# Polymeric Composites as Catalysts for Fine Chemistry

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## 1 Introduction

For the past three decades, conjugated polymers (CPs) have been studied intensively ever since the discovery of the conducting polyacetylene (PAc) in 1976 [41]. Among CPs, Polypyrrole (PPy) and polyaniline (PANI) are often studied. Later, a variety of CPs has been developed and extensively used due to their high conductivity, as listed in Table 1. These CPs are normally stable in air, widespread availability, cheap, chemically inert, and can be effectively prepared as a host for incorporating various catalysts which having intriguing properties. New generations of these materials find its application in the various sectors such as chemical sensors, biosensors, energy storage (super capacitors, dielectric capacitors, batteries, solar cells, fuel cells), biomedical devices, optical devices, electromagnetic interference shielding, anticorrosion and antistatic coatings, electro active devices and catalysis.

In recent times, these CPs was recognized as suitable candidate for supporting heterogeneous catalysts (e.g., noble metals) as well as for basic research and practical applications owing to their intrinsic properties, for example, chemical stability, superior electrical conductivity, special optical properties, better carrier mobility, enhanced electrochemical activity, reusability, high accessible surface area, chemical functionalities (like solvation, templating effect, wettability and so on) and bio-compatibility [14, 28]. Most of the catalytic processes which are

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**Table 1** Some reported conducting polymers [1, 12]

| Polymer | Label | Band gap (eV) | Conductivity (S $cm^{-1}$) | Year[a] |
|---|---|---|---|---|
| Polyacetylene | Pac | 1.5 | $10^3$ to $1.7 \times 10^5$ | 1977 |
| Poly(p-phenylene) | PPP | – | 500 | 1979 |
| Poly(p-phenylenevinylene) | PPV | 2.5 | 3 to $5 \times 10^3$ | 1979 |
| Polypyrrole | PPy | 3.1 | $10^2$ to $7.5 \times 10^3$ | 1979 |
| Polyaniline | PAni | 3.2 | 0–200 | 1980 |
| Polythiophene | PT | 2.0 | 10 to $10^3$ | 1981 |
| Polyfurane | PF | – | – | 1981 |

[a] Reported for the first time (in the year) as conducting polymer

followed in industrial applications are found to be so complex because individual catalysts cannot meet the demand in terms of catalytic activity, selectivity and resistance towards deactivation. Hence, the introduction of composite catalyst, which has at least two components clubbed together attracted many researchers [60]. Among composite catalyst, CPs based composites show outstanding performance as an effect of synergistic performance which is derived from individual component anchored on them. Therefore, in this chapter, the applications of polymer composite as a catalyst in wider fields such as fuel cells, cross-coupling reaction, photocatalysis and 4-nitrophenol reduction are discussed briefly.

## 2 Electrocatalytic Activity of Polymer Composite

Low-temperature fuel cells are receiving substantial interest due to an eco-friendly approach of direct electrochemical oxidation of hydrogen/alcohols (mostly, low molecular weight) into either $H_2O$ or $CO_2$ or both, which produces electricity in the fuel cell. For oxidative and reduction reactions in a fuel cell, platinum or platinum catalysts supported on a conductive material are frequently utilized as electrode materials [4, 7]. In those catalysts, the surface to volume ratio of metal particles is very high which promotes the accessible area for the reactions. The cost of fuel cell operation usually relies upon the morphology and dispersal behaviour of these metal particles because they are assumed as a key part in decreasing the loading rate of the catalyst. The main prerequisites of a proper catalyst support to be used in a fuel cell are

(a) appropriate void fractions for supporting gas flow,
(b) high stability during fuel cell working environments,
(c) high surface to volume ratio, for achieving high metal dispersion, and
(d) high specific conductance.

Currently, in low-temperature fuel cells, carbon, specifically Vulcan XC-72 carbon blacks, is usually preferred for supporting electrocatalyst nanoparticles because of its substantial specific conductance and surface area [3]. A primary issue associated with the utilization of carbon blacks as a cathode catalyst support in a fuel cell is their less resistivity towards corrosion due to the electrochemical oxidation of carbon surface. The carbon support instability leads to platinum particle coalesce and platinum detachment which results in reducing platinum surface area. On the other hand, the similar corrosion was to be found higher in the anode catalyst, during the reversal of the cell voltage caused by fuel starvation. Likewise, platinum catalysts appear to stimulate the carbon corrosion rate [4, 42, 49].

