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## Polymer nanocomposites for energy storage, energy saving, and anticorrosion

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Polymer nanocomposites exhibit unique physicochemical properties that cannot be obtained with individual components acting alone. Polymer nanocomposites have attracted significant research interests due to their promising potential for versatile applications ranging from environmental remediation, energy storage, electromagnetic (EM) absorption, sensing and actuation, transportation and safety, defense systems, information industry, to novel catalysts, etc. In particular, polymer nanocomposites have attracted intensive research interest for solving both energy and environmental issues. This review paper mainly focuses on the most recent advances in polymer nanocomposites for energy storage (*i.e.*, electrochemical capacitors and batteries), energy saving (*i.e.*, electrochromic devices and carbon dioxide capture), and anticorrosion (conductive and non-conductive polymer nanocomposite anticorrosive coatings) applications.

Received 14th April 2015  
Accepted 21st May 2015

DOI: 10.1039/c5ta02707a

www.rsc.org/MaterialsA

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### 1 Introduction

Nanocomposites are defined as, “two or more materials with different properties that remain separate and distinct on a macroscopic level within one unity and with any dimension in any phase less than 100 nm”.<sup>1,2</sup> If polymers, that is, long-chain molecules composed of large numbers of repeating units of identical structure, serve as the matrix reinforced by different types of nanofillers, the nanocomposites are called polymer nanocomposites (PNCs).<sup>3,4</sup> Compared to polymer composites where micron-scale fillers such as glass or carbon fibers are



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storage, anticorrosion, and environmental remediation applications.

employed, PNCs exhibit substantial enhanced properties at much lower loadings, which ultimately give rise to lower component weight and simplified processing.<sup>5</sup>

As a continuous phase to bond nanofillers together, the polymer matrix plays an important role in determining the processability, transverse tensile properties, compressive properties, shear properties, heat resistance and resistance to environmental media of the PNCs.<sup>6</sup> Typically, conventional polymers can be classified into different groups based upon their processing characteristics, the type of polymerization mechanism, or the polymer structure.<sup>7</sup> For example, they can be grouped into addition polymers (polymers formed by many monomers *via* rearrangement of bonds without the loss of any atom or molecule) or condensation polymers (a molecule, usually water, is lost during the polymerization) according to their mechanism of polymerization. Also, polymers can be homochain or heterochain depending on whether the main

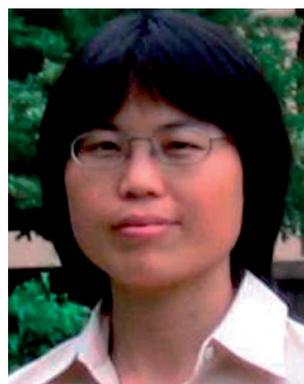
chain is constructed from atoms of a single element or not. The most common classification method is on the basis of their thermal processing behavior where polymers can be divided into thermoplastics and thermosets. Specifically, thermoplastics are those with a linear structure that can be heat-softened in order to be processed into a desired form, the typical examples of which are polystyrene and polyolefins. Thermosets are usually featured with a cross-linking structure and cannot be thermally processed. Principle examples of thermosets include epoxy, phenol-formaldehyde resins, and unsaturated polyesters.

With the invention of conductive polyacetylene in the 1970s, intrinsically conductive polymers (ICPs) have received significant attention from both science and engineering communities.<sup>8–10</sup> ICPs generally include polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(*para*-phenylene) (PPP), poly(phenylenevinylene) (PPV), polyfuran



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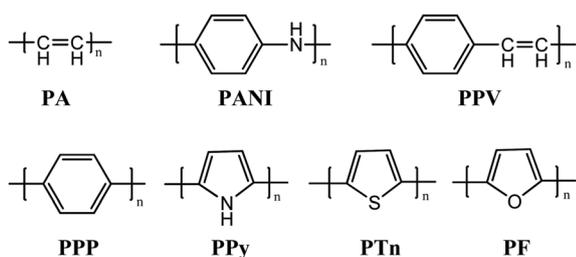
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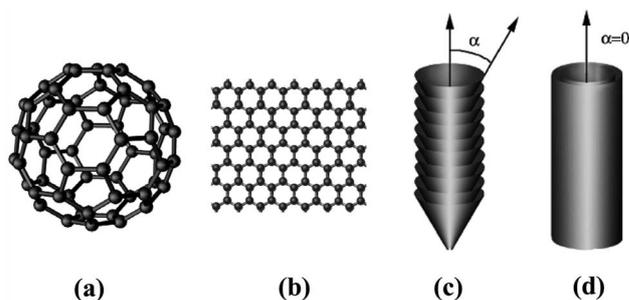
(PF), *etc.*,<sup>11</sup> and their structures are depicted in Scheme 1. These conjugated polymers can be electrical insulators, semi-conductors or conductors, depending on the doping level and nature of the dopants. Upon being treated with dopants and/or subjected to chemical or electrochemical redox reactions, the electrical conductivity of these conjugated polymers can be increased by several orders of magnitude. Apart from the wide range of electrical conductivity, ICPs also have advantages of mechanical flexibility and high thermal stability.

The other important dispersed phase in PNCs is nanofillers that function as the reinforcing component.<sup>12</sup> Nanofillers have been employed to improve the mechanical, magnetic, thermal, electrical, gas barrier properties, and flame retardancy of polymers.<sup>13–17</sup> Compared to conventional fillers, namely, glass fibers, carbon fibers, wood sheets, metal particles, and inorganic mineral particles, nanofillers are usually advantageous due to their greatly increased specific interfacial area, both higher achievable loads and overall compliance, and more controllable interfacial interactions.<sup>18</sup> The types of nanofillers explored in PNCs so far include quantum dots (semiconductors, metals, and metal oxides), nanotubes (carbon nanotubes or CNTs), nanowires (conducting metals or semi-conducting carbons), polyhedral oligomeric silsesquioxane (POSS), dendrimers, layered silicates, and metal oxide nanoparticles.<sup>19</sup> Carbon nanostructures, starting from carbon nanofibers (CNFs) that might have been discovered as early as in 1889,<sup>20</sup> followed by fullerene in the mid 1980s by a research team led by Kroto,<sup>21</sup> then CNTs by Iijima in 1991,<sup>22</sup> and finally graphene by Andre Geim and Kostya Novoselov in 2004,<sup>23</sup> have promised ultra-strong-conducting polymer nanocomposites.<sup>24</sup> The structure of carbon nanofillers, *i.e.*, fullerene, graphene, CNFs, and CNTs, is illustrated in Scheme 2. Specially, graphene is considered as a rising star on the horizon of materials science.<sup>25</sup> With its two-dimensional (2D) atomic crystal structure consisting of a one-atom-thick fabric of carbon, graphene possesses extremely high mechanical strength (Young's modulus: 1 TPa; intrinsic strength: 130 GPa), exceptionally high electronic conductivity (room temperature electron mobility:  $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and thermal conductivity (above  $3000 \text{ W mK}^{-1}$ ), impermeability to gases, as well as many other supreme properties, all of which render it extremely attractive for numerous applications.<sup>26</sup>

