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POTENTIAL APPLICATIONS OF CONDUCTING POLYMER/TUNGSTEN DISULFIDE COMPOSITES: A MINI REVIEW

(Aplikasi Potensi Konduktif Polimer/ Tungsten Disulfida komposit: Ulasan Mini)

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Abstract

Recent works on many types of synergistic conducting polymers/tungsten disulfide (CP/WS_2) composites are thoroughly covered in this mini review. Data were gathered from over 60 scientific research papers from all over the world and published within the last decade (2012-2021). CPs are as versatile materials because of their remarkable advantages over other traditional materials. These advantages include wide and adjustable electrical conductivity, high mechanical flexibility, high capacitance, and low manufacturing cost. However, CPs do possess limitations in terms of stability, processability, and mechanical strength. As a result, CPs are frequently integrated with inorganic fillers such as metal sulfide. WS_2 has garnered significant attention among metal sulfides when combined with CPs, where it improves chemical/thermal stability and provide good processability to the CPs/WS_2 composites. Hydrothermal procedures and solvothermal techniques were all mentioned and discussed as relevant synthesis methods. As a result, hybridized CP/WS_2 composites have shown prospects in terms of functionality and applicability. Sensors, energy storage, and electrical applications are among the areas that experienced enhanced performance by using CP/WS_2. A brief discussion of the mechanisms underlying these successful applications is also included. This mini review is meant to provide readers with information on CP/WS_2 and, as a result, instill interest in new research topics.

Keywords: conducting polymer, tungsten disulfide, sensors, supercapacitors, photocatalyst

Abstrak

Terdapat banyak jenis komposit yang terdiri daripada konduktif polimer/tungsten disulfida (CP/WS_2) telah dibincangkan di dalam ulasan mini ini. Data yang telah dikumpulkan telah diperolehi dari lebih 60 penyelidikan saintifik dari seluruh dunia selama sepuluh tahun sebelumnya. CP merupakan bahan kimia yang serba boleh kerana mempunyai kelebihan yang luar biasa berbanding bahan tradisional yang lain, termasuk kekonduksian elektrik yang luas dan boleh laras, fleksibiliti mekanikal yang tiggi, kapasitans yang tinggi dan kos pembuatan yang rendah. Walau bagaimanapun, CPs mempunyai batasan dari segi kestabilan, kebolehkerjaan dan kekuatan mekanikal. Oleh itu, CP sering digunakan bersama dengan pengisi bukan organik seperti sulfida logam. Di antara sulfida logam, WS_2 telah mendapat perhatian yang signifikan jika digabungkan dengan CP kerana dapat meningkatkan kestabilan kimia/haba serta menambahbaik ciri-ciri pemprosesan dalam komposit CP/ WS_2. Antara kaedah sintesis yang relevan yang telah dibincangkan dalam kajian mini ini adalah proses hidrotermal dan teknik solvotermal.

Hasilnya, komposit CP/WS_2 yang dihibridisasi telah menunjukkan penningkatan dari segi fungsi dan kebolehgunaan. Penggunaan CP/WS_2 dalam bidang sensor, penyimpanan tenaga dan aplikasi elektrik dapat meningkatkan keupayaan mereka. Perbincangan ringkas mengenai mekanisme aplikasi yang berjaya turut disertakan. Akhir sekali, tujuan kajian mini ini adalah untuk memberi maklumat kepada pembaca mengenai CP/WS_2 dan menarik minat mereka untuk menghasilkan suatu kajian penyelidikan yang baharu.

Kata kunci: konduktif polimer, tungsten disulfida, pengesan, superkapasitor, fotomangkin

Introduction

Conducting polymers (CPs) are a unique class of materials with a π-conjugated system that corresponds to its electrical conductivity. The success of CPs as synthetic metals was discovered in the late seventies by Hideki Shirakawa and his team by accidental addition of excess halides in the reaction medium of polyacetylene. Since then, CPs were widely studied upon in terms of their significant properties such as large conducting mechanisms, electrical properties, adjustable electrochemical properties, and easy processing. Currently, the CPs family consists of polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), poly(phenylene vinylene) (PPV), poly(3,4-ethylene dioxythiophene) (PEDOT), polyfuran (PF), and other polythiophenes (PTh) and its' derivatives [1]. Due to their fascinating properties, CPs have received widespread attention from both the industrial community and researchers, especially in the study of supercapacitors, sensors, fuel cells, and photocatalysis for their wide range of applications. Figure 1 summarizes far-famed CPs that correspond to their applications.

Although CPs have become the interest of many communities, they still possess a few drawbacks such as high recycling instability [2], high defect sites from poor temperature tolerance [3], slow exchange of ions [4], and inconsistent solubility [5]. Therefore, enormous effort has been undertaken to incorporate various types of filler such as carbon materials, polymers and inorganic compounds into the CPs' matrix to enhance its properties. Particularly, in recent decades, many attempts were made to produce CPs-inorganic hybrid materials, where the integration of inorganic fillers into CPs may enhance the stiffness, toughness, and dimension stability of the resulting hybrid materials [6]. Among the inorganic fillers, transition metal dichalcogenides (TMDC) were the most favored due to considerable bandgaps in the range of 1-2eV, which is applicable for sensing, nanoelectronics, and photonics [7]. Considering metal sulfides are a class of TMDC, it is an excellent candidate to improve the CPs' properties in terms of conductivity, thermal stability [8], capacitance activity, and cyclic stability[9]. This is because by supplying electrons or withdrawing electrons to or from the transition state of reaction, the transition metal retains a good source of electrons from the partially filled d-subshell. CPs eventually have more free-moving electrons obtained from metal sulfide and therefore exhibits better electrical conductivity. In a study reported by Ramesan 2013, it was found that when PPy and cadmium sulfide (CdS) were combined, the nanocomposite's alternating current conductivity was greater than pristine PPy. Meanwhile, the highest generated direct current electrical conductivity was obtained when a higher amount of CdS were added [10].

