Charge transfer of carbon nanomaterials for efficient metal-free electrocatalysis

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Abstract
Recently, carbon-based metal-free electrocatalysts (C-MFECs) have drawn considerable research attention because of their attractive physicochemical characteristics, cost-effectiveness, and ability to convert and store energy efficiently. Efficient intramolecular charge transfer among different parts of the carbon electrocatalyst and/or intermolecular charge transfer between electrocatalyst and electrolyte dictate the ultimate energy conversion performance. Experimental results and theoretical analyses have demonstrated that rational design of metal-free carbon nanomaterials, coupled with proper intramolecular charge transfer through heteroatom doping, incorporation of Stone–Wales defects, and/or intermolecular charge transfer through adsorption of appropriate molecules/moieties, can promote efficient electrocatalysis. In this article, we will first provide the related theoretical principles and then present an overview on the rational design and development of C-MFECs for efficient charge transfer, followed by elucidating charge-transfer processes for different electrocatalytic reactions related to renewable energy conversion and environmental remediation technologies. Finally, the current challenges and future perspectives in this exciting field will be discussed.

KEYWORDS
carbon, catalyst, charge transfer, defect, doping

1 | INTRODUCTION
Effective charge transfer in carbon-based nanomaterials can be caused by inhomogeneous charge distribution induced by adsorbing ions and electron-accepting/donating molecules on the carbon lattice or by incorporating defects and/or heteroatoms having a different electronegativity from that of carbon atom into the carbon structure.\(^1\) When heteroatoms are doped into carbon nanomaterials, the bonding strength is governed by their relative electronegativities. Similarly, an adsorbed molecule or ion containing heteroatom(s) of an electronegativity different from that of carbon can affect the local electronic energy density at the adsorption site on the surface of carbon nanomaterials.\(^2\) The local electronic configuration of a crystalline solid, like graphitic carbon, can also be tuned temporarily by applying an electric or magnetic field, which gives rise to numerous interesting functional applications. This can also be achieved by introducing heteroatoms into their lattice through substitutional doping or simply by adsorbing appropriate molecule(s) or atom(s) on their surfaces.

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Even after numerous reports on heteroatom-doping and/or adsorption-induced intramolecular and intermolecular charge-transfers favorable for various electrochemical and catalytic reactions, the rational design principles and in-depth understanding of the underlying mechanisms are essential for further advancement of carbon nanomaterials based technologies, including carbon-based metal-free electrocatalysis.\[^5\text{-}7\]

Doping of heteroatom(s) into a carbon lattice has been demonstrated to deteriorate its charge carrier transport characteristics.\[^1\text{-}3\]

Therefore, adsorption-induced intermolecular charge transfer in carbon nanostructured materials are more attractive due to its simplicity in fabrication and promise for large-scale production with sustained transport properties.\[^6\text{-}9\] Furthermore, the electronic modulation of carbon nanomaterials induced by physical adsorption is even more favorable as compared to chemical adsorption. Unlike chemical adsorption, Carbon surfaces with physically adsorbed moieties can easily be recovered. In this paper, we present a systematic overview on the efficient charge transfer processes associated with carbon nanomaterials by heteroatom-doping and also through atomic or molecular adsorption with an emphasis on the interfacial charge transfer in layered carbon structures. Methods for heteroatom-doping and adsorption-induced charge transfer and related functional applications are summarized in a comprehensive manner. A special focus is given to charge transfer induced by physical adsorption and the corresponding theoretical understanding. Current challenges and future perspectives concerning charge-transfer-based carbon nanomaterials for metal-free electrocatalysis are also discussed.

## 2 THEORETICAL ASPECTS OF INTERMOLECULAR CHARGE TRANSFER VERSUS CHARGE MIGRATION

The intermolecular charge transfer is the driving force for various catalytic and electrochemical reactions and therefore it should be well understood at the fundamental level. Electronic charge migration is the fundamental process in which a time-dependent charge-density oscillation, including pure electronic dynamics originating from electronic coherence, takes place.\[^10\]

Charge migration occurs in the attosecond time scale (\(10^{-18}\) of a second), and, therefore, its experimental observation requires very sophisticated laser systems.\[^11\]

Recently, Kraus et al.\[^12\] have observed the modulation and manipulation of attosecond charge migration in the iodoacetylene cation. Other theoretical studies have revealed a general coherence window, indicating that strong-field ionization by 800-nm fields could trigger charge migration with periods down to \(-1\) fs (\(10^{-15}\) of a second).\[^13\]