The incorporation of nanofillers into polymers can give rise to distinct properties from synergistic effects of each component in the PNCs. PNCs can be synthesized by various methods



Scheme 1 Chemical structure of typical ICPs including PA, PANI, PPV, PP, PPy, PTn, and PF.



Scheme 2 Schematic structure of (a) fullerene, (b) graphene layer, (c) stacked cone herringboned CNFs, and (d) CNTs.  $\alpha$  is the angle between the fiber axis and the graphene sheet near the sidewall surface.  $\alpha > 0$  for CNFs and  $\alpha = 0$  for CNTs. (b), (c), and (d) are reprinted with permission from ref. 26. Copyright [2005], AIP Publishing LLC.

that can be generally divided into four categories: melt intercalation, template synthesis, exfoliation adsorption, and *in situ* polymerization intercalation.<sup>27</sup> The aspect ratio of the nanofiller, the nature of the nanofiller/matrix interface, and the percolation threshold are key aspects in the PNCs design and behavior.<sup>28</sup> Nanofillers are capable of imparting both structural and functional reinforcement to the PNCs. For example, significant enhancements in mechanical strength have been witnessed in PNCs by the addition of nanofillers with intrinsic high modulus. Uniform dispersion of nanofillers and strong interfacial interactions between the matrix and the nanofillers are mainly responsible for the significantly enhanced mechanical properties. Covalent bondings between the filler and matrix are considered as the most effective means to increase interfacial shear stress for improving stress transfer. Moreover, attributed to the excellent thermal/electrical conductivity in nanofillers (*i.e.*, carbon nanostructures), thermally and electrically conductive polymers have been prepared with extended applications for sensors, EMI shielding materials, electrodes, and stimuli responsive materials. Bulk conductivity of typical engineering polymers is reported to increase by  $10^{10}$  to  $10^{14} \text{ S m}^{-1}$  at very low filler concentrations ( $<1 \text{ vol}\%$ ).<sup>29</sup> The percolation theory, describing the connectivity of objects within a network structure, is employed to study conductivity changes in the PNC systems. PNCs transit from insulator to conductor at a certain loading that is called the percolation threshold, or critical fractional volume. This percolation threshold strongly depends on the aspect ratio of the conductive nanofillers. Other theoretical efforts, namely, integral equation theories (Polymer Reference Interaction Site Model, PRISM), density functional theory (DFT), self-consistent field theory (SCFT) and field theoretic approaches, have been developed as well to understand the structure and phase behavior in PNCs.<sup>30</sup>

So far, PNCs have been widely studied for versatile applications ranging from environmental remediation, energy storage, electromagnetic (EM) absorption, sensing and actuation, transportation and safety, defense systems, and information industry, to novel catalysts, *etc.*<sup>31–39</sup> (Fig. 1).

In this review paper, the main focus is on PNCs for energy storage, energy saving, and environmental remediation

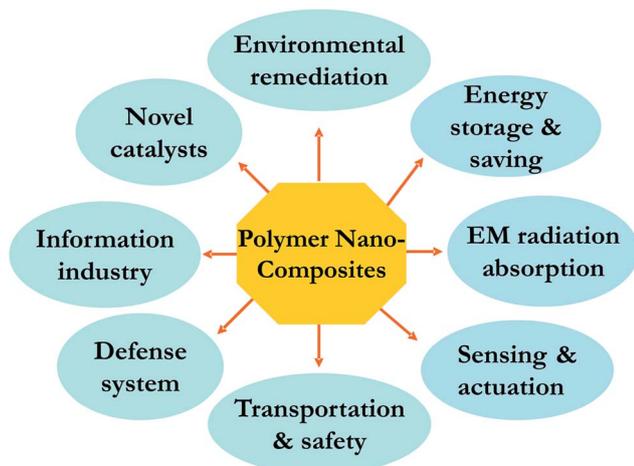


Fig. 1 Polymer nanocomposites for different applications.

applications. A brief review will be given in the most recent advances in these three areas.

## 2 Polymer nanocomposites for energy storage applications

The development of sustainable and renewable energy storage resources from renewable energy reservoirs such as wind and solar is in urgent demand due to the ever increasing energy crisis arising from depletion of conventional fossil fuels.<sup>40–43</sup> Due to the intermittent nature of these renewable energy resources, reliable energy storage systems are an urgent need to store and output energy in a stable way.<sup>44</sup> Electrochemical energy storage systems (EES) that include electrochemical capacitors (ECs), batteries,<sup>45</sup> and fuel cells<sup>46</sup> have attracted remarkable research interest among various energy storage systems; for example, pumped hydro storage, thermal energy storage, compressed air energy storage, and flywheel energy storage.<sup>47,48</sup>

An important application for PNCs is lithium-ion batteries (LIBs).<sup>19</sup> With advantages of high working voltage, high capacity, low toxicity and long cycling life, LIBs have become the most important and widely used rechargeable batteries.<sup>49</sup> In LIBs, graphite, Si, and metal oxides are usually used as the anode materials and  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{Li}[\text{NiCoAl}]\text{O}_2$ ,  $\text{Li}[\text{MnNiCo}]\text{O}_2$ , and  $\text{LiMn}_2\text{O}_4$  as the cathode materials.<sup>50</sup>