In addition, metal sulfide is outstanding because it generates excellent characteristics due to its two-dimensional (2D) structure that exhibits tunable band gaps in the visible to near-infrared spectrum [11] and exceptional physicochemical properties [12]. Among the metal sulfides, tungsten disulfide (WS_2) possesses considerable advantages too, which is comparable to other existing metal sulfides. Tungsten is a d-block element from period 6 and sulfur is a p-block element from period 3. Interestingly, the band-gap of WS_2 changed from an indirect band-gap of 1.4 eV to a direct band-gap of 20 eV when a 2D material was isolated by a simple mechanical exfoliation technique from the bulk material. Due to the wide bandgap, WS_2 is seen as an interesting material for many areas of application, especially in the industry of solid lubricant, lithium-ion battery, catalytic degradation, and electronic devices. By considering the pros and cons of both CPs and WS_2, numerous synthetic approaches have been developed with different morphologies, structures, and properties to satisfy the demands of different applications. WS_2 has been investigated with several types of CPs such as PANI, PPy and PEDOT. In the past decade, CP/ WS_2 composites have been found to have potential in several applications such as in supercapacitors, electronic components and sensors and actuators. However, a simple search in the SCOPUS database with a combined search string specifically on CPs and WS_2 only resulted in less than 50 papers, indicating that more extensive research is needed to cultivate and promote the CP/WS_2 binary composites. Therefore, this mini-review is an attempt to scrutinize the potential applications of CP/WS_2 composites and its benefits.

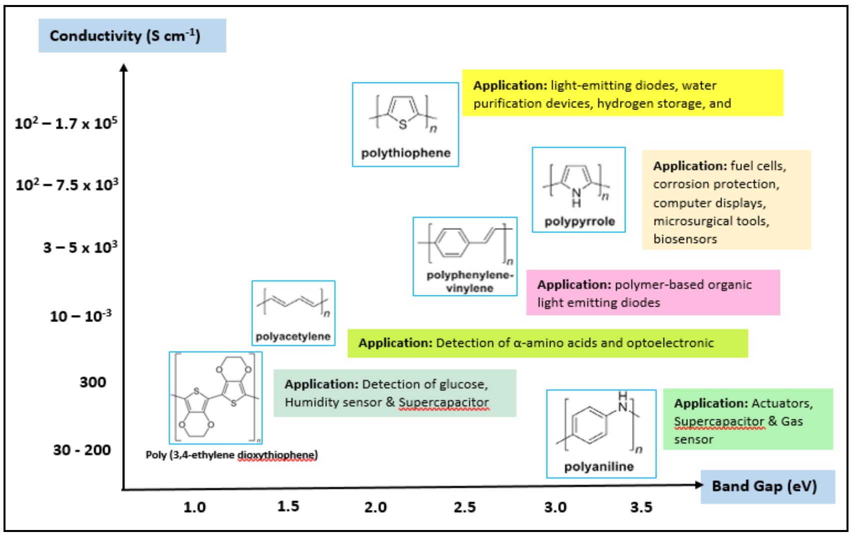

Figure 1. Various types of CPs assigned to a specific range of conductivity and band gap including their existing applications

Brief history of tungsten disulfide composites

Tungsten disulfide (WS_2) or also known as tungstenite is an inorganic compound which is composed of tungsten and sulfur with a molar mass of 247.98 g/mol. In the past, WS_2 has shown great potential for a high-temperature solid lubricant used in space as jotted in the National Aeronautics and Space Administration (NASA) record (History of Tungsten Disulfide (WS_2), 2018). The idea was initiated due to inefficient spacecraft mechanisms which cannot be inspected or maintained after launched. It was discovered that some parts of the spacecraft were not well-lubricated. On top of that, any satellite components that are subject to sliding wear must be properly lubricated to withstand the requirements of the mission. In that sense, WS_2 became the promising candidate due to its anti-friction properties that attributed by its crystal structure, which consists of hexagonal close-packed atomic tungsten layers sandwiched between two hexagonally closed atomic layers of sulfur. Weak Van der Waals forces that hold two adjacent sulfur layers allow them to slide for lubrication purposes [13]. Progressively, the success of WS_2 as a layered structure has expanded due to their interesting anisotropic behavior, great diversity in other physical properties and its advantages for various applications when added to base oil under specific laboratory test conditions. The composition of WS_2 with folded triple-layer of S-W-S sheets enables the atoms within each triple layer to be held by potential carbon-carbon bond. Each bond is clenched by weak Van der Waals interactions. This anisotropic nature of WS_2 therefore opens an opportunity to be incorporated into different types of polymer matrices, resulting in high strength moduli and a good ability for shock absorption [14].