On the other hand, charge transfer refers to a process that involves in permanent relocation of charge from a donor to an acceptor. Charge transfer could occur between two different atomic sites within a molecule, two different molecules, the central atom and a ligand in metal complexes, an atomic or a molecular solute and a solvent, different sites within a nanoparticle, or between two nanoparticles.\[^14\] For simplicity, charge transfer can be classified into intramolecular charge transfer (within a molecule) or intermolecular charge transfer (between two molecules or more).\[^15\] Intermolecular charge transfer was classically conceived by Marcus\[^16,17\] back in 1955, which was recognized by the 1992 Nobel Prize in Chemistry. It was proposed that for intermolecular charge transfer between two interacting molecules to occur, only a slight overlap of the electronic orbitals is necessary. Charge transfer takes place when the system advances from an initial state of “charge on the donor” to a final state “charge on the acceptor,” through a reaction coordinate, as presented in Figure 1. Such evolution is usually driven by an energetic stabilization and is most frequently described by classical laws for reaction rates. According to Marcus theory, the rate of charge transfer is given by Equation (1),

\[
\begin{align*}
\kappa_c &= A e^{-\frac{\Delta E}{k_B T}}.
\end{align*}
\]

The prefactor, A, depends on the nature of charge transfer (e.g., intramolecular or bimolecular) and Gibb’s free energy for activating the molecule or activation energy (\(\Delta E\)), which can be expressed as:

\[
\Delta E = \frac{\lambda}{4} \left( 1 + \frac{\Delta G^0}{\lambda} \right)^2,
\]

\(\Delta G^0\) is Gibb’s free energy for the reaction (values zero for a self-exchange reaction) and \(\lambda\) is a reorganization energy (this energy is required to help the reactants to acquire the same nuclear configuration as the products without any electron transfer, as shown in Figure 1, related to a solvational (\(\lambda_s\)) and vibrational (\(\lambda_v\)) contributions as \(\lambda = \lambda_s + \lambda_v\).

In a two-sphere model of the reactants, the solvational reorganization term \(\lambda_s\) is expressed as:

\[
\lambda_s = (\Delta e)^2 \left( \frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left( \frac{1}{D_{op}} - \frac{1}{D_s} \right),
\]

\(a_i\) and \(D_{op}\) are the radius and the distance between the two atoms, respectively, and \(D_s\) is the dielectric constant of the solvent.\[^3\]

Therefore, the rate of charge transfer is given by Equation (2),

\[
\begin{align*}
\kappa_c &= A e^{-\frac{\Delta G^0}{k_B T}}.
\end{align*}
\]
where, $a_1$ and $a_2$ are two ionic radii, $R$ is the center-to-center separation of the reactants, $D_s$ and $D_{op}$ are the static and optical dielectric constants of the solvent, and $\Delta e$ is the transferred charge.

The vibrational reorganization term $\lambda_v$ can be written as below:

$$\lambda_v = \frac{1}{2} \sum_j k_j \left( Q_j^r - Q_j^p \right)^2,$$

where, $Q_j^r$ and $Q_j^p$ are the values for the $j$th normal mode coordinate $Q$ after equilibrium, and $k_j$ is a reduced force-constant $2k_j^r k_j^p/(k_j^r + k_j^p)$ associated with it, and the superscripts $r$ and $p$ refer to the reactants and the products.\textsuperscript{[16,17]} Marcus theory emphasizes the rate of the overall charge-transfer process, including structural and electronic rearrangements, but does not tailor with any type of coherence (electronic or vibrational). Therefore, the time scale of charge transfer presented by the Marcus theory is limited only to that of nuclear motion, that is, several tens of femtosecond, but in many practical cases, charge transfer occurs in a microsecond time scale, or even at a much slower rate. However, Marcus theory can guide us for understanding the importance of coherence in charge transfer that has recently been reported through few experimental observations. Examples include the electronic coherence that was solicited to explain the quantum beats for charge-transfer oscillations in photosynthetic complexes.\textsuperscript{[18]} The quantum beats observed in photovoltaic blends were also tailored to the combined electronic and nuclear coherences.\textsuperscript{[19]}

Quantum mechanical considerations accounting for the nonadiabatic effects and tunneling through the barrier modify the electron transfer rate proposed classically by Marcus as follows:\textsuperscript{[20]}

$$k_{ct} = Ae \left[ \frac{(\Delta G^e + J)^2}{4k_B T} \right],$$

with a nonlinear expression of the prefactor

$$A = \frac{2\pi |J|^2}{\hbar \sqrt{4\pi \lambda k_B T}},$$

where, $J$ is related to the electronic coupling of donor and acceptor.\textsuperscript{[20]} Interestingly, nonlinear behavior is therefore anticipated for the dependence of the electronic transfer rate on the driving force for the forward transfer, that is, the reaction-free energy.

