J Solid State Electrochem (2010) 14:1939–1945
DOI 10.1007/s10008-010-1076-y

REVIEW

Hybrid organic–inorganic materials: from child's play to energy applications

**Pedro Gómez-Romero · Omar Ayyad ·
Jullieth Suárez-Guevara · David Muñoz-Rojas**

Received: 5 February 2010 / Accepted: 5 April 2010 / Published online: 2 May 2010

Abstract The field of hybrids has boomed since its initial conception with silicones as structural materials to the wealth of different types of hybrid materials studied nowadays as functional materials. Hybrids based on conducting polymers and a great variety of inorganic species constitute a growing area of this field. We present a brief review of the intersection between conducting polymer hybrids and electrochemical applications to energy storage and conversion. But beyond examples of hybrids active in batteries, supercapacitors, solar or fuel cells, we have tried to convey the standing challenges concerning the design of chemically (and electrochemically) complex hybrid systems with components and building blocks ranging from extended oxides or nanoparticles to carbon or oxide nanotubes, to clusters and to molecules and the opportunities arising from their integration with conducting polymers.

Keywords Hybrid materials · Conducting polymers · Energy storage and conversion · Nanocomposites · Polyoxometalates

Introduction

The intersection between the field of hybrid materials and that of electrochemistry is a quickly expanding area with strategic applications ranging from sensors to energy storage and conversion [1, 2].

The original thrust for hybrid formulations came from the quest of materials with the best properties of glass and plastics and led to the discovery and optimization of polysiloxanes or silicones, among which, silly putty has served as an American favourite modelling paste for child's play since the 1950s.

But hybrids span much further than organically substituted –Si–O–Si–O– backbones typically prepared by sol–gel chemistry. And every year more so. A glimpse of this variety, including intercalates [3–6], grafting [3], sol–gel [7, 8], electrodeposition [9] or polymer-based hybrids [2, 10], among others, can be found in the chapters of the book "Functional Hybrid Materials" [1] and in a continuous series of reviews steadily updating information on this expanding field. Indeed, just reviewing recent reviews on different applications of hybrid materials is an extraordinary exercise. One can find reviews on functional hybrid materials [2], on general applications [11] or reviews with emphasis on electrochemical properties [12], reviews and papers on luminescent hybrid materials [13–15], on photochromism [16], on catalysis [15], on sensors [17, 18], on actuators, on opto-electronic devices [19], on hybrid solar cells [20] or fuel cells [21–24]

This paper, based on an expanded version of an invited contribution at WEEM2009 aims at providing an appealing overview of the many research targets lying at the intersection between the field of hybrid materials and the vast and multifaceted field of energy storage and conversion. Several of the case examples included in this review

P. Gómez-Romero (✉) · O. Ayyad · J. Suárez-Guevara ·
D. Muñoz-Rojas
Centro de Investigación en Nanociencia y Nanotecnología,
CIN2 (CSIC-ICN),
Campus de la UAB,
08193 Bellaterra, Barcelona, Spain
e-mail: pedro.gomez@cin2.es

Present Address:
D. Muñoz-Rojas
Department of Materials Science and Metallurgy,
University of Cambridge,
Pembroke St.,
Cambridge CB2 3QZ, UK

were originated in our laboratory, but we have intended to include also other inspiring examples of how to put hybrids to work for energy applications directly related to electrochemical devices. The result is by no means exhaustive. This is not a comprehensive review, but tries to be an inspiring one.

In order to focus this review, we will concentrate our discussions on hybrid materials based on conducting polymers. In combination with them, a myriad of inorganic compounds can be used to design and prepare hybrid materials: from extended phases or metals, nanoparticles, clusters to molecular species. This variety leads in turn to a wealth of different possible interactions, and structures at different length scales, between the polymers and the inorganic components, as shown in Fig. 1 for just a few representative examples.

