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Review Article

Tailored organic–inorganic hybrid systems for energy, environment, and beyond

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ABSTRACT

Organic-inorganic hybrid materials are a class of advanced materials paramounting towards sustainable development. They are revolutionary materials comprehending the synergistic properties of the constituents, which is crucial in their development. Nanostructured conducting polymer metal oxide/mixed metal oxide hybrid composites (NCPMMOS) are receiving increased research attention in recent years owing to their potential applications in fields of energy storage and conversion, environmental remediation, catalysis, sensors, actuators, flexible electronics etc., empowering sustainability across different sectors. In energy storage, NCPMMOS are utilized in supercapacitors and batteries due to their high capacitance, energy density, and cyclic stability. Presence of conducting polymer in NCPMMOS contributes towards processability, light weight, flexibility, and low cost, whereas the metal oxide can augment optoelectronic, chemical, and thermo-mechanical properties. This review article comprehends the recent developments in the field of NCPMMOS of conducting polymers, various design strategies, synthetic aspects, fundamental properties and applications. By harnessing the power of conducting polymers and inorganic nanomaterials, NCPMMOS pave the way for innovative solutions to global challenges, contributing to a more sustainable future.

1. Introduction

Nanostructured conducting polymer metal oxide/mixed metal oxide hybrid composites (NCPMMOS) are receiving lots of attraction in recent years due to its fascinating multifunctional properties such as opto-electronic, thermo mechanical and so forth. They find potential applications in various fields such as energy storage devices, photocatalysis, etc. They possess combined advantages of inorganic fillers (e.g., metal oxides, metal nanoparticles, and layered materials) and organic polymeric matrix (e.g., conjugated oligomers and polymers). Recently researchers have taken significant efforts towards enhancing the properties of these nanocomposites by accomplishing excellent percolation of multifunctional inorganic nanoparticles within the polymer matrix [1]. The percolation results in an intimate contact between matrix and filler, which may help to increase the interfacial area between the two phases and allows a controlled distribution of the filler within the matrix. The interaction of the components in the nanolevel results in materials with improved self-organization, ordered structure, crystallinity, and well-defined morphologies. Functionalizing and stabilizing inorganic component with organic conducting polymers can emphasize sustainability, induce chemical changes, and enhance physico-chemical properties, broadening their applications.

Moreover, NCPMMOS were endowed with enhanced electrical conductivity, dielectric properties, thermomechanical

properties. They play a crucial role in the development of advanced functional materials which are expected to revolutionize the emerging field of technologies such as EMI shielding, photovoltaics, supercapacitors, photocatalysts, sensors and so forth. They possess synergetic properties of inorganic particles and organic conducting polymeric counterparts. The interpenetration of the two phases on the nanoscale can yield advanced performances compared to their constituent phases. It has been reported that a large number of various metal and metal oxide nanoparticles such as Pt, Pd, TiO₂, V₂O₅, MnO₂, SiO₂, Fe₂O₃, Fe₃O₄ can be encapsulated into the core of conducting polymers to give multifunctional polymeric-inorganic hybrid composites which may exhibit excellent optical, electronic and thermo-mechanical properties, dimensional stability, optical clarity and other related functional properties. In nano composites barrier properties may undergo substantial improvements which include decreased permeability to gases, water and hydrocarbons, and chemical resistance when compared with the virgin polymer.

2. Nanostructured conducting polymer metal oxide/mixed metal oxide hybrid composites (NCPMMOS)

Inorganic metal oxide/mixed metal oxide of different size and shape can be combined with the conducting polymers



giving rise to nanocomposites with interesting functional properties and important application potential. The matrix and filler in the composites are held together by either weak forces, such as vander Waals or hydrogen bonding interactions or strong covalent bonds. The organization of them in nanoscale will help to tailor the optoelectronic behaviors of the material, other related functional properties.

