous solutions with a limit of detection (LOD) of 4.5 μM. The sensor was tested also in simulated wastewater coming from the fertilizer industry, showing proper operation and excellent selectivity.

Introduction

In recent years, the presence of ammonia in industrial wastewater has become a critical issue (Sekhar and Kysar, 2017), especially due to its frequent usage in farming as fertilizer (Lòpez de Mishima et al., 1998). Therefore, nowadays, the development of efficient methods for detecting and monitoring of NH_3 has become of fundamental relevance. The detection process should be specific and fast, and the sensor should possess features, such as small dimensions, low cost, quick response, and high sensitivity and selectivity. Among all types of sensors, electrochemical sensors better meet the aforementioned requirements (Jiang and Zhang, 2017). Catalytic oxidation of NH_3, occurring at the anode of the electrolytic cell, is the reaction at the basis of the electrochemical detection of ammonia. The NH_3 oxidation occurs through several steps involving the N-H bond cleavage and the formation of gaseous nitrogen. Platinum (Vidal-Iglesias et al., 2006) is the best candidate for this reaction in alkaline solutions, however, it suffers from deactivation by N_{ads} poisoning intermediate (Silva et al., 2017; Sarno et al., 2019). The energy of N_{ads} on the catalyst surface is too high (−394 kJ mol^{-1}) to enable the N_2 formation (de Vooys et al., 2001). As a consequence, these strongly adsorbed intermediates block surface active sites and prevent continuous oxidation of ammonia on deactivated Pt surfaces. In order to overcome the deactivation of platinum by poisoning reaction intermediates and to increase the current density, different Pt-binary electrocatalysts have been reported in the literature (Moran et al., 2008). In particular, PtRu showed superior catalytic activity and stability towards ammonia oxidation compared to monometallic Pt, but the PtRu alloy sensor performances have been never evaluated. Moreover, 2D nanomaterials have attracted increasing attention, especially MoS_2. MoS_2 possesses hexagonal close-packed layered structure, where Mo atoms are covalently linked to upper and lower layers of S atoms in trigonal prismatic morphology. Molybdenum disulfide has different remarkable properties (Mao et al., 2018): high surface area, significant electron mobility and high density of electronic states, so it shows higher sensing properties. Hyper-cross-linked (HCL) polymers, network polymers composed of rigid molecular linkers, represent a class of advanced porous polymer materials with high surface area and porosity and physicochemical stability, arouse increasing attention because of simple chemical preparation and low cost (Castaldo et al., 2017a; Castaldo et al., 2017b, Castaldo et al., 2017c, Castaldo et al., 2019a). Here, for the first time, in order to form a 3-dimensional network, combining the beneficial effects of HCLP in reagents pre-concentration, the PtRu binary alloys, and the MoS_2 nanosheets, we report a polystyrene-based HCLP

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material embedded by PtRu-MoS_2 for ammonia detection at trace level. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy–Energy-dispersive X-ray spectroscopy (TEM-EDS) and X-ray diffraction (XRD) were employed for materials characterization.

1. Experimental Section

1.1 Materials

Platinum (III) acetylacetonate (97%), ammonium tetrathiomolybdate (>99%), Ruthenium (III) acetylacetonate (>97%), oleic acid , oleylammine, 1,2–hexdecanediol, 1-Octadecene, Vinylbenzyl chloride (VBC, >95%, mixture of isomers, ∼70% meta + ∼30% para), *p*-divinylbenzene (DVB, 85%, meta isomer ∼10 wt %), 2,2'-azobis(2-methylproprionitrile) (AIBN, >98%), $FeCl_3$ (> 97%), were purchased by Sigma Aldrich (Milan, Italy), and used without further purifications.