The complex nanostructure shown on the left (Fig. 1a) corresponds to crooked core–shell silver "nanosnakes" coated with a layer of polypyrrole [25]. The structure shown features approx. 50-nm-wide cores and many microns long lengths, but there are other of these nanostructures composed of different materials, such as Cu2O/PPy [26] or Cu/PPy nanowires of varying thicknesses and lengths. Figure 1b shows silver nanoparticles (approx. 12 nm) grown in a biopolymer matrix (agar) [27]. There are also many recent studies on the synthesis and properties of metal nanoparticles/conducting polymer nanocomposites [28–34] which would belong to this category of domain size. Figure 1c represents the (anisotropic) growth of conducting polymers, in particular polypyrrole (PPy), within the channels of a mesoporous silica matrix. The synthesis [35, 36] and electrochemical properties [37] of this type of hybrids have been recently reported. In this case, the "host" is inorganic and the "guest" polymeric, and thus, this is described as an inorganic–organic hybrid (I–O) [2]. Other examples of I–O hybrids with smaller domain size of the polymer (at least in one dimension) is given by the intercalate hybrid compound presented in Fig. 1d. Xerogels of V$_2$O$_5$ intercalated with PPy or PAni were prepared [38] and their application as cathodes in lithium batteries demonstrated [39]. Not only oxides but also extended coordination compounds of the Prussian Blue type have been extensively studied in hybrids [40–43]. The final example of hybrids based on conducting polymers in Fig. 1e shows the material prepared by anchoring polyoxometalate (heteropolyanions) within the framework of conducting polymers either PPy [44], PAni [45, 46] or PEDOT [47, 48]. These represent examples of I–O hybrids in which the matrix is polymeric and the inorganic species are clusters [44] or even smaller molecules [49, 50]. Our work showed that the large molecular weight and charge of these anions are enough to keep them anchored within the framework of p-doped polymers, although work has also been conducted on the covalent linking of this type of clusters in polymers [51]. As it will be detailed below, these materials were successfully shown to act as efficient electrodes for electrochemical supercapacitors [52].

Energy

If we shift our perspective from the world of materials to the world of energy, we will find an incredible land of

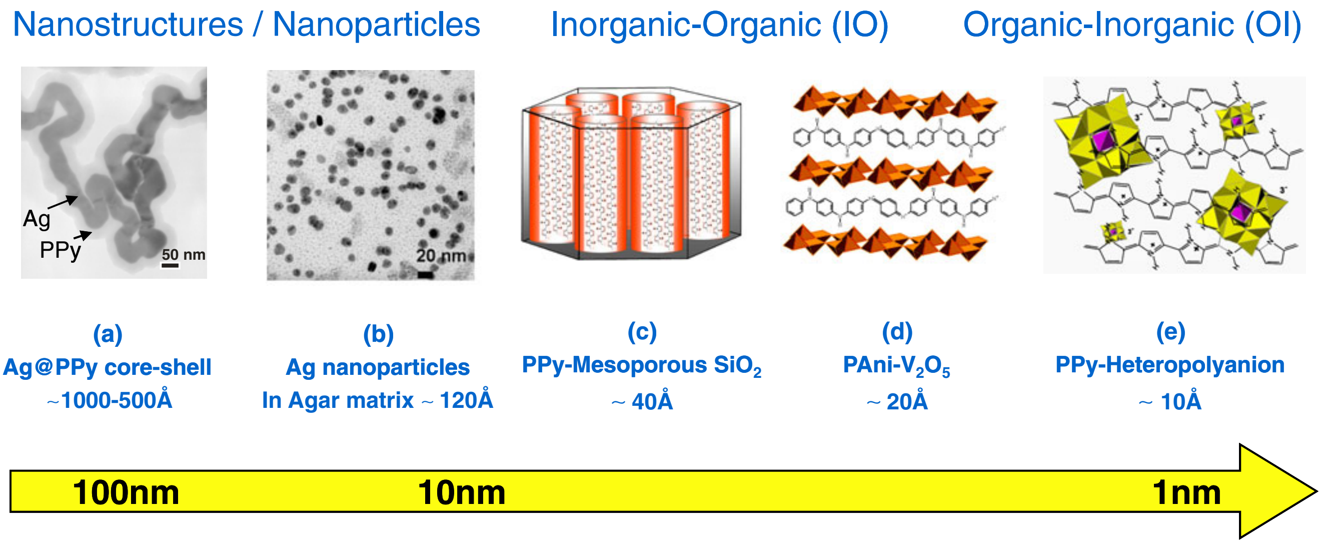

Fig. 1 Length scales of interaction and domain sizes between conducting polymers and inorganic species can vary widely depending on the type of material considered: from complex core shell nanostructures or nanoparticles spanning a few hundred nanometers to mesoporous or intercalation hybrids to molecular species down to 1 nm

opportunities. All the pieces of the energy puzzle are urgently demanding scientific breakthroughs related to the world of materials or nanoscience [53], and among them, hybrid nanocomposite materials take a good share of research [20].

Conversion (generation) of energy Whether you are an engineer and call it "generation" or you are a scientist and call it "conversion", this corner of the energy field is in bad need of help from materials scientists. Solar energy conversion could be taken as the paradigm of this need. Frequently put off as a "not so efficient" technology, solar conversion is actually a dragon with many heads (thermal, photovoltaic, photoelectrochemical), for most of which the main problem is NOT efficiency but price. After all, even the 10% of free is free, and the real question is how long it will take for that thing we put on our roof to pay off. Way too many years so far for solar energy to compete with cheap and dirty good old oil.