Current research is dedicated to further refining the design, processing, and dispersion of these nanocomposites to fully harness their potential in diverse technological applications. The ongoing exploration of hybrid nanocomposites is leading to revolutionary progress in a broad spectrum of technological arenas. NCPMMOS can be prepared through both ex-situ and in-situ synthetic methods.

In ex-situ synthesis, conducting polymer and inorganic species are synthesized separately, and the blending of them results in composites in which interfacial interaction between the two components determines their properties. Here the two components are prepared by the well-established synthetic procedures, and for the blending process, there are various robust strategies ranging from effortless methods such as mechanical mixing of the two components to more sophisticated techniques such as ligand exchange or layer-by-layer fabrication procedures. In in-situ strategy, the conducting polymer is synthesized by the in-situ polymerization of the

monomer in the presence of the inorganic nanostructures. However, the alternative sequence is also possible; namely, the inorganic component is generated in situ inside the NCP, either through chemical or electrochemical methods.

3. Polymer-metal nanocomposites

Polymer-metal nanocomposite systems comprising nanoparticles of metals or metal oxides like Au, Ag, Pd, TiO₂, ferrites, Ni, V₂O₅ etc and polymers are receiving considerable research attention, since they can be tailored to exhibit novel electrical, magnetic and optical properties along with right film-forming property and mechanical stability. Pt, Cu, Zn, Cu₂O, and CdS have been successfully fabricated on CP surfaces or embedded in CP matrices through the electrodeposition technique. Here MNPs can be directly synthesized through a conjugated polymer (CP) mediated method utilizing the redox chemistry of CPs to chemically reduce the metal ions and modulate the size, morphology, and structure of the MNPs. The as-prepared multifunctional CP-MNP nanocomposites have shown application potentials in surface-enhanced Raman spectroscopy (SERS) substrates, active heterogeneous catalysts, and critical components for electronic and sensing devices.

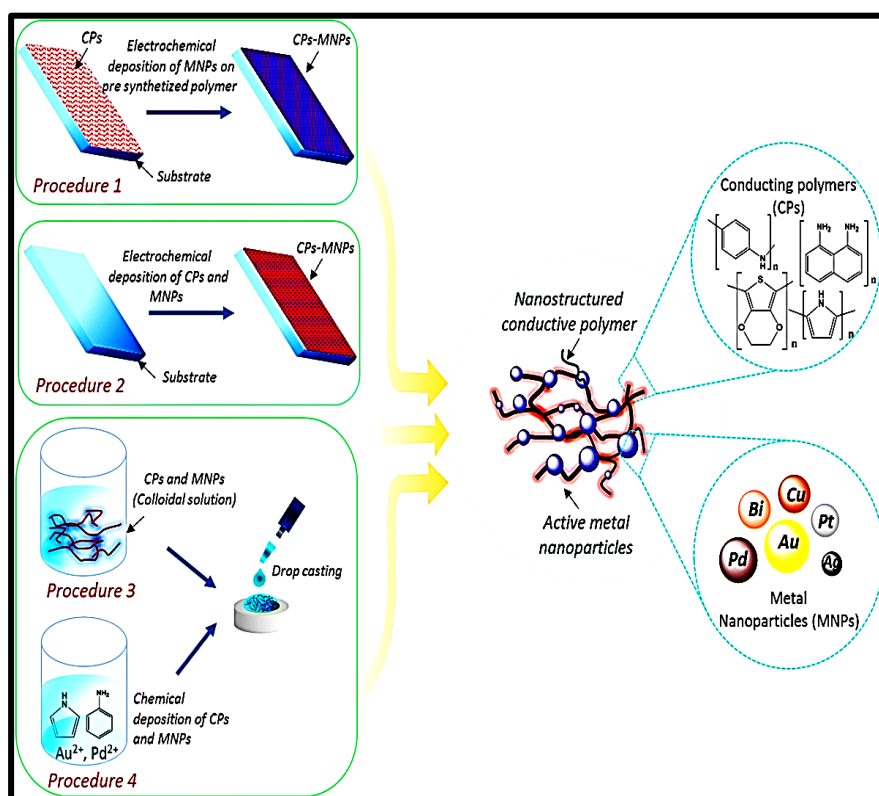


Figure 1: Synthetic methods for NCP-Metal Hybrid Composites (Rhazi et al., 2018).