In addition, the existence of more numbers of micropores will leads to the low accessible surface area for the dispersion of particles and uneven transport of the fuel to the surface. Thus, carbon blacks having a huge surface area comprising mainly micropores (<1 nm) becomes a burden to act as a catalyst support. Eventually, carbon does not conduct protons that restricts the performance achievements. A proton-conducting polymer (e.g., Nafion$^{®}$) is typically blended with a catalyst for the maximum usage of the catalyst because it mainly assists the transport of protons within the catalyst layer. In response to that, several substitutes of electrocatalyst supports are being investigated. Among them, mesoporous carbon and carbon gels received a greater attention as a fuel catalyst supports due to the presence of high quantity of mesopores and high surface area, which permits for high flow of reactant and metal dispersion [4].

Catalysts deposited on aforementioned carbons exhibited catalytic activity much higher than similar catalyst deposited on carbon black support. Their stability during fuel cell operational condition is nearly the same as that of carbon blacks. Lately, carbon-based nanostructures, for example, carbon nanofibers (CNFs) and carbon nanotubes (CNTs) were explored as a supporting material for a catalyst in fuel cells. Platinum/bimetallic Pt-based catalysts deposited on CNT and CNF exhibited catalytic activity much higher than similar catalysts deposited on carbon blacks support, because of the exceptional morphology and features like high chemical stability, high accessible surface area and high electrical conductivity [3]. Investigations performed using carbon-based nanostructures in polymer electrolyte membrane fuel cell (PEMFCs) conditions demonstrated that these nanostructures can be more robust and can replace the traditional carbon black [54]. Though, these supporting materials do not inhibit corrosion due to the oxidation of carbon surface instead merely reduce the rate.

In such a case, non-carbon materials have been explored as a support for the catalyst. Conducting oxides are developing as a suitable candidate for catalyst support due to their oxidative resistance. Additionally, during fuel cell operation, these materials exhibited electrochemical and thermal stability and delivered remarkable resistance towards corrosion in different electrolytic media. Unlike carbon, conducting oxides cease to improve electro-catalysis, but rather acts just as a mechanical support, in some cases several metal oxide supports will be able to serve as co-catalysts. Certainly, it is notable that several metal oxides, for example, $SnO_2$, $WO_3$, and $RuO_2$ can able to enrich the catalysis of platinum for oxidation of alcohol [20, 37, 40]. However, a major issue associated with the ceramic oxides is their low surface area, which influences the metal dispersion and, thereby resulting in a reduced catalytic activity. Additionally, the electrical conductivity of some metal oxides, for example, $TiO_2$ and $SnO_2$ are low at temperatures beneath 200 °C.

Depending on the morphology features, conducting polymers (CPs) have been employed in a fuel cell as a supporting material for catalysts. Normally, CPs satisfies the main prerequisites of a proper catalyst support to be used in a fuel cell that is mentioned earlier. Some of the CPs are proton- as well as electron-conducting materials, so they can be alternative to catalyst incorporated with Nafion® and deliver improved performance. The most commonly used CPs are heterocyclic polymers such as polypyrrole (PPy), polythiophene (PTh), polyaniline (PAni) and their derivatives. Table 1 shows the conductivities of some common conjugated polymers. The catalyst activity seems to be higher in PPy and PAni that is mainly due to the synergistic effect of the host matrix and the metal particles [3, 14]. Under fuel cell environment, polymer-supported catalyst usually exhibits a satisfactory stability (e.g., catalytic activity and film integrity). But, in both PAni and PPy, chemical degradation was found during metal doping and the catalysis. In addition, under both oxidizing and reducing conditions, the deposition of the catalyst particles resulted in the degradation of electrical conductivity of the polypyrrole.

And the intermediate products (aldehydes) formed during alcohol oxidation degraded the polyaniline. Furthermore, the use of PAni and PPy as electrocatalyst supports are limited due to loss of electrical conductivity [4].

In summary, the utilization of either carbon or ceramic or polymer materials as a catalyst support in a fuel cell is not totally satisfactory. Accordingly, composite of polymer–carbon, ceramic–carbon and polymer-ceramic materials have been proposed in the most recent years as catalyst supports in fuel cells. These composite may have more reasonable properties than the individual materials when used as a supporting material for the catalyst. Gomez-Romero [12] divided them into two major categories, as per the inherent features of the host and guest phases. Thus, organic-inorganic (OI) materials signify composites with organic hosts and inorganic guests, whereas in inorganic-organic (IO) materials, the organic phase is guest to an inorganic host. In OI hybrids, generally, the inorganic molecules will contribute their chemical activity and requires the structural support from CPs to form a useful solid material. On the other hand, in IO hybrids, the inorganic phase will be providing the structural task even though embedded CPs can also imprint their polymeric nature onto the materials acquired.