Simpler and less expensive processes for the fabrication and purification of solar silicon could help therefore turn the balance towards affordable photovoltaic conversion. But if 99.999% Si has reached an absolute minimum for its production costs (does anyone believe it?), materials scientists have an alternative plan. Actually many alternative plans, almost as many as scientists working on the field, because the race is open for the discovery of alternative materials and the development of novel conversion devices based on them. They would just need to be at least as efficient (and durable!) as silicon, but much cheaper. Hybrid materials have a big role to play in this game, as shown by several reviews and noted papers [1, 20, 54]. But solar is not just photovoltaics. Thermal solar conversion, though a more mature technology, could also benefit from innovation in materials. This innovation could involve the design of a wide variety of materials, such as selective absorbers, refractory materials or self-cleaning coatings for the panels, as well as novel systems for thermal energy storage like molten salts or silicones or latent heat compounds.

Finally, in the photoelectrochemical corner of solar energy, (photo-) electrochemistry is obviously the reigning tool.

Besides solar cells, other wide field related to energy conversion is that of fuel cells. Direct conversion of chemical into electrical energy has not been a big commercial hit in the past (apart from aerospace applications) due to our high tolerance of exhaust gases in exchange for the use of cheap and dirty good old fossil fuels on earth (again, apart from aerospace applications). Low-temperature fuel cells like proton-exchange membrane are the technologies with a potentially higher input from hybrid materials. Indeed, besides organic polymers conventionally used for the task, hybrid materials are beginning to show their potential for the fabrication of high-performance electrolyte membranes in this type of polymeric fuel cells [21–23].

Energy storage

Notwithstanding the importance of energy conversion, energy storage is another field of utmost importance for our upcoming sustainable energy model and a field in which electrochemistry is traditionally dominant and in which hybrid materials are beginning to show as powerful contenders.

Electrochemical energy storage has been traditionally and conventionally divided into batteries and supercapacitors. Originally, the distinction was meaningful. Conventional capacitors used a purely electrophysical mechanism to store minimal amounts of energy, but with the capability of providing it fastest, that is, at high current and high power. The introduction of double-layer supercapacitors was an ingenious way to harness charge separation at an electrode–electrolyte interphase and provided a way to store more energy than with conventional capacitors due to the high surface area and the minimal charge separation distance (Angstroms at the double layer). Batteries, on the other hand, exploited purely electrochemical reactions and provided high-energy densities but low power densities, the latter a consequence of the involvement of ions in the redox reactions. The electro-ionic nature of battery reactions was leading to slower processes in comparison with faster, purely electronic processes in conventional capacitors.

The advent of electrochemical supercapacitors has recently blurred all those distinctions [55]. These devices share features from batteries (the electrochemical nature of the processes involved) and from capacitors (the interfacial nature of those processes). Thus, following the introduction of hydrous RuO_2 as a prototypical active material for electrochemical supercapacitors [55, 56], a wealth of research has been devoted to the study of many different inorganic phases with high surface area, such as MnO_2 [57], but also to the study of conducting polymers for the same task [58]. At the conceptual interface between inorganics and conducting polymers or carbon nanotubes [59], it has been natural to find examples of hybrid materials which can harness the electroactivity and conductivity of the latter and combine it with the electroactivity of the former.

In our laboratory, we did explore the possibility to use polyoxometalates in combination with conducting polymers to be used as hybrid materials for supercapacitors. Polyoxometalates are inorganic oxide-like clusters typically formed by Mo or W oxide units which constitute the closest example of an oxide quantum dot. They are both structural and functional models of electroactive oxides reduced to their minimal size [60, 61] (Fig. 2). Indeed, all 12 MO_6 units conforming to the so-called Keggin structure are outer "surface" moieties. There is no bulk. They are so small and heavily charged that they are soluble in many solvents and, therefore in principle, useless as active electrode materials.

The integration of polyoxometalates in conducting polymers led to the development of a new class of electroactive hybrids which resulted in a new concept material for application in electrochemical supercapacitors [52, 62]. Figure 3 shows the electrochemical performance of a solid-state, symmetrical supercapacitor cell based on the hybrid $PMo_{12}O_{40}$/PAni as active electrode. The main data show the evolution of capacitance upon cycling (up to 120 F/g), whereas the inset shows how the electroactivity of both polymer and cluster are used during cycling. The steady increase of capacitance during the first 300 cycles should be commented. This apparent "activation" of the electrode is due to the progressive impregnation of the electrode with the electrolyte [52], which reminds us that the final performance of any supercapacitor material will be optimal only after an optimization of the microstructure which would lead to maximal electrode–electrolyte interface. Whether this optimization was achieved for this particular material is an open question

In addition to inorganic clusters, extended inorganic phases have also been used to synthesise hybrid materials with conducting polymers. The hybrids based on V_2O_5 xerogels and different intercalated conducting polymers (Fig. 1d) were early examples of this type which were studied in detail, with PAni [38, 63, 64], PThi [65] and PPy [66, 67], and later proposed as cathodes for rechargeable lithium batteries [39, 66, 68, 69]. Also, other early candidate oxides for Li batteries, such as MoO_3, were studied as intercalative matrices to form hybrids with PPV [70, 71] and PAni [72, 73]. Finally, inorganic phases such as $LiFePO_4$, which are well established as active cathode materials, can benefit from their integration in hybrid electrodes in combination with conducting polymers [74].