ICPs have attracted significant research efforts to improve the performances of conventional LIB electrode materials.<sup>51</sup> The electroactive organic functional groups in ICPs intrinsically have faster redox reaction kinetics than conventional inorganic LIB electrode materials.<sup>50</sup> Besides, the flexible polymer chain structure is more stable than rigid crystalline particles during the fast charge–discharge process and therefore possesses better cycling stability. ICPs coatings *via* an *in situ* polymerization method are usually utilized to form a conductive polymer framework in PNCs-based LIB electrode materials. For example, PNCs-based anode materials including  $\text{CuO}@PPy$ ,<sup>52</sup>  $\text{SnO}_2@PPy$ ,<sup>53</sup> and  $\text{Si}@PANI$ ,<sup>54</sup> as well as cathode materials of

$\text{PPy}@LiFeO_2$ ,<sup>55</sup> exhibit much better performances attributed to the fast electronic and ionic transfer channels and maintained mechanical integrity from coated ICPs.

Recently, Chao *et al.*<sup>56</sup> have done further work by combining carbon nanostructures and ICPs into an “all-in-one” highly integrated polymer nanocomposite cathode for LIBs.  $\text{V}_2\text{O}_5$  nanobelt arrays (NBAs) were directly grown on three dimensional ultrathin graphite foam (UGF), (Fig. 2a and b), and then subsequently coated by a mesoporous thin layer of the conducting polymer of poly(3,4-ethylenedioxythiophene) (PEDOT) (Fig. 2c). The  $\text{V}_2\text{O}_5$ , with a high capacity of  $294 \text{ mA h g}^{-1}$  in the voltage range of 4.0–2.0 V (*vs.*  $\text{Li/Li}^+$ ), served as a good host for the reversible  $\text{Li}^+$  insertion/extraction. UGF acted as both a lightweight scaffold for the growth of  $\text{V}_2\text{O}_5$  NBAs and the current collector. A conductive homogeneous layer of PEDOT (around 15 nm thick) was specially designed with the purpose to facilitate the electron transfer around the  $\text{V}_2\text{O}_5$  and to preserve the whole NBAs mechanical structure during the long term cycling. Meanwhile, the introduction of PEDOT was expected to decrease the polarization of electrodes and prolong the discharge plateau above 3.0 V, which would ultimately give rise to an increased proportion of high-voltage capacity and energy density. Capacity enhancement by the PEDOT coating was confirmed by the charge–discharge curves in Fig. 2d ( $300 \text{ mA g}^{-1}$  is equivalent to 1 C, which is defined as discharging the entire capacity of  $\text{Li}_2\text{V}_2\text{O}_5$  in 1 h at a current density of  $300 \text{ mA g}^{-1}$ ). Apparently, the UGF- $\text{V}_2\text{O}_5$ /PEDOT core/shell electrode exhibited lower charge voltage plateaus and higher discharge voltage plateaus than the UGF- $\text{V}_2\text{O}_5$  sample without PEDOT coating, indicating a higher energy density for the former. Accordingly, the UGF- $\text{V}_2\text{O}_5$ /PEDOT core/shell electrode showed an ultrastable high-rate profile with specific capacities ranging from  $297 \text{ mA h g}^{-1}$  at 1 C to  $115 \text{ mA h g}^{-1}$  at  $80^\circ\text{C}$ , higher than those of its counterpart of UGF- $\text{V}_2\text{O}_5$  (Fig. 2e). The reduction in the charge transfer resistance,  $R_{ct}$ , fitted from the equivalent circuit model that was derived from the electrochemical impedance spectroscopy (EIS) data (Fig. 2f) also explained the high rate capability attributed to the PEDOT coating in the UGF- $\text{V}_2\text{O}_5$ /PEDOT electrode.

Besides LIBs, the Li/S batteries, another important type of batteries, have now attracted significant attention with respect to their possible use as high energy density storage devices in the next generation of power storage systems.<sup>57</sup> The theoretical energy density of Li/S batteries reaches as high as  $2600 \text{ W h kg}^{-1}$ , which is almost three times the energy density of the current LIBs.<sup>58</sup> The problems for Li/S batteries lie in the large volumetric expansion of sulfur upon lithiation, dissolution of lithium polysulfides in the electrolyte, and low ionic/electronic conductivity of both sulfur and lithium sulfide.<sup>59</sup> The ICPs including PANI, PPy, and PEDOT have been subjected to numerous investigations as promising matrices to replace carbon for sulfur entrapment.<sup>60</sup> The ICP/sulfur nanocomposites are capable of forming a complex conductive network and a unique soft and porous structure (Scheme 3), which is beneficial for improving cell performances in terms of long-term cycling stability and high-rate performance.<sup>61</sup>

