ABSTRACT

Spintronics is gaining recognition as a promising alternative to traditional electronic devices by utilizing spin degree of freedom than charge currents. Despite this potential, the current state-of-the-art non-magnetic metals and heavily doped conjugated polymers, which are essential for effective spin manipulation, are plagued by fundamental performance and stability issues when converting spin currents into transverse electrical currents through the Inverse Spin Effect (ISHE). The rapid development of radical polymers has spanned a wide range of applications in energy storage and electronic systems. Despite their promising attributes, their potential for spin transport has not been extensively explored. These polymers, distinguished by their unique radical-radical exchange interactions and paramagnetic properties, could play a pivotal role in advancing spintronic technologies. Nevertheless, their spin transport capabilities have remained largely overlooked in contemporary research. This oversight presents a substantial gap in the literature, underscoring the need for a focused and rigorous investigation into their properties. This dissertation aims to address these gaps by utilizing various radical polymers in multiple spintronic devices and establishing structure-function relationships that advance our fundamental understanding of spin transport in these materials.

In the initial phase of this study, the spin transport properties of a nonconjugated radical polymer known as poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO) were examined. PTEO exhibited a notable spin-filtering capability, resulting in a significant giant magnetoresistance (GMR) effect of approximately 80% at 4 K. This substantial GMR is facilitated by the combination of its high electrical conductivity, its topology, the efficient and rapid radical-radical exchange interactions, and the robust magnetic interactions of the radical polymer at the interface with ferromagnetic electrodes. Moreover, under ferromagnetic resonance spin pumping conditions, these exchange interactions play a crucial role in facilitating the propagation of pure spin currents. This dynamic process resulted in extremely large effective spin mixing conductance (~ 1019 m–2) and spin diffusion lengths (~ 90 nm) that rivals the high-performing inorganic and metallic systems. The effect of radical content on spin transport was also investigated, establishing a direct correlation between ISHE voltages and radical loadings. This study is the first-ever-demonstration of spin transport in nonconjugated radical polymers and provided exciting insights

on spin transporting capabilities of radical polymers and fundamental mechanisms that govern transport in these systems.

Building upon these findings and motivated by radical polymer design rules, we synthesized new nonconjugated radical polymer named as poly[3-(4-(1-(3-methoxy-2-methylpropyl)-1H-1,2,3-triazol-4-yl)phenyl)-1,5-dimethyl-1H-1,2λ2,4,5-tetrazin-6(5H)-one], poly(verdazyl ethylene oxide) (PVEO) to further deepen our understanding of spin transport in radical polymers. Temperature-dependent ISHE measurements and spin pumping experiments revealed that spin diffusion lengths in radical polymers remain unchanged across wide range of temperature, indicating that exchange interactions between radicals predominantly govern spin transport. This contrasts with conventional conjugated polymers, where spin currents typically involve a combination of hopping and exchange mediation mechanisms. Additionally, the observation of longer spin diffusion length (~ 100.5 nm) compared to previous system suggested that radical-radical alignment could assist the successful transfer of spin angular momentum. This provided further design rules of radical polymers pertaining to spintronic applications. Motivated by this, we further investigated the role of radical-radical alignment in propagating spin currents and this was achieved leveraging stereoselective cationic polymerization to design a polymer with stable persistent radical in each repeat unit. After comprehensive material and device characterization, we showed that isotactic radical polymers with well-defined radical-radical alignment exhibited longer spin diffusion length compared to the atactic radical polymer. These findings reveal that polymer stereochemistry can be readily utilized to design these materials to meet spintronic device standards and such an ease in synthetic modularity is not readily available from conjugated polymers.

To summarize, this dissertation presents compelling evidence of exchange-mediated spin transport in radical polymers and proposes potential design principles to improve the spin transport characteristics of radical-based materials. Furthermore, these findings provide a pathway for future directions in utilizing these polymers in vast majority of thermoelectric and spin caloritronics applications.