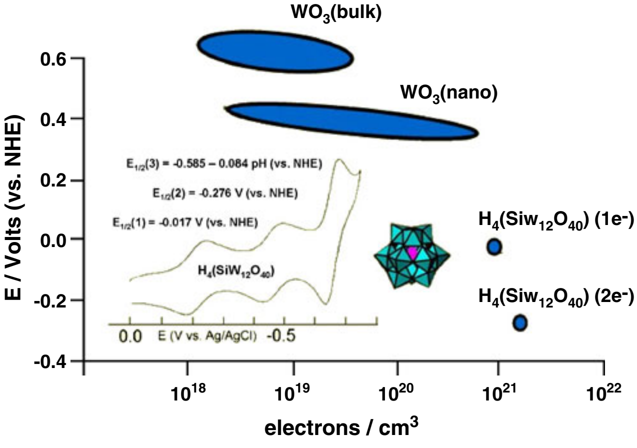

Fig. 2 Reduction potential vs. electron concentration for bulk and nano-WO_3 and for silicotungstate anions reduced with one and two electrons. The figure shows how polyoxometalates constitute the quantum limit (both structurally and functionally) for the corresponding oxides. The *inset* shows a cyclic voltammogram of silicotungstic acid showing the first ($1e^-$), second ($1e^-$) and third ($2e^-$) reduction waves (data from [60, 61]

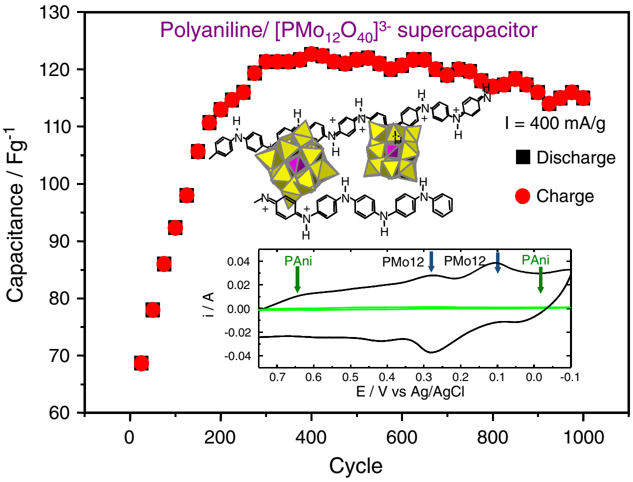

Fig. 3 Capacitance as a function of cycle number for a symmetrical supercapacitor cell with the hybrid PAni/PMo_{12} as electrode material. The *inset* corresponds to a cyclic voltammogram of these electrodes showing the added contributions of the polymer and the inorganic cluster in comparison with plain carbon

The path to complexity As a final section to this brief overview, we would like to mention an emerging contender in the field of hybrid materials and a trend towards complexity. Since their discovery, carbon nanotubes (CNTs) showed great promises with their unique combination of mechanical, electronic and chemical properties. They have been the subject of many reviews, including a recent critical review on their electrochemical properties [75], and soon they were the subject of prospective research to develop hybrid materials containing them, in particular with conducting polymers [76]. With the advent of CNTs as valuable components, the circle of possible hybrid combinations for energy storage is closed with hybrids made with conducting polymers and oxides or polyoxometalate clusters (as described above), with conducting polymers and CNTs [77, 78] and finally with CNTs and electroactive oxides [79] as well as CNTs and polyoxometalates [80].

The path to further complexity is also beginning to be explored. A few examples are electrocatalytic films of conducting polymer/polyoxometallate/Pt nanoparticles grown layer by layer [81, 82], triple hybrid materials integrating conducting polymers, oxides and inorganic molecules [83] or ternary nanocomposites of multi-walled CNTs, PAni and noble metal nanoparticles [84].

Conclusions

We have discussed a few case examples of how to build hybrid electroactive materials with conducting polymers and a wide variety of inorganic compounds, with emphasis on their possible application in energy storage and conversion. But beyond these applications, this brief review has tried to show the importance of exploring novel combinations of dissimilar materials to form more complex systems through simple chemical methods. Challenges are open concerning further control of complex composition, structure, microstructure, as well as fundamental electrochemical properties of materials with combined electronic conduction, electron transfer and varied redox chemistries. Many opportunities remain whilst exploring these fascinating topics or devising new materials based on new building blocks such as graphenes. Working to meet these challenges will certainly not be a child's play. But it will be as fun.