1.2 Nanocomposite preparation

Platinum (III) acetylacetonate (1.271 mmol), ammonium tetrathiomolybdate (1.153 mmol) and ruthenium (III) acetylacetonate (0.753 mmol) were loaded into the reagent mixture, consisting of 20 ml of 1-octadecene, oleic acid (6 mmol), oleyl ammine (6 mmol) and 1,2-hexadecandiol (10 mmol) as reducing agent. The temperature was increased to 200°C for 2 h and then the mixture was heated up to 285°C for 1 h, in inert ambient (Sarno et al., 2015; Sarno et al., 2016). After synthesis had occurred, PtRu-MoS_2 NPs obtained were purified alternating ethanol and hexane washing and separating by centrifugation (Sarno et al., 2019; Sarno and Ponticorvo, 2018a). The hyper-crosslinked poly(divinylbenzene-*co*-vinylbenzyl chloride) based nanocomposites containing PtRu-MoS_2 NPs were prepared through a two-step procedure. DVB and VBC (molar ratio 2:98) were mixed with PtRu-MoS_2 NPs. To ensure an effective nanofiller dispersion, the mixture was sonicated for 50 min with a 500 W tip sonicator at 25% power, with a 10 s/50 s ON/OFF cycle. Therefore, 0.5 phr of AIBN was added, and the mixture was kept under stirring at constant temperature (80°C) under nitrogen for 30 min. Polymerization was completed in an oven for 24 h at 80°C. The obtained nanocomposite and polymer precursors were repeatedly washed with methanol, acetone and diethyl ether, and then dried in a vacuum oven at 40 °C for 24 h (Castaldo et al., 2019b). For the synthesis of the hyper-cross-linked systems, the precursors were swollen in 1,2-dichloroethane for 2 h, then the systems were cooled to 0 °C by means of an ice/water bath. $FeCl_3$ was added, and stirring was continued for 2 h. After that, the reaction flask was heated to 80 °C and kept at this temperature for 18 h. The obtained hyper-cross-linked resin and nanocomposite were washed with methanol and dried in a vacuum oven at 40 °C.

Table 1: Simulated wastewater solution chemicals

Chemical	**Quantity [g]**
Primary molecules	
Glucose	0.2
Monopotassium phosphate	0.05
Nutrient solution	
Chemical	***[g/L]***
Calcium Chloride dehydrate	6.3
Iron chloride hexahydrate	1.5
Cobalt chloride hexahydrate	1.9
Cupper chloride dehydrate	0.1
Magnesium sulphate heptahydrate	85
Manganese chloride tetrahydrate	7.1
Nickel sulphate	6.6
Yeast extract	1

1.3 Characterization methods

Bright-field transmission electron microscopy (TEM) analysis was performed on the precursor nanocomposites by means of FEI Tecnai G12 Spirit Twin (LaB_6 source). TEM images were acquired through FEI Eagle 4k CCD camera. Electrochemical characterization was carried out by means of Autolab PGSTAT302N potentiostat/galvanostat. In detail, traces of ammonia detection was performed through cyclic voltammetry

(CV) experiments at 20 mV/s in 1 M KOH with different NH_3 amounts. To obtained the electrodes, 4 mg of synthesized nanocomposites were dispersed into 80 µl of a 5 wt% Nafion solution, 200 µl of ethanol and 800 µL of distilled water. Limit of detection (LOD) was calculated starting from the calibration curve with the following equation:

$$LOD=\frac{3*\delta}{b} \quad (1)$$

Where δ is the standard deviation and b is the slope of the calibration curve. Furthermore, a simulated wastewater solution coming from the fertilizer industry was prepared by adding to 1L of bidistilled water: (i) ammonium nitrate (NH_4NO_3); (ii) primary molecules as reported in Table 1; and, (iii) 10 mL of the nutrient solution reported in Table 1. KOH was added in order to achieve pH=14. Free ammonia in the wastewater is typically present in equilibrium with the ammonium ions (NH_4^+) (Jia et al., 2017), the equilibrium depends on pH and temperature: at pH 7, only NH_4^+ ions are present, yet at pH 12 mainly NH_3 is present.

2. Results and discussion

The X-ray diffraction pattern (Figure 1) shows a Pt peaks up-shift, indicating the PtRu alloy formation (Roth et al., 2001), due to the lattice contraction caused by the incorporation of Ru into the Pt lattice. Furthermore, the typical MoS_2 nanosheets peak was observed at 59.10°, corresponding to (110) plane (Sarno and Ponticorvo, 2018b). The absence of (002) plane and the broadness of peak indicate that the obtained MoS_2 is a single layer or few-layer graphene-like MoS_2.