## *2.1 Composite Polymer-Carbon Black Supports*

Usually, the electrochemical activity of catalysts supported on composite polymer–carbon blacks (normally Vulcan XC-72), is higher than that of the similar catalysts supported on either carbon or polymer. This enhancement is mainly due to the higher accessible surface area and electrical conductivity of the support and the polymer/electrolyte interface with simpler charge-transfer which permitting the use of almost all the deposited metal nanoparticles. Xu et al. [61] basically examined the influence of PAni on carbon characteristics (IO material) and found the optimum mass ratio of PAni to C (PAni: C = 0.25:1). An excess amount of PAni will reduce the conductivity of the composite, whereas a limited amount of PAni will reduce the anti-poisoning ability of the catalyst. Subsequently, the produced CO poisoning intermediate compound contributes 61.5% of the reduction in methanol oxidation current on the Pt/C catalyst, after 200 potential cycles, however, just 20% reduction is observed while using the Pt/PAni–C composite catalyst. This implies that the anti-poisoning ability of Pt/PAni–C was three folds greater than the Pt/C. In addition, the presence of PAni encourages ability of the catalyst to absorb more water and generates an active oxy-compound (Pt–OH), which elevates oxidation of carbon monoxide into carbon dioxide.

The work of Wu et al. [55] addressed the impact of using conventional carbon particles (Vulcan XC-72) along with CP (PAni) (OI material). They demonstrated that the integration of carbon particles into PAni film not just increases the electron conductivity, yet additionally reduces charge-transfer resistance across PAni/electrolyte interfaces. In both cases, for methanol oxidation, the activity of platinum supported on PAni–C (polymer-carbon) composite was considerably higher than that of the single host component.

Mokrane et al. [35] synthesized conducting polypyrrole (PPy)/C (Vulcan XC-72) composite material with different PPy/C ratios via chemical polymerization method. They noticed that the composite firmly affected the electrochemical activity of supported platinum toward the oxygen reduction reaction (ORR) in acid medium. The variation of the PPy/C ratio decides the so-called substrate effect for electrocatalysis. Thus, ORR is indirectly proportional to PPy content in the composite.

## 2.2 *Composite Polymer-CNT Supports*

Among many varieties of carbons, carbon nanotubes were commonly used as the carbon material in polymer-carbon composite due to their attracting features. To understand the different characteristics of polymer–CNT composites, comprehensive knowledge of the morphology, properties, and chemistry of CNT is significant. CNTs are prepared by single sheets of hexagonally arranged carbon atoms, called graphene and represented in the form of 3D cylindrical nanostructures. There are two basic classifications of CNT, that is, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [4]. SWCNT can be pictured as a rolled-up graphene sheet (tubular), which comprises of benzene molecules, including hexagonal rings of carbon atoms, whereas MWCNT contains a stack of graphene sheets that are rolled up into concentric cylinders. The unique properties related with CNT is usually influenced by various parameters, such as nanotube synthetic method, quality of nanotubes, chirality, size, shape, alignment of nanotubes, defect density, and degree of crystallinity [36]. In most cases, polymer–CNT composites are OI materials, where CNT are dispersed in the polymer matrix to enhance the electrical and mechanical properties of the polymer. The probability of attaining high conductivity at low CNT content makes them a suitable candidate for many potential applications. Moreover, in order to achieve the desired CNT properties, the system is designed in such a manner to create a uniform dispersion of CNT in the composites with high stability.

The major problems associated with the synthesis of polymer-CNT composites exist in the effective integration of CNT into a polymer matrix, the control over the alignment of CNT in the matrix and the evaluation of the dispersion. Accordingly, several techniques have been proposed for the incorporation of CNT in the polymer matrix includes melt mixing, in situ polymerization, electrospinning, chemical functionalization of the carbon nanotubes and solution mixing [43]. Besides, at existing phase of technology growth, CNT production methods are too expensive and not reasonable for manufacturing at pilot scale. Additionally, because of the complex synthesis approach, the quality of CNT differs from one supplier then onto the next and even with the same vendors at various times, making them unreliable for pilot-scale use [31].