Very recently, a prolonged charge-separated state was visualized while two electrons were accumulated on the charge acceptor in a molecular system.\textsuperscript{[21,22]} The accessibility of two redox equivalents and related long lifetime of the charge-separated state ($\sim$870 ns) designate this system very promising for the artificial photosynthesis, such as water oxidation and/or CO$_2$ reduction.\textsuperscript{[1,6]} In fact, proper expression of electronic or vibronic coherences during charge transfer needs a quantum-mechanical analysis that overtakes the classical Marcus theory. Furthermore, ionization-induced charge migration triggers a coherent superposition among multiple electronic states for the cation, which in turn initiates motions of nuclear wave-packet for every electronic state, resulting in dephasing of electronic dynamics.\textsuperscript{[15,23,24]}

Therefore, for understanding the permanent charge transfer, a mechanism of electronic decoherence or dephasing aided by the nuclear motions must be conceived. Henceforth, electronic charge transfer may not be completely independent of electronic charge migration. Therefore, the effects of electronic coherence on charge transfer, the lifetime of such electronic coherences accompanied by the nuclear motion, and their influences on the nuclear dynamics must be established to clearly formulate and perhaps control effective charge transfer for advanced technological applications. Prosperity in experimental set-ups with high-harmonic sources for highly accurate time-resolved characteristics in the soft
X-ray domain and the free-electron-laser sources for acquiring those in the hard X-ray region can culminate in enormous advancement in X-ray spectroscopy to realize attosecond/femtosecond spectroscopy and to unravel charge migration and transfer in near future.\(^{[25-29]}\) Below, we will focus on the charge separation and transfer within carbon nanomaterials induced by heteroatoms doping of and molecular adsorptions on carbon-based metal-free electrocatalysts (C-MFECs).

### 3 | Charge Transfer in Carbon Nanomaterials

Among three basic types of carbon materials, namely amorphous carbon, diamond and graphitic carbon, graphitic carbon nanomaterials with conjugated structures have been widely used for various applications.\(^{[30,31]}\) While the delocalized \(\pi\) electrons along the graphitic plane can provide highly conducting properties for graphitic carbon nanomaterials,\(^{[31,32]}\) the graphitic carbon lattice with a homogenous electronic state is not catalytically active. Henceforth, various techniques have been applied to form inhomogeneous electronic states, which include heteroatom(s) doping, defect incorporation, allotropic hybridization, and adsorption.

#### 3.1 | Heteroatom doping induced charge transfer

Doping of graphitic carbon networks by heteroatoms having a size and/or electronegativity different from that of a carbon atom can impose electronic modulation through charge redistribution and/or transfer across the graphitic basal plane.\(^{[1-3,33]}\) Thus, heteroatom-doping of graphitic carbon materials is capable of imparting new optoelectronic properties and can induce catalytic activities through doping-induced charge transfer. Since its discovery in 2009,\(^{[34]}\) therefore, heteroatom(s) doping of graphitic carbon lattices has been widely performed to activate graphitic carbon materials for catalytic applications.\(^{[1-3,33-38]}\) In general, the ultimate electrochemical and catalytic performance of heteroatom-doped carbon nanomaterials depends strongly on the relative charge transfer or separation at the doped sites, which is also greatly influenced by their synthesis and heteroatom doping methods. Owing to the considerable difference in electronegativity between N (3.0) and C (2.5) atoms and their similar sizes with a minimized structural distortion upon doping, N-doped carbon materials have been demonstrated to be efficient for numerous electrocatalytic reactions.\(^{[33]}\) When N atoms are incorporated as dopants into graphitic carbon materials, partial charge transfer occurs between each of the nitrogen atoms and adjacent carbon atoms in the graphitic lattice.\(^{[39]}\) Thus, the electronic structure of N-doped graphitic lattices is modified only within several lattice spacing of the N-dopant sites to impart favorable energy states for the reactants to overcome the activation energy barrier for catalytic reaction(s). Figure 2 presents the scanning tunneling microscope images and the related dI/dV spectra for an N-doped graphene, showing the modulation in electronic states after N-doping within the graphene lattice.\(^{[39]}\)