Acknowledgements Funding for some of the work presented here was possible by a grant from the Spanish Ministry of Science and Innovation (MICINN, CTQ2008-06779-C02-01). OA gratefully acknowledges a loan from Al-Quds University. DMR thanks CSIC and the European Social Fund for financing through the I3P Program.

References

1. Gomez-Romero P, Sanchez C (2004) Functional hybrid materials. Wiley-VCH, Weinheim
2. Gomez-Romero P (2001) Hybrid organic–inorganic materials—in search of synergic activity. Adv Mater 13(3):163–174
3. Ruiz-Hitzky E (2003) Functionalizing inorgnic solids: towards organic–inorganic nanostructured materials for intelligent and bioinspired systems. Chem Rec 3(2):88–100
4. Ruiz-Hitzky ER, Darder M, Aranda P (2005) Functional biopolymer nanocomposites based on layered solids. J Mater Chem 15(35–36): 3650–3662
5. Pomogailo AD (2005) Hybrid intercalative nanocomposites. Inorg Mater 41:S47–S74
6. Pomogailo AD (2006) Synthesis and intercalation chemistry of hybrid organo-inorganic nanocomposites. Polym Sci Ser C+ 48:85–111
7. Shea KJ, Loy DA (2001) A mechanistic investigation of gelation. The sol–gel polymerization of precursors to bridged polysilsesquioxanes Acc. Chem Res 34(9):707–716
8. Ogoshi T, Chujo Y (2005) Organic–inorganic polymer hybrids prepared by the sol–gel method. Compos Interface 11(8–9):539–566
9. Yoshida T, Zhang JB, Komatsu D, Sawatani S, Minoura H, Pauporte T, Lincot D, Oekermann T, Schlettwein D, Tada H, Wohrle D, Funabiki K, Matsui M, Miura H, Yanagi H (2009) Electrodeposition of inorganic/organic hybrid thin films. Adv Funct Mater 19(1):17–43
10. Althues H, Henle J, Kaskel S (2007) Functional inorganic nanofillers for transparent polymers. Chem Soc Rev 36(9):1454–1465
11. Sanchez C, Julian B, Belleville P, Popall M (2005) Applications of hybrid organic–inorganic nanocomposites. J Mater Chem 15(35–36): 3559–3592
12. Malinauskas A, Malinauskiene J, Ramanavicius A (2005) Conducting polymer-based nanostructurized materials: electrochemical aspects. Nanotechnology 16(10):R51–R62
13. Binnemans K (2009) Lanthanide-based luminescent hybrid materials. Chem Rev 109(9):4283–4374
14. Guo XM, Guo HD, Fu LS, Carlos LD, Ferreira RAS, Sun LN, Deng RP, Zhang HJ (2009) Novel near-infrared luminescent hybrid materials covalently linking with lanthanide [Nd(III), Er (III), Yb(III), and Sm(III)] complexes via a primary beta-diketone ligand: synthesis and photophysical studies. J Phys Chem C 113 (28):12538–12545
15. Cunha-Silva L, Lima S, Ananias D, Silva P, Mafra L, Carlos LD, Pillinger M, Valente AA, Paz FAA, Rocha J (2009) Multi-functional rare-earth hybrid layered networks: photoluminescence and catalysis studies. J Mater Chem 19(17):2618–2632
16. He T, Yao JN (2006) Photochromism in composite and hybrid materials based on transition-metal oxides and polyoxometalates. Prog Mater Sci 51(6):810–879
17. Hatchett DW, Josowicz M (2008) Composites of intrinsically conducting polymers as sensing nanomaterials. Chem Rev 108 (2):746–769
18. Rajesh, Ahuja T, Kumar D (2009) Recent progress in the development of nano-structured conducting polymers/nanocomposites for sensor applications. Sensor Actuat B-Chem 136(1):275–286
19. Holder E, Tessler N, Rogach AL (2008) Hybrid nanocomposite materials with organic and inorganic components for opto-electronic devices. J Mater Chem 18(10):1064–1078
20. Guenes S, Sariciftci NS (2008) Hybrid solar cells. Inorg Chim Acta 361(3):581–588
21. Asensio JA, Gomez-Romero P (2005) Recent developments on proton conducting poly(2,5-benzimidazole) (ABPBI) membranes for high temperature polymer electrolyte membrane fuel cells. Fuel Cells 5(3):336–343
22. Herring AM (2006) Inorganic–polymer composite membranes for proton exchange membrane fuel cells. Polym Rev 46(3):245–296
23. Jones DJ, Roziere J (2008) Advances in the development of inorganic–organic membranes for fuel cell applications. Fuel Cells I 215:219–264
24. Kundu PP, Sharma V, Shul YG (2007) Composites of proton-conducting polymer electrolyte membrane in direct methanol fuel cells. Crit Rev Solid State 32(1–2):51–66
25. Muñoz-Rojas D, Oro-Sole J, Ayyad O, Gomez-Romero P (2008) Facile one-pot synthesis of self-assembled silver@polypyrrole core/shell nanosnakes. Small 4(9):1301–1306
26. Muñoz-Rojas D, Oro-Sole J, Gomez-Romero P (2009) Spontaneous self-assembly of Cu_2O@PPy nanowires and anisotropic crystals. Chem Commun 39:5913–5915
27. Ayyad O, Muñoz-Rojas D, Oró-Solé J, Gómez-Romero P (2010) From silver nanoparticles to nanostructures through matrix chemistry. J Nanopart Res 12:337–345
28. Shu JH, Qiu W, Zheng SQ (2009) Polyaniline/gold nanoparticle composites. Prog Chem 21(5):1015–1022
29. Reddy KR, Lee KP, Lee Y, Gopalan AI (2008) Facile synthesis of conducting polymer–metal hybrid nanocomposite by in situ chemical oxidative polymerization with negatively charged metal nanoparticles. Mater Lett 62(12–13):1815–1818
30. Pacios R, Marcilla R, Pozo-Gonzalo C, Pomposo JA, Grande H, Aizpurua J, Mecerreyes D (2007) Combined electrochromic and plasmonic optical responses in conducting polymer/metal nano-particle films. J Nanosci Nanotechnol 7(8):2938–2941
31. Li WG, Jia QX, Wang HL (2006) Facile synthesis of metal nanoparticles using conducting polymer colloids. Polymer 47 (1):23–26
32. Pillalamarri SK, Blum FD, Tokuhiro AT, Bertino MF (2005) One-pot synthesis of polyaniline—metal nanocomposites. Chem Mater 17(24):5941–5944