Baikeri and Maimaitiyiming [5] revealed that poly(9,9-dioctyl fluorine-alt-2-amino-4,6-pyrimidine) (oligomer) acts as an effective dispersant for SWCNTs. Pt particle was doped on the Py-SWCNT films by $H_2PtCl_6$ via coordination reaction. Furthermore, the incorporation of SWCNT also lead to higher catalytic activity due to the higher accessible surface area and the electrical conductivity of Py-SWCNT composite was considerably higher. Zhu et al. [68] prepared homogeneous PAni-MWNT nanocomposites by functionalizing the MWCNT by the means of diazotization reaction. The 4-carboxylicbenzene group was altered on MWCNT surface via a C–C covalent bond, which helps the dispersion of carbon nanotubes in aniline. Later, electrochemical polymerization was performed by cyclic voltammetry in sulphuric acid containing aniline and 0.8 wt% MWNT. The functionalization of the MWNT can prevent separation of microscopic phase in the nanocomposite and thereby ensure the adaptability of CNTs in the PAni matrix. Compared to pure PAni film, the Pt-modified PAni–MWNT composite exhibited long-term stability with a higher activity for formic acid oxidation. On this basis, the Polymer–CNT composites can serve as excellent host matrices for fuel cell catalysts.

## 2.3 *Composite Polymer-Ceramic Supports*

A recently developing field of materials, so-called “nanohybrid” or “nanocomposite” materials, produced by coordinating interactions of different organic and inorganic materials at the molecular level to obtain new materials with enhanced features and unique functions. This strategy has been effectively utilized currently for the production of new nanocomposite materials by a redox intercalation approach to get hybrid lamellar transition-metal oxides possessing improved synergistic activity. It is renowned that intercalation prompts alteration in the spacing between the layered structures. For instance, a few conducting polymers, for example, PAni, PPy, and PTh are known to oxidatively polymerize in presence of strong oxidizing transition-metal oxides (like $V_2O_5$).

In low-temperature fuel cells, ceramic materials (includes carbides and metal oxides which acts as a carbon-alternative) have been studied as oxidation resistant supports for catalysts [4]. During fuel cell operational condition, these materials are highly stable and exhibited exceptional resistance towards corrosion (under different electrolytic medium). In some cases, various metal oxide supports also acted as co-catalysts. Mesoporous ceramic materials are effectively utilized as a support of fuel cell catalyst because they possess high accessible surface area, large pore volumes with controllable sizes. On these bases, PANI-doped mesoporous metal oxides have been studied as anode materials in fuel cell applications.

Maiyalagan and Viswanathan [30] prepared a stable conducting PEDOT-$V_2O_5$ nanocomposite material via the intercalation of poly(3,4ethylenedioxythiophene) (PEDOT) in $V_2O_5$ matrix. PEDOT-$V_2O_5$ was used as the support for Pt in formaldehyde reduction method. For methanol oxidation, the electrochemical activity and stability of the Pt/PEDOT-$V_2O_5$ electrode were greater than that of Pt/ C electrode, under the electrochemical operating conditions. Pang et al. [39] synthesized PAni-$SnO_2$ composites via chemical polymerization of aniline in presence of $SnO_2$. The Pt has supported the PAni-$SnO_2$ matrix and on $SnO_2$ for comparative study. The characterization study using XRD (X-ray diffraction) indicated that the nanoparticles Pt were evenly deposited on PAni-$SnO_2$ than the other one. In comparison with the Pt/$SnO_2$ electrode, the Pt supported-PAni-$SnO_2$ electrode exhibited better electrochemical characteristics (larger electrochemical surface area (ESA), better anti-poisoning ability and higher electrocatalytic activity for methanol oxidation) under the same operating parameters.

## 3 Catalysing Cross-Coupling Reactions

In the coupling reactions like Mizoroki-Heck, Suzuki-Miyaura and Sonogashira-Hahihara reactions, homogeneous palladium catalysis has garnered vast significance. This kind of catalysis offers high turnover numbers (TON), high reactivity and frequently provides high yields and selectivity. With the help of ligands (such as phosphines, amines, carbenes, dibenzylideneacetone (dba), etc.), the Pd catalysts properties can be enhanced.

Recent development in ligand-free Pd catalysts has replaced ligand assisted techniques. In another aspect, homogeneous catalysis has various disadvantages, such as difficulty in reuse or recycling the catalyst. This resulted in the loss of precious metal and ligands. Additionally, the impurities and the residual metals in the end-products have to be expelled [11]. These issues are to be resolved in order to catalyse the coupling reactions in the industry using homogeneous Pd-catalyst which are still an as challenging task. Heterogeneous Pd catalysis was found to be a feasible alternative. In this technique, Pd is attached to a solid support, such as zeolites and molecular sieves, activated carbon, metal oxides (mainly alumina or silica and also ZnO, MgO, $ZrO_{2,}$ $TiO_2$), alkali, clays and alkaline earth salts ($BaSO_{4,}$ $CaCO_3$, $SrCO_{3,}$ $BaCO_3$), organic polymers, porous glass or polymers implanted in porous glass. In another aspect, Pd can also be converted to composite material by attaching it directly to a solid support; or by covalently bounding Pd to the supports with the help of ligands. These two methods of solid support permits to reuse or recover the heterogeneous catalyst after the process until the catalyst get deactivated. However, heterogeneous catalysis requires more extreme reaction conditions than homogeneous catalysis without causing a problem to the stability of the catalysts, because Pd catalyst is often thermally stable.