It was also found that the N atoms doped within graphitic carbon lattice could form various configurations, such as graphitic-N, pyridinic-N, pyrrolic-N, and N-oxides.\(^{[40]}\) Graphitic and pyridinic-N create marginal influences on the graphene lattice structure due to the similar bond lengths of C–N (1.41 Å) and C–C (1.42 Å).\(^{[41]}\) However, pyrrolic N disrupts the planar structure of graphene significantly. Later, it has also been proposed that the electrons and holes in heteroatom(s) containing carbon-based materials are shared by neighboring carbon atoms to enhance the charge mobility and conductivity.\(^{[42,43]}\) As an illustration, each graphitic-N atom in N-doped graphene can impart ~0.5 electron to the \(\pi\) network of graphene lattice, making it a n-type semiconductor. In contrast, pyrrolic and pyridinic N are formed at the defect sites and impose p-type doping effect by taking electrons away from the neighboring C atoms in the graphene sheet.\(^{[41]}\) Furthermore, a crossover behavior of transition from the p-type to n-type was also observed with an increasing N-doping level in pyridinic and pyrrolic-N dominant carbon lattice, which was attributed to the hydrogenation of pyridinic and pyrrolic N to transform them from the p to n type.\(^{[44,45]}\)

Recently, it has been demonstrated that N-doping at the zigzag edge of nanoribbons can culminate active charge transfer for oxygen reduction reaction (ORR) efficiency superior to the uniform N-doping, which is also supported by ball-milled edge-functionalized carbon platelets.\(^{[46,47]}\)

Due to the difference in atomic sizes and electronic configurations for various heteroatoms, the extent of charge transfer is different for different heteroatom(s) doped in the carbon lattice plane. The content and location of heteroatom-doping also dictate the charge transfer in graphitic carbon materials (e.g., graphene and carbon nanotubes [CNTs]).\(^{[41,43]}\) As such, with the same doping element and content, the electrocatalytic activities of the heteroatom-containing graphitic carbon could differ with the dopant location (e.g., plane or edge) in the carbon lattice. P atom, having a bigger size than that of N and a lower electronegativity (~2.1) than that of C (2.5), while doped into graphene can transfer about 0.21e charge to the graphene lattice.\(^{[42,56]}\) In fact, P dopant overhangs from the graphene plane by 1.33 Å, along with a 24.6% enlargement in the P–C bond length (~1.76 Å).
with respect to the C–C bond (1.42 Å) in the pristine 
graphene.\[41\] For B-doped CNTs, electrons accumulate in 
the vacant 2pz orbital of the B dopant and from 
π* 
electrons of the conjugated C–network, which then 
transfer to the ORR intermediates.\[57\] To get a com-
parative view, the Mulliken electron population on N, S, B, and P-doped graphene has been presented in 
Figure 3.\[58\] Unlike B, N, and P doping, there exists a 
negligible charge transfer in S-doped graphene lattice 
because of the similar electronegativities of S (\( \sim 2.58 \)) and 
C (\( \sim 2.55 \)) atoms.\[59\] However, in contrast to the zero 
electronic spin density of the pristine graphene lattice, 
the mismatch of the outermost orbitals of S and C atoms 
introduces a nonuniform electronic spin density dis-
tribution on the S-doped graphene with a large S–C bond 
length (\( \sim 1.78 \AA \)), which in-turn provides active catalytic 
functionalities to graphene useful for energy conversion 
applications, including ORR.\[42\] First principles density-
functional theory study also revealed that the covalently 
bonded S atoms and oxidized S atoms situated at both the 
zigzag and armchair edges of C-lattice can enlarge the 
electronic spin density considerably compared to the 
graphene nanoplates synthesized through ball milling 
technique.\[60\] In addition, the oxidization of sulfurized 
graphene nanoplatelets further increased their electro-
catalytic activities, owing to 5–10 times increase in the 
magnetic moments.

As one of the most reactive elements, F-doping in 
carbon lattice elongates the C–C bond length to 
1.57–1.58 Å and the C–F bonds stick out of the graphene 
basal plane.\[61\] Theoretical calculations have shown that 
a negative chemisorption energy exists for F doping in 
graphene even when the graphene is fully covered by F 
atoms, which is called fluorographene. Fluorographene 
is known as the thinnest insulating material with a band 
gap of about 3 eV, where the F atoms are covalently 
bonded to sp3 hybridized C atoms, and hence the gra-
phene basal plane is buckled locally because the F