A metal ion having enhanced reduction potential than a CP can be spontaneously reduced by the CP to form zero-valent metal. Electron transfer from CP to metal ions also results in the oxidation of CP to a higher oxidation state. This

synthetic platform utilizes the CP as both the template and reducing agent, without the involvement of any other organic solvents and reducing agents.

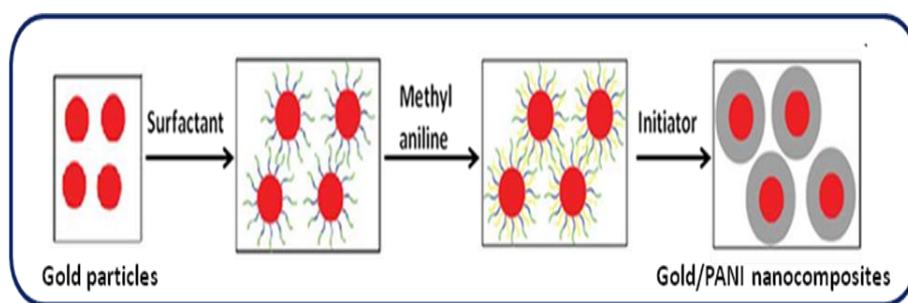


Figure 2: Schematic representation for the preparation of gold/PANI nanocomposites (Han et al., 2010).

Han et al. in 2010 [2] described a versatile two-step method for the preparation of gold/PANI core/shell nanocomposites with the aid of a nonionic surfactant as represented in Figure 2. Initially, the surfactant and monomer were introduced to gold colloids followed by the addition of oxidant to initiate the polymerization to create an ICP shell around each gold nanoparticle. These composites are becoming the research focus not only from fundamental scientific interest but also from practical applications like in plastic digital memory.

4. Polymer- metal oxide nano composites

Conducting polymer/metal oxide nanocomposites are a burgeoning class of hybrid materials that offer a wide array of applications in optoelectronic devices, supercapacitors, sensors, and more [3, 4]. These composites combine the advantages of conducting polymers, such as ease of processing, with the high specific capacitance and variable oxidation states of metal oxides [5]. Research has shown that incorporating nanostructured materials like carbon derivatives, metal oxides, and MXene into conducting polymers enhances their electrochemical performance significantly [6]. The fabrication of conductive polymer/metal oxide composite nanostructures, such as nanofibers and nanotubes, has paved the way for innovative applications in energy, electronics, healthcare, and environmental sectors [7]. Despite these advancements, there are still research gaps in optimizing the synthesis methods, understanding the long-term stability, and exploring novel applications for these nanocomposites, presenting opportunities for further research and development in this field.

5. Applications of Electrically conductive hybrid nanocomposites (ECNHCs)

(a) Energy storage

Metal oxide composites, such as MnO_2 , SnO_2 , titanium dioxide (TiO_2), and cadmium oxide (CdO), have shown promising results for supercapacitor applications. These composites exhibit enhanced electrochemical performance, including high specific capacitance, good cyclic stability, and improved energy density. The incorporation of metal oxides promotes faradaic capacitance, while PANI provides pseudocapacitance and redox reactions, leading to improved overall performance [8, 9, 10]. Additionally, the development of PANI composites with graphene oxide (GO) has demonstrated high specific capacitance, energy density, and power density, making them suitable for energy storage devices [11]. The utilization of PANI-based materials in supercapacitor electrodes, especially in nanocomposites with carbon materials or metal compounds, has shown significant advancements in achieving higher electrochemical

performance, addressing the limitations of pure PANI electrodes [12].