## *3.1 Suzuki-Miyaura Reactions*

For the modern synthetic organic chemistry especially in the synthesis of biaryl compounds, Suzuki-Miyaura reaction was turned into the backbone. In recent times, the biaryl compounds are synthesized by catalysing arylation through Suzuki-Miyaura reaction using Pd/C catalyst and they also exist in heterocyclic. Furthermore, Suzuki-Miaura reactions can utilize for coupling variety of organic compounds which are different from aryl compounds (such as alkynes, alenes or alkenes). Marck et al [32] reported about the Pd/C catalysed Suzuki reaction for the first time in 1994.

Generally, in catalytic applications, some of the expected outcomes are evenly dispersion of nanoparticles, easy recovery and reusability, and control in particle size. However, nanoparticles often get aggregated and influenced the selectivity and catalytic activity of the catalyst. Hence, these nanoparticles should be anchored on a host complex such as macromolecular organic ligands or polymer. Esmaeilpour et al. [10] investigated the Suzuki–Miyaura reactions using $Fe_3O_4@SiO_2$-polymer-imid-Pd magnetic nanocatalyst without added phosphine ligands. So-produced Pd nanoparticles provided better accessibility for reactants without getting aggregated. In addition, they offered the easy separation of the catalyst using a magnetic field, short reaction times, easy purification, higher product yields and reduced Pd leaching. Sun et al. [46] prepared the magnetic polymer-supported catalyst by dispersing of Pd on the surface of the orange-like $Fe_3O_4$/polypyrrole (PPy) composite and investigated their application in Suzuki cross-coupling reaction in water. The PPy provided two functions: (i) protection of the magnetic particles against corruption and oxidation by acids and oxygen; (ii) presence of numbers of functional groups (–NH–) on the surface facilitated the immobilization of catalytic active species. Furthermore, the easy separation of magnetic $Fe_3O_4$ (seeds in composite) was achieved and reused for 6 times during a reaction turn without any loss.

### *3.2 Heck Cross-Coupling Reactions*

The first Mizoroki-Heck cross-coupling reactions were discovered separately by Mizoroki et al. [33] and Heck and Nolley [15] where the palladium-catalysed arylation of olefins. In presence of palladium catalyst, an aryl (pseudo) halide reacts with an alkene along with a base to form an arylated alkene. This reaction has been employed in many fields, including fine chemicals syntheses, bioactive compounds, drug intermediates, natural products, antioxidants, UV absorbers, and other industrial applications Esmaeilpour et al. [10].

For Heck cross-coupling reactions, soluble palladium compounds such as phosphine palladium complexes are found to be the effective catalyst [21, 45]. The advancement of the catalyst with non-phosphine ligands [18, 29] gathered the attention of many researchers as phosphine ligands are found to be unfit to our environment due to its cost, toxicity, sensitivity to air and moisture. In recent studies, several efficient eco-friendly matrices were reported for supporting heterogeneous catalysts (Palladium) such as carbon nanotubes/nanofibers, clay, ionic liquids, silica, zeolites, metal oxides, graphene, d-glucosamine, magnetic materials and polymers. For the efficient separation of catalyst for recycling and organic end-products, immobilization of metal catalyst on solid matrix considered to be an efficient tool. In most cases, polymers are used a solid matrix because it provides different combinations of metal bonding to the matrix of the polymer by a non-covalent or covalent bonding, through hydrogen bridges, hydrophobic or specific fluorous interactions as well as ionic bonding.