Synthesis method of WS_2

The synthesis of WS_2 composite usually involves multiple steps. Pristine WS_2 must be prepared prior to the integration with a specific CP. Then, WS_2 can be utilised to synthesise CP/WS_2 composite commonly via chemical oxidative method [15]. Every synthetic route for metal disulfide (MS_2) synthesis offers different outputs. The synthesised material can be tailored in order to develop various functions and applications for the metal sulfide [16]. For WS_2, every type of synthetic methods conducted possess several pros and cons depending on the processes involved. Hydrothermal and solvothermal syntheses are a few of the existing methods to synthesise WS_2 that have different synthetic route and its own significance.

Hydrothermal synthesis

Hydrothermal synthesis has been reported as an appealing method due to its simple procedure and productivity. Due to its advantages of low temperature, large-scale development and simple synthesis, it is an environmentally friendly technique for the preparation of various nanostructures [17]. In addition, hydrothermal method leads to the development of nanoscale products under supercritical pressure, which is cumbersome via classical routes. In this method, sodium thiosulfate and hydroxylamine sulfate are the important chemical ingredients. Hydroxylamine sulfate not only acts as the source of sulfur, but is also utilised as a strong acid to establish an acidic state for the nanoparticles that may form. Moreover, WS_2 can also be produced with a chrysanthemum-like nanostructure via hydrothermal synthesis. According to Tang et al. [18], the addition of pluronic and cetyltrimethyl ammonium bromide (CTAB) significantly affect the growth and final morphology of the WS_2. The resulted self assembled chrysanthemum-like nanostructures were grown prior to a fast nucleation of amorphous primary particles and slow aggregation of nanosheets [19]. Prominently, this method is interesting since large-scale metal sulfide composite can be achieved via this technique. However, this method is limited to aqueous precursors which might restrict the control over certain optimisations like temperature, reaction time, and type of solvent.

Solvothermal synthesis

Typically, solvothermal synthesis is a technique for preparing a variety of materials such as ceramics, polymers, metals and semiconductors. It might imitate the hydrothermal synthesis method but what differentiate both of them is the precursor type. Both hydrothermal and solvothermal synthesis use aqueous and non-aqueous precursor solution, respectively [20]. This method may adjust certain experimental parameters including temperature of reaction, time of reaction, type of solvent, type of surfactant, and type of precursor to ensure precise control of the size, distribution of shape and crystallinity of the nanostructure product. Focusing on WS_2, one step exfoliation-restacking technique is invalid to be employed even though WS_2 has similar chemical structure with MoS_2. The reason why this restacking technique makes the WS_2 layered nanocomposites difficult to obtain is because the precursor does not have optimum concentration. Hence, the solvothermal method is used to increase the amount of lithium introduced in WS_2 in order to improve processability [21].

Applications of conducting polymer/tungsten disulfide

The electrical properties of polymeric materials have piqued researchers' attention in the field of solid-state electronics. Generally, CPs by nature reveal poor electrical conductivity due to the absence of free moving electrons to enable the conduction process. However, when the CPs undergoes doping treatment with oxidizing or reducing agent, they can exhibit reasonable conductivity [22]. As a result of the presence of both the polymer and the filler material, a range of inorganic materials may be integrated into CPs with improved characteristics. Metal sulfide appears to be a superior alternative for making hybrid CP composites than metal oxide and other carbon derivatives. Metal sulfide is not only inexpensive and abundant in nature, but it also performs well in faradic redox reactions, making it useful in the fuel cell business. When it comes to the WS_2 nanostructure, the weak Van der Waals interactions indicate that it is anisotropic, and it is well known for its high strength moduli and shock absorption capabilities [14]. However, WS_2 has a drawback in the form of short cycle stability, which causes the capacitance to rapidly degrade. As a result, including WS_2 into CP matrices might be a promising method to improve the stability and combine favourable physical properties of both organic and metallic components while retaining capacitance in a single composition [23].

Polyaniline/Tungsten Disulfide (PANI/WS_2)

Since PANI is one of the most promising CP with enhanced properties, researchers actively synthesize and analyze the PANI composites in numerous applications. A lot of papers were published on the preparation of conducting composites of PANI, such as PANI/TiO_2, PANI/ZrO_2, PANI/Fe_3O_4, PANI/MoO_3, PANI/zeolite, PANI/WO_3, PANI/MnO_2 and PANI/WS_2 from metal sulfide groups [24]–[31]. Despite many papers have been published regarding PANI composites, PANI/WS_2 are still lagging in terms of research and have limited source of information. Only a few reports were found using PANI/WS_2 in the fabrication of micro supercapacitor microrobots and its incorporation with chlorin e6 (Ce6) to give a triple-synergistic strategy in tumor treatment [32]. In a study by Stejskal et al. [33] PANI/WS_2 was fabricated through in situ polymerisation. The flake-like semiconducting particles of WS_2 were coated with a thin film of PANI during the oxidation of aniline. In addition, scanning electron microscopy (SEM) analysis of PANI/WS_2 revealed a porous nature and seems to be robust, where the WS_2 particles interlinked the PANI nanorods. This is probably due to the fact that, WS_2 naturally exists as a stack layered material, where the incorporation of PANI provides additional strength to the whole structure.