Polyaniline (PANI) mixed with metal oxide composites, such as MnO_2 , SnO_2 , titanium dioxide (TiO_2), and cadmium oxide (CdO), have shown promising results for supercapacitor applications. [13] These composites exhibit enhanced electrochemical performance, including high specific capacitance, good cyclic stability, and improved energy density. The incorporation of metal oxide promotes faradaic capacitance, while PANI provides pseudocapacitance and redox reactions, leading to improved overall performance. Additionally, the development of PANI composites with graphene oxide (GO) has demonstrated high specific capacitance, energy density, and power density, making them suitable for energy storage devices. The utilization of PANI-based materials in supercapacitor electrodes, especially in nanocomposites with carbon materials or metal compounds, has shown significant advancements in achieving higher electrochemical performance, addressing the limitations of pure PANI electrodes. The continuous research and development in supercapacitor technology are paving the way for more efficient and powerful energy storage solutions. The continuous innovation in supercapacitor technology is driving the evolution towards more efficient and powerful energy storage solutions, revolutionizing the field of energy AC supercapacitor with enhanced performance.

Metal oxide nanostructures coated with polyaniline, utilized in asymmetric supercapacitors, exhibit enhanced capacity owing to the combined effects of double-layer capacitance, pseudocapacitance, and redox reactions. [14] Polyaniline-wrapped metal oxide nanostructures used in asymmetric supercapacitors. Higher capacity due to double-layer capacitance, pseudocapacitance, and redox reaction. Synthesized polyaniline-wrapped metal oxide/organic framework-derived carbon ternary composites. Achieved high capacities, stable performance, and powering LED with 4.4V.

High capacity electrodes for asymmetric supercapacitors long cycle life and ability to power electronic devices efficiently Polyaniline-wrapped metal oxide nanostructures used in asymmetric supercapacitors. [15] Higher capacity due to double-layer capacitance, pseudocapacitance, and redox reaction. Double-layer capacitance from NC - Pseudocapacitance from polyaniline, redox reaction of metal oxides Polyaniline-wrapped metal oxide/organic framework-derived carbon composites show high capacitance. The asymmetric supercapacitor achieved a specific energy of 36-41 Wh kg^{-1} . Lack of comparison with other similar composite materials. Need for further investigation into long-term stability and scalability.

The PANI@ TiO_2 -CuO ternary composite demonstrates improved performance as a supercapacitor. A straightforward

synthesis method offers enhanced charge storage capabilities. The study involves the fabrication and evaluation of a PANI@TiO₂-CuO ternary composite. It reveals enhanced electrochemical properties suitable for supercapacitor applications [16]. The research explores hybrid material composites for their potential applications. Incorporation of metal oxide nanoparticles enhances environmental stability. The PANI@TiO₂-CuO ternary composite exhibits increased capacitance and stability. Uniform dispersion of TiO₂-CuO within the PANI matrix significantly improves its properties. Optimization of ternary nanocomposite synthesis is needed for better supercapacitor performance. Further studies are required on the long-term stability and scalability of the electrodes.

Synthesis of PANI-NiO nanocomposites for supercapacitor applications. PANI-NiO³ demonstrated a specific capacitance of 623 Fg⁻¹. Synthesis of nickel oxide and polyaniline nanocomposites for supercapacitor applications. PANI-NiO³ showed a specific capacitance of 623 Fg⁻¹ at a current density of 1 Ag⁻¹. Nickel oxide-enhanced polyaniline nanocomposites are potential electrode materials for supercapacitors. PANI-NiO nanocomposites show high specific capacitance and cyclic stability. There is a lack of comparative analysis with other supercapacitor electrode materials. There is no detailed discussion on the scalability and commercial viability.