Many types of research recently reported that under phosphine-free conditions polymer-anchored palladium composites were active for the Heck reaction. Under the phosphine-free condition, Islam et al. [18] examined the catalytic activity of Pd (II) supported on poly (N-vinyl carbazole) in the heck reaction (cross-coupling reaction) of terminal alkenes with aryl halides. The polymer-anchored metal complex found to be air-stable, non-polluting and active under different reaction parameters while optimization of the reaction conditions. The simple reaction conditions and in operation, higher yield, easy regeneration of the catalyst and rapid conversion makes them a suitable candidate for industrial application. Sarkar et al. [44] prepared a heterogeneous poly(hydroxamic acid) Pd(II) complex by utilizing corn-cob cellulose waste as a solid matrix with a reusable ability. Cellulose (biopolymer) is considered as a supporting material due to various attracting features such as low-density, inexpensive, insolubility, better stability while using organic solvents and wide availability. Under ambient reaction conditions, the cellulose-poly(hydroxamic acid)-Pd(II) catalysed the reaction of aryl/heteroaryl halides and arenediazonium tetrafluoroborate with a different olefins and without a loss during recycling of the catalyst.

### 3.3 Sonogashira-Hagihara Reaction

The sonogashira cross-coupling reaction is well-known for the construction of c-c bonds, especially for the formation of alkynes. Generally, the catalyst used for this type of transformation includes Pd/C, CELL–Pd(0), Pd(dmba)Cl(PTA), $PdCl_2(PCy_3)_2$, $PdCl_2/PPh_3$ and $PdCl_2(PPh_3)_2$ together with CuI as co-catalyst [25, 34]. In recent decades, modification in the conventional Sonogashira protocol has been done. Notable among them are phase transfer and copper-free condition; and catalyst utilization, which includes N-heterocyclic carbene (NHC) ligands mostly used for reaction with less reactive bromo- and chloroarenes. The consequence of various solvent such as ionic liquids, aqueous-organic solvent mixtures in presence of water-soluble phosphine ligands is explored. (Bhattacharya and Sengupta [6].

Tamami et al. [48] developed a catalytic system by anchoring palladium nanoparticle on poly (N-vinyl imidazole) (PVI) grafted silica through an eco-friendly approach. This catalytic system showed exceptional activity in copper-free Sonogashira-Hagihara reaction of phenylacetylene with aryl halides, under short reaction times with high yields. Furthermore, seven consequence cycles demonstrated that the polymer-supported catalyst retained its activity and recyclability without any loss. Heravi et al. [17] combined copper- and solvent-free Sonogashira coupling for the different reaction of alkynes with several aryl halides in presence of recyclable and reusable $PdCl_2$ catalyst which is supported on modified poly(styrene-co-maleic anhydride). In addition to higher activity, the catalyst also produced a wide variety of coupling products with remarkable yields. Moreover, without any pre-activation steps, the catalyst was reused for a minimum of five consecutive cycles.

## 4 Photocatalytic Degradation of the Pollutant

Due to the properties like higher catalytic activity, structure-based optical and electronic property, rapid reaction rate, and higher surface area, nanoparticles have high in potential as catalyst as well as redox active media, which attracted many researchers in designing of photo/chem-catalytic materials with greater efficiency especially for the purification of water and gases which are contaminated. Nanosized semiconductor materials such as nano-$TiO_2$ [24, 50], ZnO [38], CdS [67], and CdO [47], zero-valence metals such as $Cu^0$ [27, 57] and $Fe^0$ [51, 52] and bimetallic nanoparticles such as Fe/Pd [53], Fe/Ni [56], and Pd/Sn [26] are commonly used catalytic nanoparticles. For a variety of contaminants which includes polychlorinated biphenyls (PCBs), halogenated aliphatics, organochlorine pesticides, azo dyes [66], halogenated herbicides and nitroaromatics are degraded using a catalyst or redox reagents. But the limitations are seen in the segregation of fine particles from the aqueous suspensions and in catalyst recovering. This limit has been rectified by immobilizing the nanoparticles onto polymer support (such as porous resins [26], polymeric membranes [9, 47, 50] and ion exchangers [27]) with minimum particle loss and coalesce. Table 2 summarizes some polymer-supported nanocomposites for photocatalytic degradation of pollutants from the various aqueous environment.

In degradation of organic pollutants, nano-$TiO_2$ usually plays as a catalyst. Ameen et al. [2] done a research on degradation of methylene blue (MB) dye by poly 1-naphthylamine (PNA)/$TiO_2$ nanocomposite prepared by in situ polymerization, where enhanced photocatalytic activity was observed. The photodegradation efficiency of MB colour might be due to the effective charge separation of the electrons ($e^-$) and hole ($h^+$) pairs at the interfaces of PAN and $TiO_{2.}$ Some bimetals (such as $Cu^0$, $Fe^0$, Fe/Pd, Pd/Sn, Ni/Fe, etc.) and nanoscale metals are found to be very efficient in degradation of different organic pollutants (such as brominated methanes, chlorinated methanes, trihalomethanes, chlorinated benzenes, chlorinated ethenes, other polychlorinated hydrocarbons, dyes and pesticides) [26, 51–53, 56, 57]. The aforementioned metal nanoparticles are found to be very higher in reactivity, for example, self-ignition of nZVI is possible when exposed to air. Hence, oxidation is inhibited in order to preserve the nature of the chemical until they are exposed to the targeted contaminants.