33. Vasilyeva SV, Vorotyntsev MA, Bezverkhyy I, Lesniewska E, Heintz O, Chassagnon R (2008) Synthesis and characterization of palladium nanoparticle/polypyrrole composites. J Phys Chem C 112(50):19878–19885
34. Xing SX, Tan LH, Yang MX, Pan M, Lv YB, Tang QH, Yang YH, Chen HY (2009) Highly controlled core/shell structures: tunable conductive polymer shells on gold nanoparticles and nanochains. J Mater Chem 19(20):3286–3291
35. Guo RR, Li GT, Zhang WX, Shen GQ, Shen DZ (2005) Superlong polypyrrole nanowires aligned within ordered mesoporous silica channels. Chemphyschem 6(10):2025–2028
36. Dong JP, Hu YY, Xu JQ, Qu XM, Zhao CJ (2009) Nanocomposite with polypyrrole encapsulated within SBA-15 mesoporous silica: preparation and its electrochemical application. Electroanal 21 (16):1792–1798
37. Fang FF, Choi HJ, Ahn WS (2009) Electroactive response of mesoporous silica and its nanocomposites with conducting polymers. Compos Sci Technol 69(13):2088–2092
38. Lira-Cantu M, Gomez-Romero P (1999) Synthesis and characterization of intercalate phases in the organic–inorganic polyaniline/V_2O_5 system. J Solid State Chem 147(2):601–608
39. Lira-Cantu M, Gomez-Romero P (1999) The organic–inorganic polyaniline/V_2O_5 system—application as a high-capacity hybrid cathode for rechargeable lithium batteries. J Electrochem Soc 146 (6):2029–2033
40. Kulesza PJ, Miecznikowski K, Chojak M, Malik MA, Zamponi S, Marassi R (2001) Electrochromic features of hybrid films composed of polyaniline and metal hexacyanoferrate. Electrochim Acta 46(28):4371–4378
41. Kulesza PJ, Miecznikowski K, Malik MA, Galkowski M, Chojak M, Caban K, Wieckowski A (2001) Electrochemical preparation and characterization of hybrid films composed of Prussian blue type metal hexacyanoferrate and conducting polymer. Electrochim Acta 46(26–27):4065–4073
42. Ernst A, Makowski O, Kowalewska B, Miecznikowski K, Kulesza PJ (2007) Hybrid bioelectrocatalyst for hydrogen peroxide reduction: immobilization of enzyme within organic–inorganic film of structured Prussian Blue and PEDOT. Bioelectrochemistry 71(1):23–28
43. Makowski O, Kowalewska B, Szymanska D, Stroka J, Miecznikowski K, Palys B, Malik MA, Kulesza PJ (2007) Controlled fabrication of multilayered 4-(pyrrole-1-yl) benzoate supported poly(3,4-ethylenedioxythiophene) linked hybrid films of Prussian blue type nickel hexacyanoferrate. Electrochim Acta 53 (3):1235–1243
44. Gomez-Romero P, LiraCantu M (1997) Hybrid organic–inorganic electrodes: the molecular material formed between polypyrrole and the phosphomolybdate anion. Adv Mater 9(2):144–147
45. Lira-Cantu M, Gomez-Romero P (1998) Electrochemical and chemical syntheses of the hybrid organic–inorganic electroactive material formed by phosphomolybdate and polyaniline. Application as cation-insertion electrodes. Chem Mater 10(3):698–704
46. Kulesza PJ, Chojak M, Miecznikowski K, Lewera A, Malik MA, Kuhn A (2002) Polyoxometallates as inorganic templates for monolayers and multilayers of ultrathin polyaniline. Electrochem Commun 4(6):510–515
47. Adamczyk L, Kulesza PJ, Miecnikowski K, Palys B, Chojak M, Krawczyk D (2005) Effective charge transport in poly(3,4-ethylenedioxythiophene) based hybrid films containing polyoxometallate redox centers. J Electrochem Soc 152(3):E98–E103
48. Vaillant J, Lira-Cantu M, Cuentas-Gallegos K, Casañ-Pastor N, Gomez-Romero P (2006) Chemical synthesis of hybrid materials based on PAni and PEDOT with polyoxometalates for electrochemical supercapacitors. Prog Solid State Chem 34(2–4):147–159