Polyaniline/graphene oxide composite used for supercapacitors in study. - No mention of polyaniline mixed metal oxide composite in study [17]. PANi/GO composites synthesized for supercapacitor electrodes with high capacitance. - PANi/GO suitable for energy storage devices application. PANi/GO composites suitable for energy storage devices application - High capacitance retention of about 76.96% after 5000 cycles PANi/GO composites for supercapacitor electrodes - High capacitance retention, suitable for energy storage devices application PANi/GO composites suitable for energy storage devices application. - PANi/GO exhibited high capacitance retention after 5000 cycles. The study highlights the effectiveness of PANi/GO composites for energy storage devices due to their high capacitance retention even after 5000 cycles.

PANI-based materials for supercapacitor electrodes reviewed for enhanced performance. - Nanocomposites of PANI with carbon or metal compounds improve performance. Enhanced energy storage with PANI-based nanocomposites - Improved performance in supercapacitors for sustainable energy solutions Nanocomposites of PANI with carbon or metal compounds improve performance. - Evaluation based on capacitance, energy, power, cycle performance, and rate capability. PANI with carbon or metal dopants enhances electrochemical performance. - Nanocomposites show improved capacitance, power, and cycle performance. Pure PANI electrodes have drawbacks in cycle life, power density. Nanocomposites of PANI with carbon or metal compounds show promise [18]. The research highlights the potential of nanocomposites to address the limitations of pure PANI electrodes in cycle life and power density. Nanocomposites offer a promising solution to enhance the cycle life and power density of pure PANI electrodes in supercapacitors for sustainable energy applications. The study underscores the significant potential of nanocomposites in overcoming the limitations of pure PANI electrodes for improved cycle life and power density in supercapacitors, paving the way for sustainable energy applications. Nanocomposites present a

viaable strategy for improving the performance of pure PANI electrodes in supercapacitors, offering enhanced cycle life and power density for sustainable energy applications. The innovative use of nanocomposites demonstrates a breakthrough in enhancing the efficiency of PANI electrodes for sustainable energy storage solutions. Utilizing nanocomposites in supercapacitors showcases a pioneering approach to boosting the efficiency and sustainability of energy storage solutions. The integration of nanocomposites in supercapacitors represents a cutting-edge advancement towards enhancing energy storage efficiency and sustainability. Implementing nanocomposites in supercapacitors not only enhances energy storage efficiency but also propels sustainable energy solutions to new heights. The integration of nanocomposites in supercapacitors is paving the way for a more sustainable future in energy storage technologies. The evolution of nanocomposites in supercapacitors heralds a promising future for sustainable energy storage innovations. The continuous development of nanocomposites in supercapacitors is revolutionizing the landscape of sustainable energy storage technologies. The ongoing progress in nanocomposites for supercapacitors is reshaping the landscape of sustainable energy storage technologies, promising a brighter future for efficient energy solutions. The innovative use of nanocomposites in supercapacitors is revolutionizing the field of sustainable energy storage, offering a glimpse into a future powered by efficient energy solutions. The advancement of nanocomposites in supercapacitors is propelling the energy storage industry towards a greener and more efficient tomorrow. The integration of nanocomposites in supercapacitors is paving the way for a more sustainable and efficient energy storage landscape.

(b) Catalysis

Photocatalysts are materials which utilize light energy and convert it to chemical energy through a series of electronic processes and surface reactions. The key to the success of photocatalyst is the development of high-performance materials having well matched photo absorption with the solar spectrum, an efficient photoexcited charge separation to prevent electron-hole recombination and an adequate energy of charges that carry out the desired chemical reactions. Semiconductor photo-catalysts such as TiO₂ and ZnO are the mostly studied photocatalysts because of their good stability, low cost, band gap and non-toxicity. However, the applications of these metal oxides are limited because of weakly absorb visible light and can only collect UV light owing to a large band gap (3.20 eV). Additionally, high recombination efficiency of the photogenerated electron-hole pairs also results in poor photocatalytic property.