Lin et al. [27] done a research using cation exchanger resin doped with nanoscale zero-valent copper (nZVC) which increases the accessible surface area of the catalyst by reducing aggregation of nZVC particles. During the reaction between $CCl_4$ and $Cu^o$, the Cu ion produced is recycled back by simultaneous cation exchange resin. The combination of sorption due to host resin and degradation by means of nZVC resulted in declination of the quantity of pollutant ($CCl_{4)}$ available in aqueous solution.

Dong et al. [8] researched a composite made by intercalating sodium carboxymethylcellulose (CMC) (serves as a stabilizer) into parallelized iron (Fe/Pd) nanoparticles. When comparing to CMC-stabilized nanoparticles, the pristine Fe/Pd particles, showed less stability against agglomeration, soil transport and chemical reactivity. It is concluded from batch dichlorination tests that CMC-stabilized nanoparticles photodegraded trichloroethene (TCE) which is found to be 17-folds faster than the non-stabilized nanoparticles.

## 5 Catalytic Reduction of 4-Nitrophenol

Recently, for the degradation of aromatic dye and nitro-compounds, various metal nanocatalysts has been developed in order to attain sustainable environment. Since 4-nitrophenol was found to be toxic, it has to be reduced to 4-aminophenol which is important in application aspect. Comparing to 4-nitrophenol, 4-aminophenol find its

**Table 2** Summary of polymer-supported nanocomposites for photocatalysts

| NPs | Polymer support | Pollutant | Preparation method | Results | References |
|---|---|---|---|---|---|
| $TiO_2$ | Polyaniline (PAni) | Phenol | Aniline polymerization in presence of $TiO_2$ | Under visible light, illumination phenol was degraded after 5 h in an aqueous solution | Li et al. [24] |
| $TiO_2$ | Poly (3-hexylthiophene) (PHT) | Methyl orange (MO) | Dispersion of $TiO_2$ nanoparticles onto the polymer matrix | Under optimum molar ratio of $TiO_2$/PHT (75:1), the removal efficiency of MO reached 88.5% under 10 h illumination | Wang et al. [50] |
| $TiO_2$ | Poly (1-naphthylamine) (PNA) | Methylene blue (MB) | In situ polymerization of 1-naphthylamine monomer with $TiO_2$ | Under visible light illumination, MB was degraded nearly 60% | Ameen et al. [2] |
| Au/ $TiO_2$ | Poly(methyl methacrylate) (PMMA) | Trypan blue (TB) | PMMA was first dissolved in tetrahydrofuran and $TiO_2$ powder suspended in a dissolved polymer | Degradation efficiency was 90% by Au-$TiO_2$/ PMMA thin film under sunlight | Elfeky and Al-Sherbini [9] |
| ZnO | PAni | Methylene blue (MB) | In situ polymerization method | % removal of MB after 1 h irradiation was 28% under UV and 82% under visible light | [38] |
| CdS | Chitosan | Congo red (CR) | Bio-mineralization simulation | 85.9% of 0.02 g/L CR was degraded using 1.5 g/L composite catalyst under 180 min of illumination | Zhu et al. [67] |
| CdO | PAni | MB and Malachite green (MG) | Chemical oxidative polymerization | MB and MG dyes were photocatalytically degraded with removal efficiency of 99% under natural sunlight irradiation | Tadjarodi et al. [47] |
| $Fe^0$ | Poly(methyl methacrylate) (PMMA) | Trichloroethene (TCE) | In situ synthesis with MMA and $FeSO_4.7H_20$ as a precursor | The observed degradation rate of TCE was 0.0034 $h^{-1}$ and dechlorination efficiency was 62.3% | Wang et al. [51, 52] |
| $Fe^0$ | Carboxymethyl cellulose (CMC) | Cr(VI) | In situ synthesis with $FeSO_4.7H_20$ as a precursor | After 1 h, higher removal efficiency was found in CMC/$Fe^0$ (94%) when compared with $Fe^0$ (22%) | Wang et al. [51, 52] |

(continued)