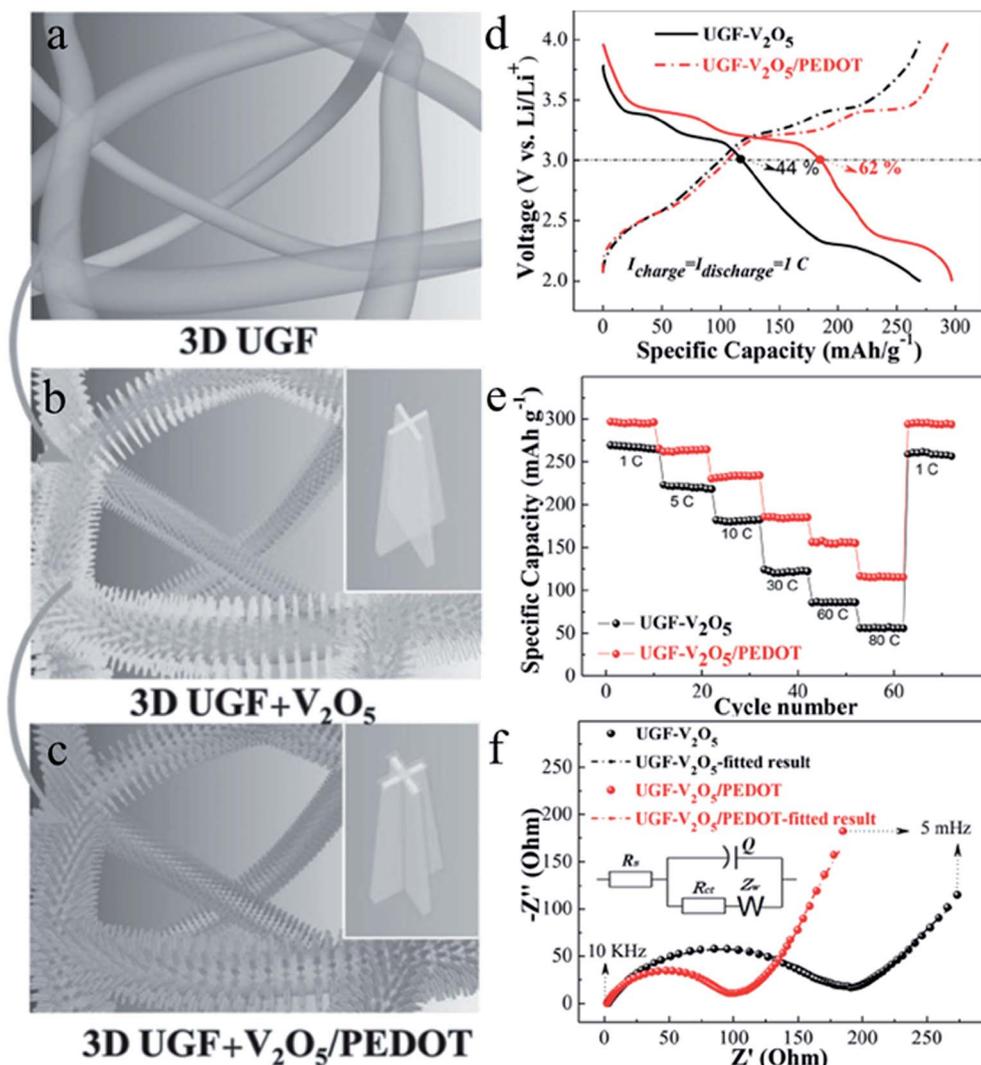
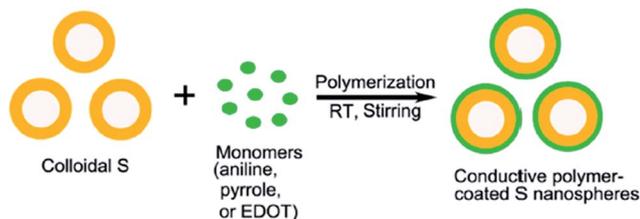


Fig. 2 (a–c) Schematics of the synthesis of the UGF-V<sub>2</sub>O<sub>5</sub>/PEDOT core/shell electrode. (d) Charge–discharge curves measured between 2.0 and 4.0 V at 1 C (ca. 300 mA g<sup>-1</sup>). (e) Rate capability. (f) Nyquist plots at fully charged stage. Inset: a simplified equivalent circuit. R<sub>s</sub>: Ohmic resistance of solution and electrodes, R<sub>ct</sub>: charge transfer resistance, Q: double layer capacitance, Z<sub>w</sub>: Warburg impedance. Reproduced from ref. 56 with permission of John Wiley and Sons.

Another important application for PNCs in EESS is electrochemical capacitors. Owing to their advantages of high energy and power density as well as long cycle life, electrochemical

capacitors have recently spurred extensive research interests for their promising potentials for future systems including portable electronics, hybrid electric vehicles, and large industrial equipment.<sup>62</sup> The electrochemical capacitors are expected to fill in the gap between batteries and conventional electrostatic capacitors, where the former has high energy density but relatively low power density whereas the latter has high power density but too low energy density.<sup>63</sup>

Based on the charge storage mechanism, electrochemical capacitors can be generally classified into two categories: electric double layer capacitors (EDLCs) and pseudocapacitors. For EDLCs, the electrical charge storage/release is based on ion adsorption/desorption at the electrode/electrolyte interface, which is a non-Faradic process. The main electrode materials for EDLCs are from carbon materials including activated carbons (ACs),<sup>64</sup> CNTs,<sup>65</sup> ordered mesoporous carbons (OMCs)<sup>66</sup> and graphene nanosheets (GNS),<sup>67</sup> which are characterized with



Scheme 3 Schematic illustration of the fabrication process of conductive polymer-coated hollow sulfur nanospheres. Reprinted with permission from (ref. 61). Copyright (2013) American Chemical Society.

large specific surface areas (SSA) and good electrical conductivity. EDLCs have the merits of high power density ( $>10 \text{ kW kg}^{-1}$ ) and long cycle life ( $>10^6$  cycles), but are low in energy densities (*i.e.*,  $3\text{--}5 \text{ W h kg}^{-1}$  for carbon based electrode materials).<sup>68</sup>

Different from EDLCs, the energy storage of pseudocapacitors is achieved *via* electron transfer that follows reduction-oxidation (redox) reactions in the material, which is a Faradic process. Typical pseudocapacitor electrode materials include transition metal oxides ( $\text{WO}_3$ ,<sup>69</sup>  $\text{MnO}_2$ ,<sup>70</sup>  $\text{RuO}_2$ ,<sup>71</sup>  $\text{MoO}_3$ ,<sup>72</sup>  $\text{Co}_3\text{O}_4$  (ref. 73) and  $\text{VO}_x$  (ref. 74)) and ICPs (PThs,<sup>75</sup> PPy,<sup>76</sup> and PANI<sup>77</sup>). The problem with respect to transition metal oxides is their relatively high electrical resistance that leads to much lower power density. In comparison, ICPs have relatively high conductivity and low cost, and have attracted significant research interests for electrode materials.<sup>78,79</sup> Particularly, PANI and PPy have received special attention by virtue of their intriguing properties such as facile polymerization in aqueous media or non-aqueous media, good stability in air, low cost, and relatively high electrical conductivity.<sup>80</sup> Compared to EDLCs, pseudocapacitors are high in energy densities but low in power densities.