Humidity sensors

Humidity is another critical parameter that significantly affects the operation of electronic components in the determination of geographical distribution and the maximum intensity of precipitation, biosphere and surface hydrology. Measurements of humidity or moisture level in the human body could be beneficial in evaluating a variety of physiological and metabolic conditions. Since low humidity has adverse effects on human health, the existence of humidity sensor is important in interpreting the growth, repair and aging mechanisms to regulate internal body conditions [34]. Manjunatha et al. [31] reported on the preparation of PANI/WS_2 composite by in situ polymerisation technique and demonstrated an excellent humidity sensing compare to pure WS_2 as reported by Guo et al [35]. Typically, PANI/WS_2 exhibits enhanced humidity sensing properties due to its porous nature. The porous nature is of paramount interest for the adsorption of water molecules, which is also an important aspect in developing humidity sensors. Consequently, the agglomerated flower-like structure with highly microporous nature of PANI/WS_2 is assumed to have an important role in the humidity sensing behaviour of the composite. Typically, the water vapour could find its way through micropores of PANI/WS2 to react and give response in the sensing mechanism. Figure 2 shows a uniform distribution of WS_2 micro-sized sheets in the matrix of PANI from the observation of a field emission scanning electron microscope (FESEM) micrograph of the composite with magnification 12kx.

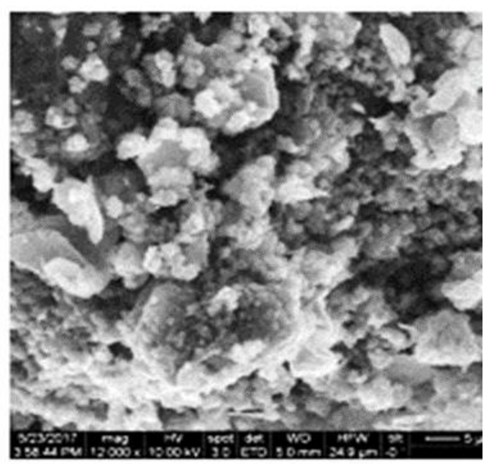

Figure 2. Field emission scanning electron micrograph of the PANI/WS_2 composite with 12000x magnification [31]

Ammonia gas sensor

The application of gas sensors in industries of environmental analysis, automotive, medical applications and indoor air quality controls have been developed for more than a decade ago due to the enforcement of the Occupational Safety and Health (OSHA) regulations against volatile hazardous gases [36]. Among the hazardous gases, ammonia (NH_3) has received major attention in the field of gas sensors due to its abundance in chemicals manufacturing industries and applied in diverse areas around the world [37]. Hybrid PANI/WS_2 composite promises a synergetic effect for NH_3 gas detection. The mechanism of NH_3 gas sensing by PANI/WS_2 can be proposed based on electron donation concept. Complementary to each other, PANI is a p-type conducting polymer with a linear conjugation of π−electronic system, while WS_2 is an n-type semiconductor whose band gap increases with the decrease in the number of stacked layers. The fact that NH_3 could donate electrons to the p-type PANI resulted in a decrease in the hole-transport concentration and next, deprotonation reaction caused the resistance of PANI to incline. Consequently, PANI/WS_2 showed high selectivity towards NH_3 gas with long term stability and repeatability [38]. The magnificent sensing capability of PANI/WS_2 sensor in humid environments and at room temperature makes it a suitable candidate for environmental monitoring devices [39].

Supercapacitor

Self-propelled supercapacitor device based on WS_2 nanoparticles-polyaniline/platinum (PANI/Pt) microrobot design opened a new insight that it can act as an on-demand reconfigurable device owing to its superior capacitance of 14000 μFcm^{-2} with energy density and power density of 0.07 $mWhm^{-2}$ and 120 mWm^{-2}, respectively [40]. Due to great capacitance result exerted by this microbot, it is expected to be proficient for on-demand construction and adjustment of the electronic devices. The fabrication of this autonomous WS_2NPs-PANI/Pt self-propelled microsupercapacitor for on-site electronics delivery in the circuit involved an electrodeposition process using cyclopore polycarbonate membrane as a template. WS_2NPs-PANI/Pt micromotors (μ-motor) fabrication process is shown in Figure 3.

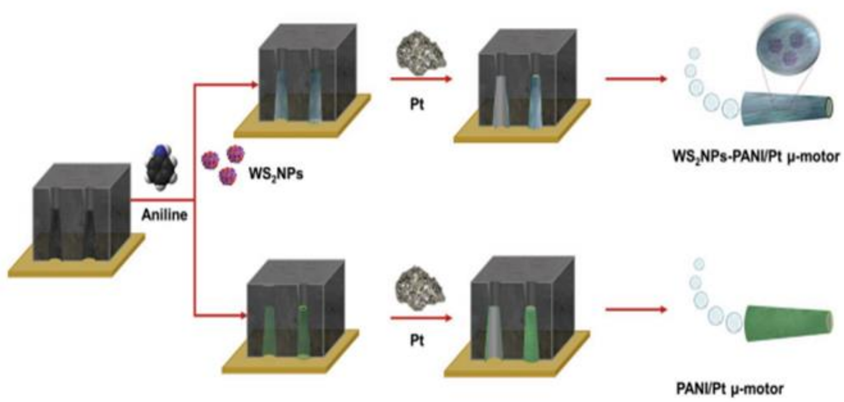

Figure 3. Schematic representation of WS_2NPs-PANI/Pt μ-motor fabrication process. Reproduced with permission from ACS [40].