**Table 2** (continued)

| NPs | Polymer support | Pollutant | Preparation method | Results | References |
|---|---|---|---|---|---|
| $Cu^0$ | Chitosan | Cr(VI) | In situ synthesis with $CU(SO_4)_2.5H_20$ as a precursor | The concentration of Cr(VI) reduced from 50 to 2.21 $mgL^{-1}$ in presence of 1 g composite after 24 h | Wu et al. [57] |
| Fe/ Pd | Poly(vinylidene fluoride) (PVDF) | Trichloroacetic acid (TCAA) | Reduction deposition | Dechlorination of TCAA was observed within 180 min | Wang et al. [53] |
| Ni/ Fe | Cellulose acetate | Trichloroethylene | Solvent-cast | Observed that reduction rate was proportional to the Ni content (0–14.3 wt%) | Wu and Ritchie [56] |
| Pd/ Sn | Resin | Trichloroethylene | In situ reduction of $Sn^{2+}$ to $Sn^0$ and the deposited $Pb^0$ via reduction of $Pb^{4+}$ | When compared to commercial Sn, the rate of dechlorination in Resin-Pd/Sn was promoted by ~2 orders of magnitude | Lin et al. [26] |

footprint as intermediate in the hair-dyeing agent, antipyretic drugs, anticorrosion lubricant and photographic developers etc. Hence, conversion of 4-nitrophenol (4-NP) by borohydride ions ($BH_4^-$) using metal nanocatalysts into 4-aminophenol (4-AP) via catalytic reduction became more significant. Various novel metal (such as Ag, Au, Pd, Pt etc.,), metal oxide (such as $Cu_2O$) and bimetal (such as Au/Ag, Au/Pt, Pd/Ag, Pd/$ZnO_2$ and Pt/$CeO_2$, etc.,) nanostructures were considered as catalyst for the reduction of 4-NP using $NaBH_4$, which is a pollutant in industrial wastewaters and non-biodegradable material, can be harmful to environment and human health [63].

For the enhancement of the activity of these type of catalysts, the particle morphology and size can be altered. Moreover, the catalytic performance is found higher while using bimetallic nanomaterials (such as Pt/Au alloy nanoparticles (NPs)) [62], Ag/Pd bimetallic NPs [19], and Au/Ag alloy nanoclusters [58]. Therefore, the important key variable for catalytic activity is considered as low-coordination sites and the elevated range of surface-to-volume ratio in nanocatalysts. In any case, these variables have the potential to reduce the surface energy of nanocatalyst and thereby increases the chance of agglomeration which influences the catalytic activity of nanocatalysts. In response to above problem, a promising technique has been proposed, that is anchoring of nanocatalyst on the support matrix, such as cellulose nanofibers [16], silica nanotubes [64], carbon nanotubes [22, 23], polymer-type matrices [13, 59], and graphene [22, 23]. Among these support materials, polymer-type carriers have received great interest for practical application because these materials contain various functional groups which act as anchor sites for loading nanoparticles (catalyst) and thereby improves the properties of nanoparticles, dispersibility and recyclability. Wu et al. [59] fabricated a composite particle of polystyrene/reduced graphene oxide@gold nanoparticles by a facile and controllable method and reported that as-prepared PS/RGO@AuNP composite has good dispersibility in water and additionally, showed excellent catalytic activity in the reduction of p-nitrophenol by sodium borohydride in aqueous solution. In Heidari [16] work, cost-effective biopolymer (nanofibrillated cellulose (NFC)) was used as support for silver nanoparticles and achieved shorter reduction period. Zhang et al. [65] immobilized silver nanoparticles in sulfhydryl functionalized poly(glycidyl methacrylate) microspheres for enhancing monodispersity and recyclability. Moreover, Ag NPs@PGMA-SH composite showed higher catalytic activity during the reduction of 4-NP, which was 1.3–1.32 times higher than reported in the literature. This catalyst also exhibited excellent reusability as a conversion higher than 92% (after 10 consecutive cycles).

## 6 Conclusions

Many researchers dedicated their work on CPs ever since the discovery of conducting polyacetylene in the 1970s and published more number of research results in this relevant field. The rapid development in the field of science and technology has led to the advancement in the CPs and their composite materials in nanoscale. The application of these polymer-based composites is found to be interesting. The well-known use of polymer-based composites in catalytic applications such as fuel cells, cross-coupling reaction, photocatalysis degradation and reduction of pollutants are discussed briefly. Among them, polymer composite as a catalyst in fuel cell and photocatalysis are often studied. Moreover, the interaction behaviour between the host polymers and the immobilized catalyst are highlighted. Others issues regarding the technology limitation and challenging tasks are also discussed.

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