To achieve better electrochemical performances, considerable efforts have been devoted to exploring innovative PNCs-based electrode materials. Carbon nanofillers including CNFs,<sup>81,82</sup> graphene<sup>83</sup> and metal oxides such as  $\text{MnO}_2$ ,<sup>84</sup>  $\text{SnO}_2$ ,<sup>85</sup>  $\text{MoS}_2$ ,<sup>86</sup> and  $\text{ZrO}_2$  (ref. 87) were reported to be incorporated into the ICP matrixes for electrochemical capacitor electrode applications. Increased electrical conductivity, enhanced mechanical strength, and improved rate capability and cycling stability were obtained due to synergistic effects in the PNCs. These PNCs can be prepared either by *in situ* oxidative polymerization in the presence of the pristine or modified nanofillers<sup>88,89</sup> or by an *ex situ* method.<sup>90</sup> Generally, the former method is more preferred since it minimizes phase separation and ensures a much more conductive network.

Zhou *et al.*<sup>91</sup> reported a supercapacitor electrode material composed of a well-aligned CoO nanowire array grown on 3D nickel foam with PPy uniformly immobilized onto or firmly anchored to each nanowire surface (Fig. 3a). The electrode architecture combines advantages of high pseudocapacitance attributions from both the CoO and PPy, high electrical conductivity of PPy, and a short ion diffusion pathway in the ordered mesoporous nanowires. Both the larger enclosed CV area in the CV curves (Fig. 3b), and longer discharge time in the charge-discharge curves (Fig. 3c), confirm an enhanced supercapacitive performance in the CoO@PPy electrode than CoO. The CoO@PPy electrode also exhibits excellent cycling stability by retaining around 99.8% of the capacitance even after 2000 cycles (Fig. 3d).

### 3 Polymer nanocomposites for energy saving applications

Energy saving is imperative in terms of reduced fossil fuel consumption, less environmental pollution, and improved economy.<sup>92</sup> It is estimated that 30–40% of primary energy has been consumed for heating, cooling, ventilation, and lighting by buildings.<sup>93</sup> Particularly, air conditioners are mainly responsible for energy usage to maintain thermal comfort in buildings. Therefore, it is of significant importance for energy savings to be able to effectively control energy exchange between the interior and exterior of buildings through windowpanes with solar heat control properties.<sup>94</sup> Smart windows are an innovative strategy to achieve this purpose. By modulating the windows' radiative and thermal properties dynamically, smart windows can increase solar heat gain at low temperature and decrease it at high temperature, and therefore are capable of reducing energy consumption and electric demand of buildings. Chromic materials have gained increasing interests for smart window coatings applications.<sup>95</sup> Based on the type of

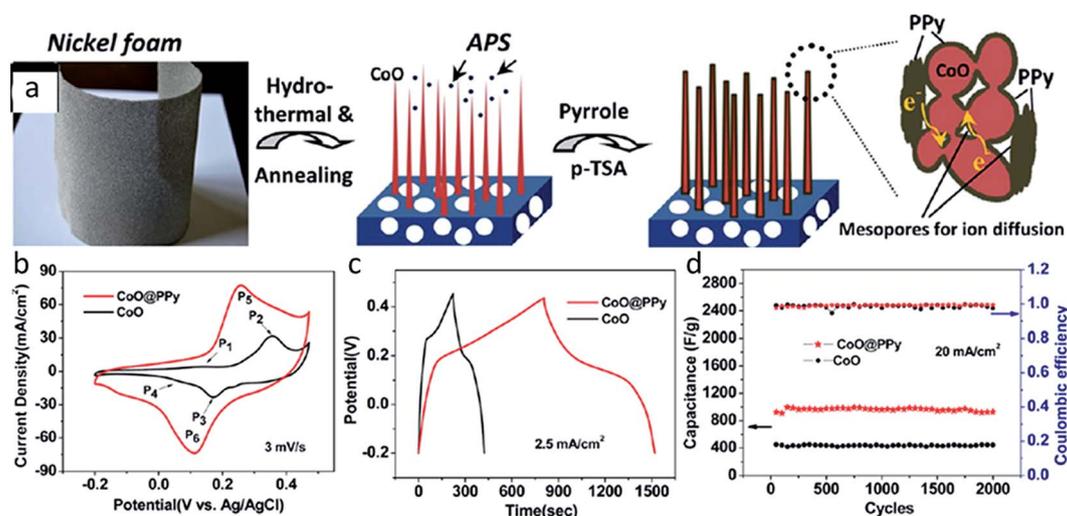


Fig. 3 (a) A representative synthetic procedure and structure details of the 3D hybrid CoO@PPy nanowire electrode. (b) CV curves, (c) charge-discharge curves, and (d) cycling performance of CoO@PPy and the pristine CoO electrodes. Reprinted with permission from (ref. 91). Copyright (2013) American Chemical Society.



Fig. 4 Electrochromism examples in PANI/GO nanocomposite thin films in aqueous solution containing 0.5 M  $\text{H}_2\text{SO}_4$ . Reproduced from ref. 107 with permission of Elsevier Ltd.

external triggering mechanism to perform the modulation in smart windows, chromic materials can be generally divided into four categories: electrochromic (EC, triggered by electricity),<sup>96</sup> gasochromic (activated by hydrogen gas),<sup>97</sup> photochromic (actuated by light),<sup>98</sup> and thermochromic (TC, induced by temperature).<sup>99</sup>

In comparison, EC windows exhibit higher controllability than photochromic or TC windows and do not require a well-controlled gas exchange processes as in gasochromic windows. So far, EC windows have been considered as the most promising technologies and are commercially available and performing well.<sup>100</sup> Herein, polymer nanocomposites based EC materials will be introduced.