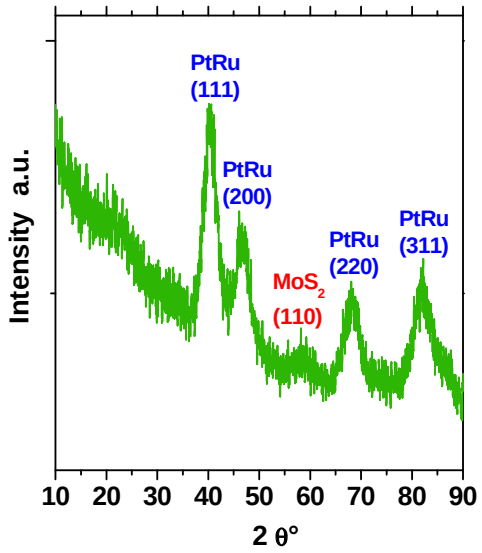

Figure 1: XRD spectrum of PtRu/MoS_2 NPs

To evaluate the morphology of the as-prepared PtRu/MoS_2 nanoparticles, TEM images at different magnifications are shown (Figure 2). The images display the formation of uniformly distributed nanoparticles with homogeneous dimensions. They are covered by molybdenum disulfide nanosheets, free MoS_2 nanosheets can also be found. The nanoparticles exhibit an average dimension of 3.1 nm with a narrow size distribution. After the Pt/Ru/MoS_2-HCL composite resin synthesis (Figure 3), which allows to “freeze” the nanomaterials in the polymer matrix, the nanoparticles result almost homogeneously dispersed.
Electrochemical sensor performance, for ammonia traces determination, was firstly evaluated by CV tests at different NH_3 concentrations with a scan rate of 20 mV/s using 1 M KOH solutions (Figure 4). The tests show that increasing the ammonia concentration the oxidation peak current density and the oxidation peak voltage increase, due to the raised percentage of adsorbed species on the electrode and number of electrons transferred for the ammonia oxidation reaction as ammonia concentration growths (Li et al., 2017; Moran et al., 2008; Moschou et al., 2000; Ji et al., 2005).