49. Torres-Gomez G, Gomez-Romero P (1998) Conducting organic polymers with electroactive dopants. Synthesis and electrochemical properties of hexacyanoferrate-doped polypyrrole. Synth Met 98(2):95–102
50. Gomez-Romero P, Torres-Gomez G (2000) Molecular batteries: harnessing Fe(CN)(6)(3-) electroactivity in hybrid polyaniline–hexacyanoferrate electrodes. Adv Mater 12(19):1454–1456
51. Peng ZH (2004) Rational synthesis of covalently bonded organic–inorganic hybrids. Angew Chem Int Edit 43(8):930–935
52. Gomez-Romero P, Chojak M, Cuentas-Gallegos K, Asensio JA, Kulesza PJ, Casañ-Pastor N, Lira-Cantu M (2003) Hybrid organic–inorganic nanocomposite materials for application in solid state electrochemical supercapacitors. Electrochem Commun 5(2):149–153
53. Kamat PV (2007) Meeting the clean energy demand: nanostructure architectures for solar energy conversion. J Phys Chem C 111(7):2834–2860
54. Nguyen TP, Lee CW, Hassen S et al (2009) Hybrid nanocomposites for optical applications. Solid State Sci 11(10):18010–14
55. Conway BE (1991) Transition from supercapacitor to battery behavior in electrochemical energy-storage. J Electrochem Soc 138(6):1539–1548
56. Miller JM, Dunn B, Tran TD, Pekala RW (1997) Deposition of ruthenium nanoparticles on carbon aerogels for high energy density supercapacitor electrodes. J Electrochem Soc 144(12): L309–L311
57. Subramanian V, Zhu HW, Vajtai R, Ajayan PM, Wei BQ (2005) Hydrothermal synthesis and pseudocapacitance properties of MnO_2 nanostructures. J Phys Chem B 109(43):20207–20214
58. Rudge A, Raistrick I, Gottesfeld S, Ferraris JP (1994) A study of the electrochemical properties of conducting polymers for application in electrochemical capacitors. Electrochim Acta 39 (2):273–287
59. Frackowiak E, Beguin F (2002) Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. Carbon 40 (10):1775–1787
60. GomezRomero P, CasanPastor N (1996) Photoredox chemistry in oxide clusters. Photochromic and redox properties of polyoxometalates in connection with analog solid state colloidal systems. J Phys Chem 100(30):12448–12454
61. Gomez-Romero P (1997) Polyoxometalates as photoelectrochemical models for quantum-sized colloidal semiconducting oxides. Solid State Ionics 101:243–248
62. Cuentas-Gallegos AK, Lira-Cantu M, Casañ-Pastor N, Gomez-Romero P (2005) Nanocomposite hybrid molecular materials for application in solid-state electrochemical supercapacitors. Adv Funct Mater 15(7):1125–1133
63. Kanatzidis MG, Wu CG, Marcy HO, Kannewurf CR (1989) Conductive polymer bronzes—intercalated polyaniline in V_2O_5 xerogels. J Am Chem Soc 111(11):4139–4141
64. Liu YJ, Degroot DC, Schindler JL, Kannewurf CR, Kanatzidis MG (1993) Stabilization of anilinium in vanadium(V) oxide xerogel and its post-intercalative polymerization to poly(aniline) in air. Chem Commun (7):593–596
65. Kanatzidis MG, Wu CG, Marcy HO, Degroot DC, Kannewurf CR (1990) Conductive polymer–oxide bronze nanocomposites–intercalated polythiophene in V_2O_5 xerogels. Chem Mater 2 (3):222–224
66. Goward GR, Leroux F, Nazar LF (1998) Poly(pyrrole) and poly (thiophene)/vanadium oxide interleaved nanocomposites: positive electrodes for lithium batteries. Electrochim Acta 43(10–11): 1307–1313
67. Wong HP, Dave BC, Leroux F, Harreld J, Dunn B, Nazar LF (1998) Synthesis and characterization of polypyrrole vanadium pentoxide nanocomposite aerogels. J Mater Chem 8(4):1019–1027