Electrochromism, which is defined as a reversible optical change, occurs upon the reduction (gain of electrons) or oxidation (loss of electrons), on the passage of an electrical current after applying an appropriate potential to the electrode material.<sup>101</sup> Electrochromic devices have been under intense study for controllable light-reflective or light-transmissive devices for optical information and storage, anti-glare car rear-view mirrors, protective eyewear for the military, controllable aircraft canopies, glare-reduction systems for offices, and 'smart windows' used in both cars and buildings.<sup>102</sup> Particularly, by controlling the amount of transmitted light and heat radiation, the electrochromism phenomena can greatly reduce energy consumption, lighting expenses and cooling/heating loads, and

therefore hold promising potential for energy saving applications.<sup>103</sup>

Electrochromism in ICPs occurs through changes in the  $\pi$ -electronic character accompanied by reversible insertion and extraction of ions through polymer films upon electrochemical oxidation and reduction.<sup>104</sup> Electrochromic properties of ICPs have gained increasing popularity both from the academia and industry owing to their easy processability, rapid response time, high optical contrast, and the ability to modify their structures to create multicolor electrochromes.<sup>105</sup>

The mechanical degradation and fading electrochemical performance caused by the swelling/shrinking during cycling redox reactions in ICP thin films have imposed a lethal limitation on their applications for their commercialization. To address the problem, Wei *et al.*<sup>106,107</sup> incorporated  $\text{WO}_3$  and graphite oxide (GO) nanoparticles in the PANI matrix. The interfacial interactions between nanoparticles and the polymer matrix help relieve the mechanical stress during the redox reactions and therefore an enhanced stability is achieved. To fabricate the nanocomposite thin films, nanofillers are spun-coated onto the transparent conductive substrate, *i.e.*, indium tin oxide (ITO) glass, and then serve as a platform for the PANI polymers growth *via* a potentiodynamic electropolymerization technique. The composite films display multicolor electrochromism, light yellow at  $-0.2$  V (reduced state), light green at  $0.5$  V, blue at  $0.8$  V (partially oxidized state), and finally dark blue at  $1.0$  V (fully oxidized state), in an aqueous solution containing  $0.5$  M  $\text{H}_2\text{SO}_4$  (Fig. 4).

The electrochromic properties of electroactive polymers synthesized from the monomer of *N,N'*-di[*p*-phenylamino(phenyl)]-1,4,5,8-naphthalene tetracarboxylic diimide (DNNTD), a bis(diphenylamine)naphthalene diimide, have also been studied. Poly (DNNTD) belongs to the class of conjugated conducting polymers with a chemical structural motif of R-X-R, where R represents the diphenylamine (DPA) group and X represents a naphthalene tetracarboxylic diimide (NTCDI) group as the electroactive center. Materials made from this monomer exhibit low dielectric, thermal/oxidative stability,<sup>108</sup> and increased bulk conductivity through  $\pi$ -stacking interactions.<sup>109</sup> Though the electrochemical and optical properties of pure poly(DNNTD) polymer thin films have been widely

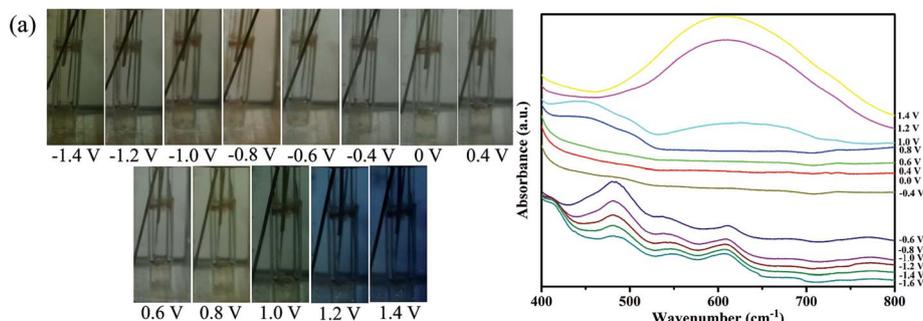


Fig. 5 (a) Color change of poly (DNNTD)/CdSe@Zn nanocomposite thin film. Reprinted with permission from (ref. 111) Copyright (2012) American Chemical Society. (b) Transmittance spectra change of poly(DNNTD)/ $\text{WO}_3$  nanocomposite thin film under applied potentials ranging from  $-1.4$  to  $+1.4$  V in propylene carbonate containing  $1$  M  $\text{LiClO}_4$  as the electrolyte. Reprinted with permission from (ref. 112) Copyright (2012) American Chemical Society.

investigated and well elucidated by cyclic voltammetry, UV-Visible spectroelectrochemistry, and electrochemical quartz crystal microbalance (EQCM),<sup>110</sup> polymer-based poly(DNTD) nanocomposite thin films for electrochromism applications have not been fully explored. Pioneering work on hybrid electrochromic nanocomposite thin films consisting of poly(DNTD) and core@shell CdSe@ZnS quantum dots (QDs)<sup>111</sup> or WO<sub>3</sub> (ref. 112) has been conducted. The nanocomposite films display multichromism at a broad working potential from -1.4 to 1.4 V in propylene carbonate organic solvent (Fig. 5a). Color switching is attributed to structure change at different potentials, as evidenced by changes in the absorbance spectra (Fig. 5b). Compared to PANI-based nanocomposites investigated in aqueous solution, poly(DNTD) exhibited a much higher working window in an organic medium and more color switching. Much more exiting work such as poly(DNTD) operated in different organic media (*i.e.*, propylene carbonate, ionic liquids, *etc.*) and the potential commercialization of poly(DNTD)-based electrochromic devices is anticipated.

Another promising application of PNCs for energy saving is carbon dioxide (CO<sub>2</sub>) capture. The increase in atmospheric CO<sub>2</sub> has been linked to increasing use of fossil fuels over the past century. Post-combustion capture has the greatest near-term potential of reducing CO<sub>2</sub> emissions. Removal of CO<sub>2</sub> can be achieved *via* solution absorption, solid sorbents, membrane separation, and cryogenic processing methods.<sup>113</sup> Solution absorption, or amine-based regenerative chemical absorption processes, have been widely practiced for several years for CO<sub>2</sub> capture from gas streams in natural gas, refinery off-gases and synthesis gas processing.<sup>114</sup> Aqueous amine solutions, such as monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP), are usually used for the absorption. 20–30 wt% aqueous MEA is currently used in the state-of-the-art process. However, the concern over this process is the high energy needs arising from the high regeneration energy requirements, which therefore reduces the implementation of the MEA process for CO<sub>2</sub> capture from the flue gas of coal-based power plants. Adsorption processes have been considered as a promising alternative separation technique for CO<sub>2</sub> capture from flue gas streams of coal-based power plants to mitigate global warming problems. Conventional physical sorbents include carbon sorbents, zeolite sorbents, carbon molecular sieves, metal-organic frameworks (MOFs), porous polymers, and nanoclays.<sup>115,116</sup> To overcome the problem of low CO<sub>2</sub> adsorption capacities at relatively low CO<sub>2</sub> partial pressure and lower selectivity toward CO<sub>2</sub> associated with physical sorbents, surface modification is necessary to incorporate basic sites such as alkaline carbonates and various amine groups, which are capable of interacting strongly with acidic CO<sub>2</sub>, in the chemisorbents.<sup>117</sup> PNCs based on polymers with rich amine groups also have been explored for CO<sub>2</sub> capture; for example, PANI incorporated with MWNTs<sup>118</sup> or magnetites,<sup>119</sup> and polyethylenimine with magadiite (a hydrous sodium silicate mineral with a formula of NaSi<sub>3</sub>O<sub>13</sub>(OH)<sub>3</sub>·4(H<sub>2</sub>O)) grafted with amine groups.<sup>120</sup> These solid sorbents were reported to demonstrate a higher CO<sub>2</sub> adsorption capability than other