The catalytic reduction with heterogeneous catalysts has received much attention due to its easy operation, high efficiency, simple processing, and low cost. The catalytic reduction and decoloration of dye pollutants and the conversion of aromatic nitro compounds to beneficial amino counterparts have been widely reported. The metal-based reductions highly depend on noble metals such as silver, gold, palladium, platinum. Electrocatalysis has the strength to be one of the ways we can use renewable energy to produce fuels for heavy transport and air travel, chemicals for fertilizers, and molecules to be used in the production of plastics.

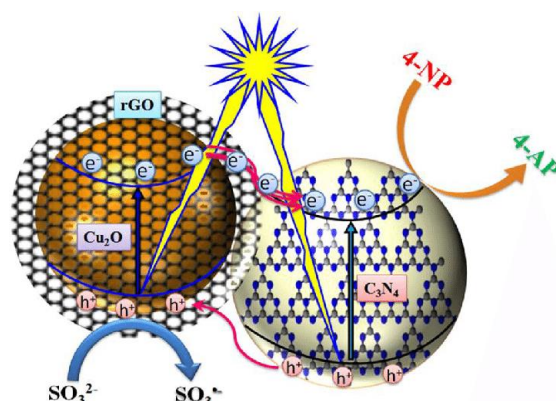


Figure 3: Photocatalytic reduction of p nitrophenol by Cu₂O–rGO– C₃N₄ photocatalyst (Zhang et al., 2010).

Zhang and coworkers reported a novel process for the synthesis of Cu₂O–rGO– C₃N₄ composites by polymerization of aniline in the presence of Cu₂O–rGO– C₃N₄ nanoparticles. These functional nanocomposites exhibited enhanced visible light photocatalytic activity and excellent antiphotocorrosion performance of Cu₂O–rGO– C₃N₄ (Figure 3). This new cadmium sulphide based photocatalysts invoke tremendous hope in solving the serious environmental and energy challenges.

(c) Water purification

Metal oxide-based organic hybrid composites have emerged as promising materials for water purification due to their high permeability, specific surface area, and photocatalytic efficiency in degrading organic pollutants. These composites offer advantages such as lightweight design, mechanical strength, and antifouling properties, making them effective in wastewater treatment processes. Additionally, the incorporation of metal oxide nanoparticles into polymer nanofibers enhances their water purification capabilities, especially in removing hazardous contaminants from water sources. Furthermore, the development of metal-organic frameworks (MOFs) as composites in photocatalytic water purification has shown potential, although challenges like weak water stability and low reutilization rates need to be addressed for wider environmental remediation applications. Overall, metal oxide organic hybrid composites represent a cutting-edge solution for efficient water treatment processes, combining the advantages of both metal oxides and organic materials for enhanced purification performance. Moreover, the continuous research and innovation in nanotechnology hold promise for further advancements in water treatment technologies, paving the way for more sustainable and effective solutions in addressing water pollution challenges. Nanotechnology research continues to drive advancements in water treatment, offering promising solutions for addressing pollution challenges and improving environmental sustainability.

6. Summary and conclusion

Conducting polymer inorganic nanocomposites offer a sustainable alternative to traditional synthetic materials, providing eco-friendly bioactive materials with enhanced opto electronic and photophysical properties. They are endowed with flexibility, processability and high specific capacitance which make them suitable for developing energy storage devices and batteries contributing to sustainable energy

solutions. Conducting polymer mixed metal oxide/metal oxide composites are opening up possibilities for the above-mentioned applications promoting sustainability. Conducting polymer graphene composites have attracted research attention towards water purification and environmental remediation applications. Moreover, utilizing bio-based natural polymers functionalized with nanofillers in conducting polymer nanocomposites can pave the way for advanced eco-friendly products in packaging, tissue engineering, antimicrobial applications, and membrane technology, reducing the environmental impact of petroleum-based plastics. However, the environmental impacts of long-term use of such composites needs further explorations.

Authors' contributions

All authors contributed equally to the conception, design, data analysis, interpretation of results, and preparation of the manuscript. All authors reviewed and approved the final version of the manuscript for publication.

Conflicts of interest

The author declares no conflict of interest.

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Data availability

No new data were created.

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