Polypyrrole/Tungsten Disulfide (PPy/WS_2)

The integration between PPy and WS_2 nanocomposites exhibited a conductivity higher than the pristine WS_2 at ambient temperature [37]. In addition, WS_2 coated with PPy has benefit of wettability. In simple words, wettability is the ability of surface to reduce the surface tension of the liquid that is in contact with it and allow the liquid to spread over the surface and wet [41]. Wettability is important in adhesion as it provides quality for adhesive bonding and coating. Besides, synthesis of PPy/WS_2 can be steered by in-situ oxidative polymerization. The oxidation of pyrrole yields water-insoluble pyrrole oligomers that is further adsorbed on an immersed surfaces and continually grow the PPy chains. Typically, the process started with adsorption where the PPy patches are reinforced into chain colonies and are then grown slowly, resulting in uniform brush-like coating on the entire film [42] to the extent whenever the substance are still available, additional PPy globules will continuously be produced. The PPy globules are produced on hydrophilic PPy films or in surrounding aqueous phase and the globules stick to the film surface. In this context, the deposition of CPs are hydrophilic or hydrophobic surface dependent [43]. The product therefore generally consists of two phases which involve a thin polymer film deposited on the substrate and globular PPy. These two phases were demonstrated by the morphology analysis where, at a composition of 23.7 wt.% of PPy content, WS_2 flakes readily become coated with PPy. Furthermore, the appearance of additional PPy globules was due to the increment of the PPy content up to 38.3%. The idea of uniform PPy coating on WS_2 is due to the different hydrophobicity of pyrrole oligomers in conjunction to the fact that WS_2 is mildly hydrophilic [41].

Hydrogen evolution reaction

Hydrogen evolution reaction (HER) is basically a water splitting technology which found importance in energy storage based on hydrogen evolution. The combination of PPy and WS_2 seems to be a promising composite in the HER catalytic process due to the enhanced conductivity and wettable properties of this composite. Stejskal and co-workers [41] prepared PPy/WS_2 in various ratio of pyrrole monomer. The study revealed that excess of PPy globules would block the active edges of WS_2 in HER, despite of improved conductivity. However, a significant result was attained upon physical mixing of the PPy and WS_2 as a result of proton abundancy which was responsible for capacitive charging process in HER.

In Vivo drug release

Traditional drug delivery medications, such as oral administration and injections, tend to deliver greater drug concentrations than necessary, which may cause side effects in patients. Therefore, externally controlled drug delivery systems are of special relevance for study because they enable for drug delivery control from outside the body [44]–[46]. Particular interest on PPy functionalized WS_2 was paid by Hsiao and co-workers [47] since the composite possesses excellent synergistic properties to fine-tune the electrical properties to enable an electrically active nanocarrier system for an effective drug delivery to the target organ. The study revealed that a large quantity of anti-cancer drug, such as 5-fluorouracil (5-FC), be effectively delivered (90%) in the presence of electrical stimulation. They also successfully reported could that no toxic effect was evident in the electrical stimulation of PPy/WS_2.

Poly (3,4-ethylenedioxythiophene: Poly (Styrene Sulfonate)/Tungsten Disulfide (PEDOT: PSS/WS_2)

Poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)/tungsten disulfide, PEDOT:PSS/WS_2 is one of the ternary CPs composites as a potential material in thermoelectric applications due to its various benefits such as adjustable electrical conductivity and solution processability [49, 50]. PSS is a polymer surfactant, which enhances the dispersion and stability of PEDOT in water and other solvents [50]. PEDOT:PSS is well-known in the thermoelectric field for its excellent mechanical flexibility, low thermal conductivity, water solubility and processability [51]. As PEDOT:PSS went through a small treatment via direct vacuum filtration, the composite has been enhanced with high electrical conductivity. Since then, research related with incorporation of inorganic nanostructures with PEDOT:PSS to enhance the thermoelectric performances has been expanding [49].

The introduction of PEDOT:PSS into WS_2 resulted in a composite that facilitated the charge carriers to move along the polymer chains, which effectively improved the charge transfer within the composite [52]. The fabrication technique was utilized due to the poor conductivity of WS_2, where the lateral transfer of electrons along the lamella structure of the WS_2 nanostructures were blocked, making the electron transfer inefficient. PEDOT:PSS also acts as spacers to avoid restacking of WS_2 and provide plenty of channels to enhance the charge transport. Moreover, synthesized the PEDOT:PSS/WS_2 thin film synthesized may easily be peeled off and transferred to another substrate, resulting in more potential applications. Therefore, stronger performing thermoelectric composite such as PEDOT:PSS/WS_2 carries better properties rather than the pristine PEDOT:PSS and pristine WS_2 [52].

Schottky diodes

In a study by Ortiz et al. [53], PEDOT:PSS/WS_2 Schottky nano-diode was constructed through hetero-junction of a hole transporting CP with an n-type semiconductor. In order to fabricate this composite, individual PEDOT:PSS was synthesized via electrospinning while the mono- and multi-layer WS_2 flakes were synthesized via chemical vapor deposition (CVD). These combination methods are developed from a previous research that implemented electrochemical polymerization techniques [54]. The previous experiment demonstrated poor device operation due to undesirable chemical reactions with the inorganic semiconductor. In terms of performance, the equations in standard thermionic emission model of a Schottky junction were used and from there it exerts an ideality parameter of 1.9 and a barrier height of 0.58 eV. Far from being ideal, the high ideality parameter measured value for this device may be contributed by the recombination of hole and electrons at the interface or the presence of interface states at the CP/WS_2 interface. Even so, upon large surface to volume ratio of the film, semiconductor carrier density is tunable via a back-gate bias and the reversible change of barrier height makes it potentially useful as a sensor [53].