solid sorbents, which is attributed to chemical interactions between CO<sub>2</sub> and the amine groups in polymer chains.

Membrane technology offers numerous advantages over solvents and solid sorbents, such as absence of a regeneration step, small footprint, low capital investment, no moving parts, ease of installation, low environmental impact, ease of scaling up, and ease of testing new membrane products as materials innovation emerges. Dense polymeric membranes have also been widely used for gas separations due to differences in permeation properties between adsorptive using membranes.<sup>121</sup> Especially, polymers with a solubility parameter equalling to 22 MPa<sup>0.5</sup> and ether oxygen linkages in their backbones are promising candidates for the fabrication of reverse selective membranes to separate CO<sub>2</sub> from light gases. Poly(ether-*block*-amide) (PEBA), a block copolymer of polyamide (PA) and polyether (PE), is a promising membrane material for CO<sub>2</sub> separation. However, PEBA membrane has a trade-off between gas selectivity and permeability. The problem can be addressed by incorporation of a nanofiller phase (carbon molecular sieves,<sup>122</sup> MOFs,<sup>123</sup> and MWNTs<sup>124</sup>) into the polymeric matrix. Ghadimi *et al.*<sup>125</sup> fabricated PEBA/SiO<sub>2</sub> nanocomposite membranes and found that *cis*-9-octadecenoic acid (OA) can be used for surface modification of the SiO<sub>2</sub> nanoparticles to restrict their agglomeration within the polymeric matrix.

## 4 Polymer nanocomposites for anticorrosion applications

Corrosion, which usually involves the oxidation of metals (*i.e.*, alloys of iron and aluminum) and the reduction of oxygen, protons (H<sup>+</sup>) and/or water, has imposed a major impact on economics of industrial nations.<sup>126</sup> Therefore, corrosion protection has become an issue of prime importance especially in the modern metallic finishing industry.<sup>127</sup>

Conventional organic coatings or paints, including polyvinyl butyral, acrylic polyurethane, vinyl, epoxy and baked phenolic containing zinc chromate or strontium chromate, are commonly used to protect metallic substrates from corrosion.<sup>128</sup> It is generally established that the coatings provide a barrier blocking the passage of oxygen and water and also increase the resistance of ion movement at the metal/electrolyte interface.<sup>129</sup>

Recently, intrinsically conductive polymer nanocomposites using PANI, PPy, polythiophene and their derivatives have become a topic of current interest for corrosion prevention of iron, steel and other metals owing to their superior performance in highly aggressive environments and their eco-friendly characteristics.<sup>130</sup> The presence of nanoscale fillers in nanocomposites significantly improves the barrier properties and prolongs lifetime of organic polymeric coatings. To explain the anticorrosive properties of ICP nanocomposite coatings, different mechanisms have been proposed. From a study of anticorrosive PANI coatings onto a steel substrate, Debberly and Wessling demonstrated that anticorrosion protection can be achieved by an anodic protection mechanism; for example, the generation of an iron oxide layer (Fe<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) with high protection ability on the interface of steel and PANI.<sup>131</sup>