68. Boyano I, Bengoechea M, de Meatza I, Miguel O, Cantero I, Ochoteco E, Grande H, Lira-Cantu M, Gomez-Romero P (2007) Influence of acids in the Ppy/V_2O_5 hybrid synthesis and performance as a cathode material. J Power Sources 174(2):1206–1211
69. Boyano I, Bengoechea M, de Meatza I, Miguel O, Cantero I, Ochoteco E, Rodriguez J, Lira-Cantu M, Gomez-Romero P (2007) Improvement in the Ppy/V_2O_5 hybrid as a cathode material for Li ion batteries using PSA as an organic additive. J Power Sources 166(2):471–477
70. Nazar LF, Zhang Z, Zinkweg D (1992) Insertion of poly(*para*-phenylenevinylene) in layered MoO_3. J Am Chem Soc 114 (15):6239–6240
71. Kerr TA, Leroux F, Nazar LF (1998) Surfactant-mediated incorporation of poly(*p*-phenylene) into MoO_3. Chem Mater 10 (10):2588–2591
72. Bissessur R, Degroot DC, Schindler JL, Kannewurf CR, Kanatzidis MG (1993) Inclusion of poly(aniline) into MoO_3. Chem Commun (8):687–689
73. Kerr TA, Wu H, Nazar LF (1996) Concurrent polymerization and insertion of aniline in molybdenum trioxide: formation and properties of a [poly(aniline)]0.24MoO_3 nanocomposite. Chem Mater 8(8):2005–2015
74. Fedorková A, Nacher-Alejos A, Gómez-Romero P, Oriňáková R, Kaniansky D (2010) Structural and electrochemical studies of PPy/PEG-$LiFePO_4$ cathode material for Li-ion batteries. Electrochim Acta 55(3):943–947
75. Dumitrescu I, Unwin PR, Macpherson JV (2009) Electrochemistry at carbon nanotubes: perspective and issues. Chem Commun (45):6886–6901
76. Baibarac M, Gomez-Romero P (2006) Nanocomposites based on conducting polymers and carbon nanotubes: from fancy materials to functional applications. J Nanosci Nanotechnol 6(2):289–302
77. Baibarac M, Lira-Cantu M, Oro-Sole J, Casañ-Pastor N, Gomez-Romero P (2006) Electrochemically functionalized carbon nanotubes and their application to rechargeable lithium batteries. Small 2(8–9):1075–1082
78. Baibarac M, Gomez-Romero P, Lira-Cantu M, Casañ-Pastor N, Mestres N, Lefrant S (2006) Electrosynthesis of the poly(*N*-vinyl carbazole)/carbon nanotubes composite for applications in the supercapacitors field. Eur Polym J 42:2302–2312
79. Chen Z, Qin YC, Weng D, Xiao QF, Peng YT, Wang XL, Li HX, Wei F, Lu YF (2009) Design and synthesis of hierarchical nanowire composites for electrochemical energy storage. Adv Funct Mater 19(21):3420–3426
80. Cuentas-Gallegos A, Martinez-Rosales R, Baibarac M, Gomez-Romero P, Rincon ME (2007) Electrochemical supercapacitors based on novel hybrid materials made of carbon nanotubes and polyoxometalates. Electrochem Commun 9(8):2088–2092
81. Kulesza PJ, Chojak M, Karnicka K, Miecznikowski K, Palys B, Lewera A, Wieckowski A (2004) Network films composed of conducting polymer-linked and polyoxometalate-stabilized platinum nanoparticles. Chem Mater 16(21):4128–4134
82. Kulesza PJ, Karnicka K, Miecznikowski K, Chojak M, Kolary A, Barczuk PJ, Tsirlina G, Czerwinski W (2005) Network electrocatalytic films of conducting polymer-linked polyoxometallate-stabilized platinum nanoparticles. Electrochim Acta 50 (25–26):5155–5162
83. Cuentas-Gallegos AK, Gomez-Romero P (2006) Triple hybrid materials: a novel concept within the field of organic–inorganic hybrids. J Power Sources 161(1):580–586
84. Sapurina I, Stejskal J (2009) Ternary composites of multi-wall carbon nanotubes, polyaniline, and noble-metal nanoparticles for potential applications in electrocatalysis. Chem Pap 63 (5):579–585