Supercapacitor

In the organic semiconducting family, PEDOT has triggered worldwide interest owing to its development as pioneer for electronically conducting polymers (ECPs). However, the fact that PEDOT has outstanding electrochemical properties is still insufficient for it to meet the needs of practical applications. To overcome the problem, WS_2 has been incorporated into PEDOT to accelerate its applications in the fields of various devices, especially for the supercapacitors [55]. Nevertheless, to excel as high-performance supercapacitors, PEDOT/WS_2 may need to form a ternary composite with another compound. The combination of the three components in nanoscale creates a synergistic effect and higher potential in the faradaic processes Xia et al. [34]. For instance, a recent study in the electrical field by Liang et al. [56]reported that the use of poly(3,4-ethyleenedioxythiophene)-poly(ethylene glycol)-tungsten disulfide (PEDOT-PEG-WS_2) as ternary compounds exhibited good performance as a supercapacitor. PEDOT-PEG-WS_2 nanocomposite was prepared via electrochemical self-assembly of PEDOT and WS_2 nanosheets in the presence of PEG.

This ternary composite has resulted in a unique three-dimension interpenetrating porous network (3D-IPN) in nano-/micro scale. The addition of 5% PEG surfactant has effectively stabilized the WS_2 nanosheets that coexist with additional electrolytes. 3D-IPN materials has gained attention for its high-volume ions transport system and utilization of limited space that allows enhancement of energy storage capacity. Moreover, the 3D-IPN confined to metal-organic framework helps to build and verify automotive hydrogen storage systems that will allow hydrogen-fueled vehicle platforms to meet customer specifications. The optimization of PEDOT-PEG-WS_2 nanocomposite has been developed from the WS_2 contents and CV cycles adjustment. Based on their CV area and specific capacity of each sample, it was found that the as-prepared PEDOT-PEG-WS_2 nanocomposite has reached maximum specific capacity by adding 2.7% WS_2 in solution and 50 electrodeposition cycles.

Other than that, electrochemical properties of the engineered 3D IPN-PEDOT-PEG-WS_2 nanocomposite were recognized and compared with PEDOT-PEG [56].

Organic photovoltaic cells

OPV is an electrical device that converts light directly into electricity by photovoltaic cells, which combine physical and chemical phenomenon. The great characteristics such as low cost, light weight, flexible and scalability through roll-to-roll coating processes make OPV is great for green technology. The performance of OPV can be improved by a few ways including device structure optimization, conversion of light to suitable absorbance wavelengths and synthesis of new short band-gap polymers. PEDOT:PSS is familiar in hole-extraction layers (HEL) which works as buffer layers between the active layer and electrode. Recently, researchers have discovered that MoS_2 based OPVs utilizing PEDOT:PSS HEL, possesses better performance due to increased hole extraction and light absorption [57]. This finding has opened a venue for WS_2 to replace traditional MoS_2 as HEL in OPVs since it is structurally similar to MoS_2 with some expectation to enhance device performance equally or better. Surprisingly, a study by Lin and co-workers [58] exhibited excellent results of the OPV device performance through the implementation of an WS_2 HEL layer combined with the indium tin oxide (ITO) anode, PEDOT:PSS layer, poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) [58]. In this study, WS_2 nanosheets were obtained by a simple ultra-sonication method and were uniformly spin coated on a ITO/glass as visualized in Figures 4 (a) and (b). Next, the hole-extraction efficiency of WS_2 was amplified by a UV-ozone treatment which at the same time empowered the OPV device.

In another study by Le and co-workers [59], the effect of WS_2 upon UVO treatment was investigated by introducing WS_2 into CP composites such as PEDOT:PSS, P3HT:PCBM and lithium fluoride/aluminum (LiF/Al) [59]. As expected, the change in work function of WS_2 due to UVO treatment enhanced its hole-extraction properties. The power conversion efficiency (PCE) of the OPV with WS_2/PEDOT:PSS was 3.07%, which is superior compared to the OPV with only PEDOT:PSS layer of 2.87%. Therefore, the study agreed on a deduction that high PCE resulted from the efficiency of charge separation and collection processes by WS_2/PEDOT:PSS.

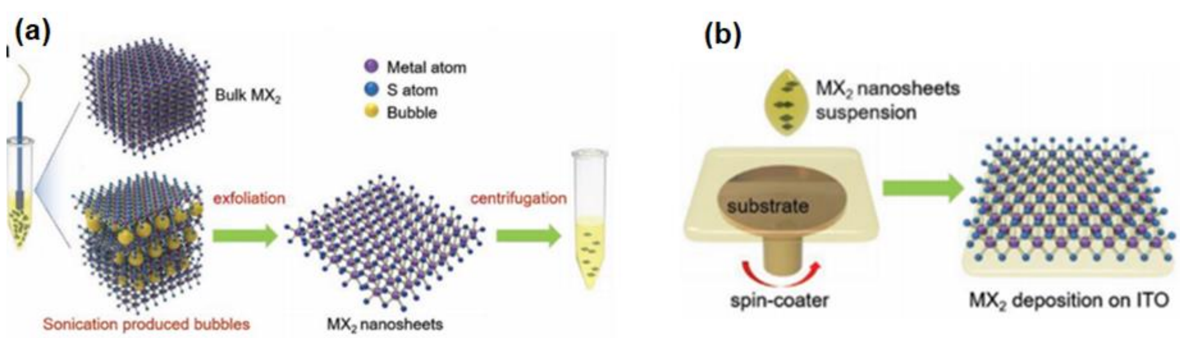

Figure 4. (a) Sonication assisted liquid exfoliation to prepare WS_2 and (b) deposition of WS_2 or MoS_2 onto ITO substrate via spin coating technique