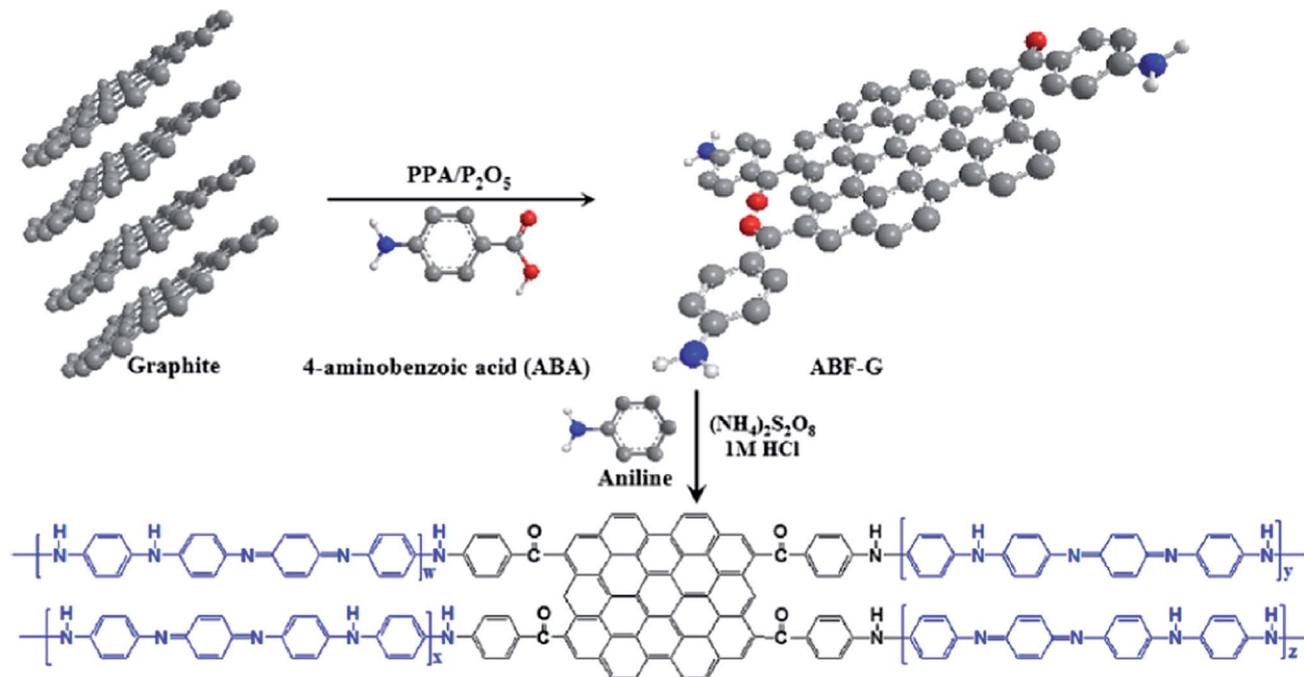


Fig. 6 Preparation of PANI/graphene nanocomposites (PAGCs). Reproduced from ref. 133 with permission of Elsevier Ltd.

It is also proposed that the corrosion process can be slowed down or prevented by a generated electric field by doped conducting polymers, which restricts the flow of electrons from the metal to the outside oxidizing species.<sup>132</sup>

Chang *et al.*<sup>133</sup> reported using PANI/graphene nanocomposites (PAGCs) for corrosion protection of steel. Graphite was exfoliated and then treated with 4-aminobenzoic acid (ABA) to obtain the conductive filler, 4-aminobenzoyl group-functionalized graphene-like sheets (ABF-G). ABF-G acts as versatile platform for polymer grafting that promotes better dispersion of the graphite within the polymer matrix. PANI/graphene nanocomposite (PAGC) was then obtained by the *in situ* chemical oxidative polymerization of aniline monomers at different loadings of ABF-G (Fig. 6). The PAGC displays a reduced corrosion rate evaluated in an aqueous electrolyte containing 3.5 wt% NaCl. Enhanced anticorrosive performance in PAGCs is attributed to a relatively higher aspect ratio of ABF-G nanofillers, which is believed to increase the tortuosity of diffusion pathways and therefore to more effectively prevent H<sub>2</sub>O and O<sub>2</sub> from accessing the metal substrate surface. However, the lower protection efficiency in these ICP nanocomposites (around 50%) still needs to be improved in comparison with the anticorrosive polyurethane nanocomposite coatings (around 97%).<sup>134</sup>

More recently, researchers have been paying more attention to smart anticorrosive coatings with self-healing properties, which are promising to address the challenges existing in current conventional coatings, for example, the susceptibility to cracks that are difficult to detect and high cost associated with maintenance.<sup>135</sup> The micron/nano capsules, that is, particles containing a core (solid, droplet of liquid, or gases) surrounded by a coating layer or a shell,<sup>136</sup> are firstly uniformly distributed

to the protective coating. By releasing active agents in a controllable manner from micron/nano capsules triggered by a local environment change (pH, wettability, heat) or other impact (mechanical induction), the smart coatings can prevent cracks propagation and heal the cracks in the protective polymer coatings (Fig. 7). So far, different types of micron/nano containers, *i.e.*, organic polymer coatings,<sup>137</sup> inorganic clays,<sup>138</sup> mesoporous silica nanoparticles,<sup>139,140</sup> and polyelectrolyte multilayers,<sup>141</sup> *etc.*, have been reported. Healing agents encapsulated by micron/nano containers can be either polymerizable components, for example, unsaturated vegetable oils,<sup>142,143</sup> dicyclopentadiene<sup>144–146</sup> and epoxy<sup>147,148</sup> or inhibitors with nitrogen-containing organics such as azole groups, amines, and amino acids.<sup>149</sup> Given increasing concerns over environment and limited reserves of fossil fuels, green and innovative smart coating systems based on sustainable and renewable energy sources, for example, vegetable oils, will gain more attention. Meanwhile, incorporating other functionalities such as self-cleaning, anti-dusting, and anti-fouling properties into smart self-healing coatings will be promising for fabricating advanced coatings with combinatorial healing abilities and multifunctional properties.<sup>150</sup>

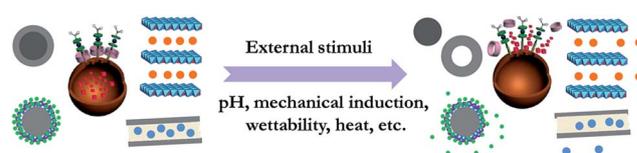


Fig. 7 Smart self-healing micron/nano containers by releasing active compounds to heal cracks in the coating in response to external stimuli. (Reprinted from ref. 150).

## 5 Conclusions and perspectives

Polymer nanocomposites used for energy storage, energy saving, and anticorrosion applications have been reviewed here. ICP nanocomposites have been attracting more research interest for their good electrical conductivity, low cost, easy processability, and environmental friendliness. Nanofillers such as graphene are emerging as promising candidates for nanocomposites. Significant progress in processing, characterization, and modeling of nanostructured materials has opened great opportunities for engineering properties of PNC systems. However, there are still many challenges that remain unaddressed. The first one regards the limited availability of high-quality nanofillers, their high production cost, and difficulty to scale up. The second challenge is related to the processing of PNCs. Careful control of dispersion and orientation of the nanofillers is crucial to optimize PNCs performances. The third challenge is lack of an in-depth understanding and predictive capability of the key process-structure-property relationships, which are required to fully utilize the commercial potential of these novel materials. The models developed often fail to predict experimental results. Meanwhile, from the point of view of sustainability, more research efforts are needed on developing novel polymer nanocomposites from clean, sustainable, and renewable energy sources.

## Acknowledgements

This work is financially supported by University of Tennessee start-up grant, National Science Foundation -Nanomanufacturing (Grant Number: NSF CMMI 13-14486); Nano-scale Interdisciplinary Research Team and Materials Processing and Manufacturing (Grant Number: CMMI 10-30755); and Chemical and Biological Separations (Grant Number: CBET 11-37441) USA, National Natural Science Foundation of China (31200439), National Science Foundation of Guangdong Province, China (10451030007004610).

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