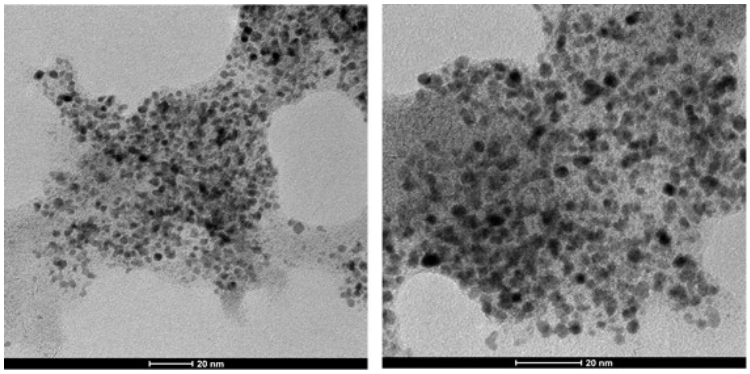

Figure 2: TEM images of PtRu/MoS_2 NPs at different magnifications

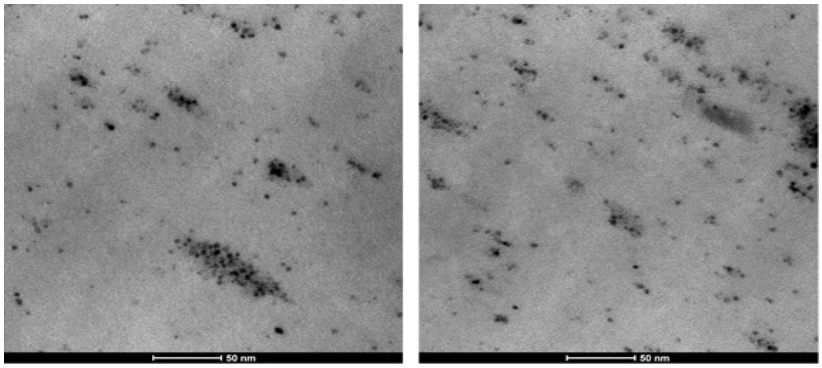

Figure 3: TEM image of dispersed of PtRu/MoS_2 NPs in HCL resin

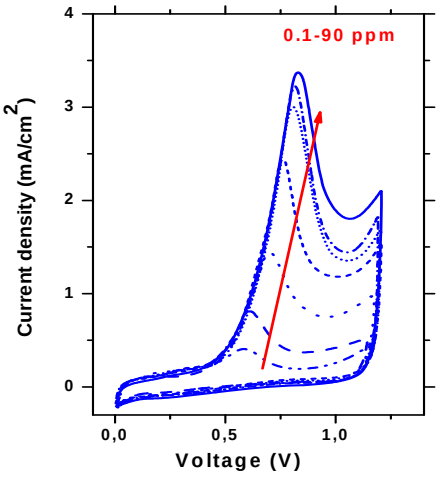

Figure 4: CV tests in the presence of different amounts of NH_3 in 1 M KOH

Amperometric experiments at different NH_3 amounts were performed and the sensitivity plot as a function of ammonia concentration, with error bars based on three trials of NH_3 exposure, is shown in Figure 5a. The calibration curve, obtained in the range 0-3 ppm, for the electrochemical sensor was constructed in Figure 5b. The collected data fitted the equation indicated in Figure 5b with a straight line, with a coefficient of determination R^2 close to one (0.987) and showing a very low LOD value of 4.5 µM. The accuracy of the analytical technique was evaluated as the percentage of recovery by the assay of the known added amount of analyte in the samples: the recovery rate calculated was 99.2 % indicating a possible utilization of the proposed material to determine NH_3 in real conditions. Aiming to evaluate the effectiveness of the PtRu/MoS_2 NPs in HCL resin-based sensors in real environments, further tests were carried out in simulated wastewater.

Amperometric oxidation peaks were recorded at different ammonia concentrations and compared with the theoretical ones, see Table 2. A close correspondence between the as-obtained experimental data and the previously made calibration curve can be detected, therefore suggesting a significant sensor performance even in a solution close to reality.

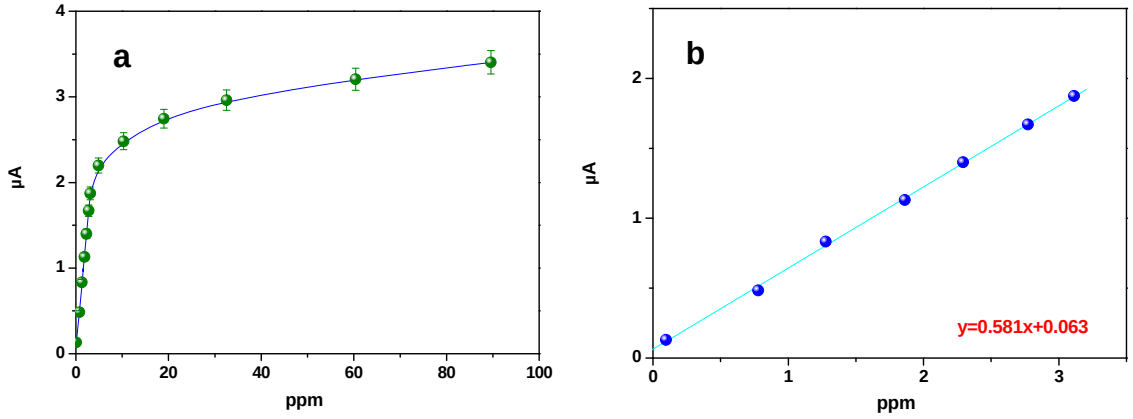

Figure 5: Amperometric sensitivity vs. NH_3 concentration (a). Enlarged view of the first part of the curve and the fit of anodic peak current vs. NH_3 concentration (b)

Table 2: Correspondence between the sensor calibration curve and the experimental data obtained by testing the sensor in a simulated wastewater solution

NH_3 concentration [ppm]	Theoretical anodic peak current [μA]	Experimental anodic peak current [μA]
0.2	0.18	0.16
0.5	0.35	0.36
2	1.22	1.21
2.5	1.52	1.55
3	1.81	1.82

3. Conclusions

In summary, a simple, and efficient modified Davankov procedure was adopted in order to synthesize hyper-cross-linked styrene-based resins filled with PtRu/MoS_2 NPs. TEM images confirmed the formation of the aforementioned nanocomposite structure, well dispersed in the HCL resin. The prepared nanocomposite has been tested as an electrochemical sensor in order to detect very small traces of ammonia in aqueous solution as established by European standards, i.e. NH_3 content must be lower than 5 ppm. PtRu/MoS_2 NPs in HCL resin showed excellent behavior as NH_3 sensor: high oxidation peak currents intensities, wide linear ranges of detection and low detection limit (4.5 μM). This can be regarded as a consequence of the multifunctional mechanism due to:

(i) the strong synergism between the two metals in the PtRu alloy enhanced also by the small size of the nanoparticles. In particular, Pt favors the adsorption of ammonia molecules and the dehydrogenation to different adsorbed intermediate species. Ru provides an abundance of OH_{ads} species, which have a key role in ammonia detection, helping the reaction with hydroxide ions, producing N_2, and avoiding the catalyst poisoning by adsorbed species.

(ii) MoS_2 carpet favoring significant electron mobility.

(iii) HCLs meso- and microporous structure favoring accessibility and wettability of the electrode active sites for ion adsorption throughout the electrolyte induced swelling.

The sensor was tested also in a simulated wastewater coming from the fertilizer industry, showing proper operation and excellent selectivity, too.

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