Polyfluorene/ Tungsten Disulfide (PFO/ WS_2)

Polyfluorene (PFO) is an attractive material for display applications such as light source in organic light emitting diodes (LED) due to efficient blue light emission, good solubility and high mobility. Light absorption of PFO in the UV region falls approximately at 380 nm. Beyond the desired blue emission at 425 nm, a green component close to 530 nm can either be attributed to intermolecular interactions or oxidation-induced keto defects that cause aggregates to form [60]. According to Luccio et al. [61], even though the energy emission is low, the removal of the inter-chain interaction enhanced the color purity and luminescence stability of PFO/WS_2. Considering WS_2, both fullerene-like nanoparticles (F-WS_2-NP) and nanotube (WS_2-NT) structures work differently. F-WS_2 is more into lubricating fluids, self-lubricating coatings and medical devices. Meanwhile, WS_2-NT is great at improving the mechanical properties of CP composites [61]. With respect to that, the addition of inorganic nanomaterial like WS_2 ensures color emission tunability. Not to mention, the exhibited optical and electrical properties of PFO/WS_2 depends on the number of WS_2 layer present [61]. The surface morphology of PFO has a smooth appearance at a glance as shown in Figure 5 (a). Meanwhile, SEM images of PFO/WS_2 nanocomposite films showed high dispersion of WS_2 nanotubes upon various WS_2 concentration from 10 wt.% to 50 wt.% as displayed in Figure 5 (b–d). It is observed that the dispersion of the WS_2-NT is quite homogeneous for all the concentrations investigated, even though some nanotube agglomerates remain. This finding suggests a further study is needed either on the purification of nanotubes or the preparation of the blend.

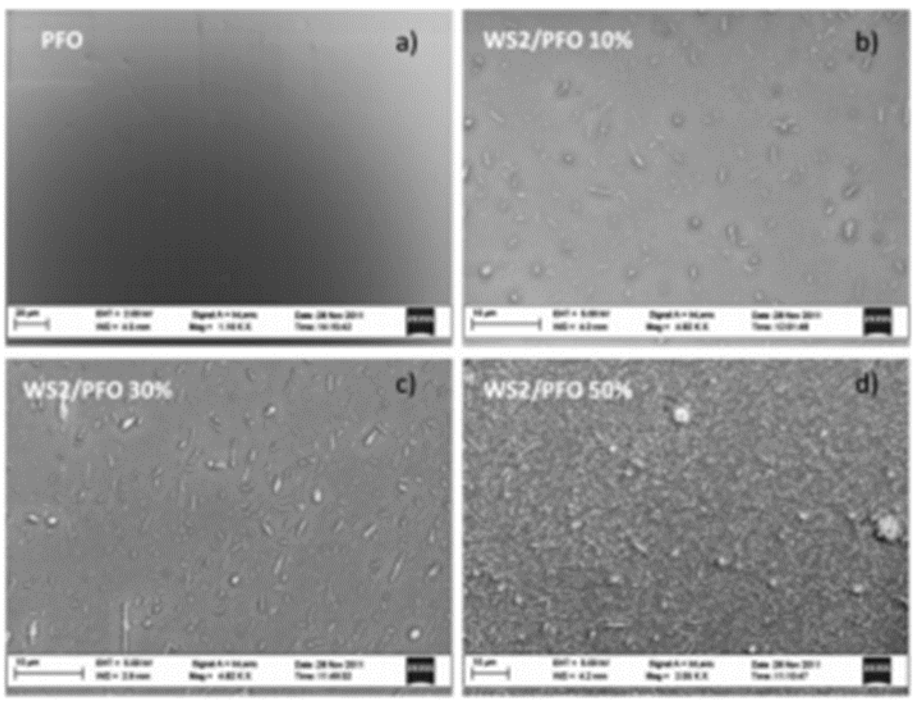

Figure 5. Scanning electron microscope images of a) bare PFO, and PFO/WS_2 nanocomposites at b) 10 wt.% c) 30 wt.% and d) 50 wt.% [61].

Organic light-emitting diode

An organic light-emitting diode (OLED) is a light emitting diode in which organic layers are responsible for light emission. The light emitted by OLED follows the basic principal of electroluminescence in which a material acts in response to the electrical field applied across it [62]. In context of CP/WS_2, PFO has recorded an investigation where PFO matrix and WS_2 nanotubes were combined to prepare PFO/WS_2 blends with various loadings of 10 wt.%, 30 wt.%, and 50 wt.%. The fabrication of these homogeneously dispersed PFO/WS_2 composites were influenced by two major steps including the WS_2 nanotube purification and the blend preparation. An optimization on the threshold voltage has recorded the highest voltage of 4.7 V when 30% of WS_2 was integrated with PFO, and surprisingly the threshold voltage depreciated at 50% of WS_2 and recorded 4.1 V which was almost similar to pure PFO. Compared to pure PFO, the devices containing the nanocomposites has poor efficiency. This is because the electrical data exhibited that the PFO/WS_2 nanocomposite device of WS_2 showed fluctuated performances with increasing wt.%. Such unsynchronized data of threshold voltage and efficiency of the tailored material might be contributed by several factors such as unbalanced charges and electrode interfaces. It also could be due to the change of the device working point or total applied power [61]. Table 1 summarizes various CPs/WS_2 composites with its respective summary on desired applications and advantages.

