The scientific interest in nanotechnology and nanomaterials can be traced back to about sixty years ago (1959, in the occasion of the Annual Meeting of the American Physical Society), when a new approach for manipulating and controlling matter on a miniaturized scale rose. The subsequent huge increment in the involvement of nanomaterials in science is due to their peculiar properties: increased surface-to-volume ratio, quantum size effects, new physical and optical features, high active surface area, enhanced or different mass transport, improved selectivity and so on. All these characteristics make nanomaterials extremely suitable for a wide range of applications, from energetics to catalysis and sensing. In the last few decades, apart from "single-component" nanomaterials, the use of "hybrids" (made of two or more components) is growing. This is connected to the fact that, since in a composite the instauration of synergistic effects is confined to the interfacial region of the materials mixed together, in nanomaterials, because of the small size, these effects may become a dominant factor. The result is the instauration of new and unexpected properties (often sought and interesting) that are not only the sum of the individual contributions. Considering all these
facts, hybrids are extremely good candidates to be applied in several fields. In this PhD Thesis Project, hybrid nanomaterials are the subject of a deep electrochemical study with the final purpose of optimizing electroanalytical sensors for organic, inorganic and biological analytes, also at trace levels. The single components of the hybrids here presented are metals, graphene and graphene-derivatives, and semiconductors. In more detail, metal-metal hybrids are gold-based bimetallic systems (AuPt, AuPd and AuAg), in different conformations (alloy or core-shell) that are characterized combining electrochemical results with those obtained by more conventional techniques (TEM, EXAFS). The use of electrochemistry for understanding the real structure of the hybrids is presented as a low-cost, easy to use and fast alternative technique, that allows also to follow in time the conformational evolution of selected bimetallic systems. The effect played also by the possible presence of a support onto the electrochemical and electrocatalytic properties of the nanoparticles is considered, showing promising results in terms of selectivity of the materials. Moreover, the enhanced performances of the bimetallics instead of the monometallics in the detection of target analytes (cinnamyl alcohol and aldehyde in the case of AuPd systems and organic halides for what concern AuAg) is verified. The interest is then moved to metal-semiconductor hybrids, particularly to Au/TiO2 based devices, in which the presence of gold nanoparticles is exploited for the electroanalytical detection of a contaminant of emerging concern (diclofenac) while the presence of TiO2 has been verified as essential in order to avoid problem of fouling and passivation of the electrode. The photo-renewability of the electrode is verified, allowing to restore the starting performances of the device even after the electroanalytical use. The instauration or not of a real interphase between gold and TiO2 is explored, analysing electrochemical results gained by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). With regard to graphene-metal hybrids, two materials made of Reduced Graphene Oxide (RGO) decorated with gold nanoparticles are involved for the detection of both organic and inorganic molecules (dopamine and arsenic). In both cases, strong enhanced properties are highlighted in the use of the hybrid with respect to its single components, with low detection limits and high sensitivities reached. A different material, also based on RGO platform, is used for the construction of a biosensor, labelled with gold nanoparticles, for the electroanalytical detection of the antigen H-IgG. In this case, the possibility to use paper-based electrodes is of particular interest for the construction of low-cost and user-friendly (in terms of facility of use) sensors. Finally, graphene-semiconductor hybrids are analysed, starting from graphene/TiO2 materials. Different electrodes modified with several layers of graphene (from one to five) decorated with titanium dioxide nanocrystals are electrochemically characterized and differences in the electrochemical response and activity are highlighted passing from a graphene to a graphitic-like structure. The presence of TiO2 nanocrystals is verified to act as a coverage of the defective site, changing again the reactivity of the device toward selected analytes. Moreover, the photo-renewability of the sensors is again exploited. Another hybrid of this group is based on RGO and PbS nanocrystals, in which the light harvesting properties of the semiconducting particles are combined with the high conductivity of graphene in order to create a promising device to be applied from electronics to sensing fields. The electronic communication between the two
materials and the hole transfer from photoexcited PbS nanocrystals to graphene is verified also allowing to claim the presence of an interphase between the two components of the hybrid. In conclusion, several hybrid materials are here investigated starting from their physico-chemical and electrochemical characterizations. Their application as electroanalytical sensors is explored, evidencing the presence of synergistic effects in the hybrid with respect to the single components, assuring enhanced properties and superior performances.

Localizzazioni e accesso

http://memoria.depositolegale.it/*/http://hdl.handle.net/2434/703446