Table 1. Summary of CP/WS_2 in various application and their significant advantages

Conducting Polymer/WS_2	**Application**	**Advantage**	**Remarks**	**Ref.**
PANI/WS_2	Dye sensitized solar cell (DSSC)	Higher conversion efficiency of WS_2 compare to platinum counter-electrode. Relatively cheaper cost compares to platinum.	Nano-sheets of WS_2 and nano-rods of PANI were used in the investigation.	[63]
	Supercapacitor	The higher composition of PANI in the WS_2 matrix has enhanced the supercapacitor performance.	Conductivity: 65.7 S/m; Specific capacitance: 441 at 0.5A/g.	[64]
	Supercapacitor	Exhibited excellent electrochemical properties and high frequency response.	High capacitance of 180 μFcm$^{-}{}_{2}$ at 1$_2$0 Hz. Potential use in energy storage device.	[65]
	Sensor	The sensor showed an excellent result under humid environment which can be utilized in the respiratory gases.	Ammonia sensor	[39]
PPy/WS_2	Drug release	Biocompatible Non-invasive electrically stimulating drug release system	5-fluorouracil (anticancer drug)	[47]
	Potential use in medium-frequency devices such as humidity and gas sensors.	Excellent operation in terms of AC conductivity and dielectric properties.	PPy with 40 wt% of WS_2 possessed highest conductivity of 5.081 x 10^{-3} S/cm.	[66]

Table 1 (cont'd). Summary of CP/WS_2 in various application and their significant advantages

Conducting Polymer/WS_2	Application	Advantage	Remarks	Ref.
PPy/WS_2	Humidity sensor	Excellent long term-stability.	Response/recovery = 5_2/58 s, respectively. Long term stability up to 60 days at 55 and 95% relative humidity.	[67]
PEDOT/WS_2	Electrochemical sensor	WS_2 has enhanced the denseness and smoothness of PEDOT morphology. The ternary composite of SWCNT/WS_2-PEDOT showed good linear response in the range of 0.00_2 – 0.9 µM with low LOD of 0.7 nM in the Vitamin B_2 detection.	The study involves molecularly imprinted polymer of WS_2-PEDOT in the presence of Vitamin B_2 as the template.	[68]
	Supercapacitor	The supercapacitor showed long-term stability up to 5000 cycles by retaining 83.3% of initial areal capacitance.	Hybrid material of ternary composites consist of PEDOT, MeOH, PEG and WS_2 were prepared using simple co-electrodeposition method.	[69]
	Schottky diode	Novel material of PEDOT/WS_2 used for the first time in nano-diodes. The perfect ambient tolerance of the diode makes it an ideal candidate for gas or light sensors.	The combination of PEDOT and WS_2 has resulted in rectification ratio of 1_2 and a turn-on voltage of 1.4 V.	[53]
	Miniature-supercapacitor	Simple and cost-effective fabrication of WS_2/PEDOT:PSS ternary composite. Improved flexibility in the miniaturized supercapacitor.	The WS_2/PEDOT:PSS supercapacitor recorded a high conductivity of 44 S/cm, high areal specific capacitance of 86 $mFcm^{-}{}_2$, and 107% capacitance retention after 5000 cycles.	[70]

Table 1 (cont'd). Summary of CP/WS_2 in various application and their significant advantages

Conducting Polymer/WS_2	**Application**	**Advantage**	**Remarks**	**Ref.**
Polythiophene/WS_2 (PTh/WS_2)	Functionally designed PTh/WS_2	Shown good magnetic effect which could find potential use in microwave absorbing materials.	Modified liquid phase oxidative polymerization that controls interface PTh-based layered material.	[71]
	Functionally designed coating method for Pth/WS_2	Electro-conductivity and mechanical properties of WS_2 has been enhanced via the tailor-made functionalization.	Potential use in drug release control.	[72]
PFO/WS_2	Organic Light Emitting Diodes	PFO with 30% of WS_2 showed a threshold voltage of 4.7 V when 30% of WS_2.	PFO/WS_2 has been tested for the first time as OLED and it opens the door for new avenues for this composite material.	[61]

Conclusion

A widespread overview of CP composites has been studied in the context of their properties and existing applications. WS_2-based CPs offer a very broad and promising field of research, not only due to its enhanced properties but also because of the chances to achieve multifunctional nano systems from the synergic effect between CP and WS_2. In this mini-review, CP/WS_2 composite showed the best performance as energy storage material followed by electronic components and sensors. CP/WS_2 is a great choice for energy storage since it shows high capacitive behaviour even in a micro-sized supercapacitor. As a matter of fact, this material composite deserves a place in electronic and biomedical industries. Based on the findings and limitation of this research, some improvement can be made on low energy emission by PFO/WS_2. As abovementioned, WS_2 nanotubes were not fully homogenous in the PFO matrix. Henceforth, future research might consider nanotube purification in the fabrication of PFO/WS_2. Besides, CP/WS_2 can also consider more formation of ternary compounds inspired from the PEDOT-PEG-WS_2 composite. This is because the initiative of using ternary compound can strengthen the connection between CP and inorganic filler, thus exhibiting remarkable performance in supercapacitors due to better electrons transport.

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