\[FIGURE 2\] Scanning tunneling microscope (STM) imaging of nitrogen dopants: (A) STM image of the most common doping form 
observed on N-doped graphene on copper foil, corresponding to a single graphitic N-dopant. (Inset) Line profile across the dopant shows 
atomic corrugation and apparent height of the dopant (\( V_{bias} = 0.8 \text{ V}, I_{set} = 0.8 \text{ nA} \)). (B) Simulated STM image of graphitic N dopant 
(\( V_{bias} = 0.5 \text{ V} \)), based on density functional theory (DFT) calculations. Also superposed is a ball-and-stick model of the graphene lattice with 
a single N impurity. (C) STM image of N-doped graphene on copper foil showing 14 graphitic dopants and strong intervalley scattering tails. 
(Inset) FFT of topography shows atomic peaks (outer hexagon) and intervalley scattering peaks (inner hexagon, indicated by red arrow) 
(\( V_{bias} = 0.8 \text{ V}, I_{set} = 0.8 \text{ nA} \)). (D) Spatial distribution of N–N distances from eight samples on copper foils with different N concentrations. 
Distributions are all fit well by a quadratic power law (expected error bands in gray) overall length scales, indicating that N dopants 
incorporate randomly into the graphene lattice. (E) \( dI/dV \) curves taken on a N atom (bottom) and on the bright topographic features near 
the nitrogen atom on N-doped graphene on copper, offset vertically for clarity. The top curve is the \( dI/dV \) spectrum taken \( \sim 2 \text{ nm} \) away from 
the dopant. (Inset) Positions where the spectra were taken (\( V_{bias} = 0.8 \text{ V}, I_{set} = 1.0 \text{ nA} \)). Reprinted with permission from Ref. [39] Copyright 
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attachment occurs on both sides of graphene sheet by sandwiching it with two F-layers.\textsuperscript{[41]} Such unique structural modulation introduces a high amount of charge separation within graphene sheets. Furthermore, it was found that O, Cl, Br, and I doping can also efficiently induce charge separation in carbon lattice, though they are comparatively less explored.\textsuperscript{[1,41]} The dopant concentration in a carbon nanomaterial often prescribes the amount of electrons transferred between the dopant atoms and carbon atoms/adsorbed intermediates. Therefore, the dopant concentration should be optimized for the best catalytic performance, which could also be predicted by density functional theory (DFT) calculations. In this regard, super-doping of heteroatoms into carbon nanomaterials would be interesting, which can be easily achieved by replacing F atoms in the fluorographene with other heteroatoms.\textsuperscript{[62,63]}

In addition, doping of carbon nanomaterials with more than one element were found to facilitate the effective charge transfer to enhance the electrocatalytic activity.\textsuperscript{[1,2,33,64–67]} Thus, the codoping and even multidoping of carbon nanomaterials with different heteroatoms became very popular to achieve higher charge transfer amount in various formulations for different electrocatalytic energy conversion applications.\textsuperscript{[1,4,6,33]} It has been indicated that when one electron acceptor element (such as N) and one electron donor element (such as P) are codoped into graphitic carbon structures, they tend to situate close to each other in the carbon lattice, and the related p-electron clouds overlap and interact with each other. Such interaction culminates in high modulation of the electronic structure, resulting in the generation of more active sites on the neighboring carbon atoms in comparison to the graphene doped with a single element only. In fact, dopants with a lower electronegativity than that of C (e.g., B, P, and S) carry positive charges (donor) in C-lattice, and vice versa. Therefore, codoping and even multiple doping of carbon nanomaterials with more than one element have often been utilized to impose efficient charge separation and transfer to impart multifunctional electrocatalytic activities for graphitic carbon materials.\textsuperscript{[4,42,68]}

Heteroatom doping within graphitic carbon backbones can be achieved during synthesis or by...
postsynthesis doping.\textsuperscript{[1,4,40,69]} During the in situ doping process, particular chemical reagent(s) containing the desired heteroatom(s) are combined with precursors of carbon source to synthesize heteroatom(s)doped carbon materials. For instance, heteroatom-doped carbon materials can be synthesized by chemical vapor deposition in heteroatom-containing gas environments mixed with methane, ethane, and/or ethylene as the carbon source.\textsuperscript{[33,40]} Of particular interest, vertically aligned nitrogen-doped CNTs (N-CNTs) were fabricated through pyrolysis (900°C) of iron(II) phthalocyanine (a metal heterocyclic molecule containing nitrogen), in either the presence or absence of additional ammonia (NH\textsubscript{3}) vapor, as the first carbon-based metal-free ORR electrocatalyst.\textsuperscript{[34]} On the other hand, postsynthesis heteroatom-doping is performed by different chemical and electrochemical reactions, including pyrolysis of nanostructured carbon materials with reagents and/or gases flow, and by reactive plasma modification of the carbon materials.\textsuperscript{[1,2]} For instance, N-doping of CNTs was achieved by the postsynthesis method through treating CNTs with N\textsubscript{2} plasma to enhance the ferromagnetism and supercapacitor performance.\textsuperscript{[69,70]} Apart from the in situ N-doping of graphene during the synthesis by feeding N\textsubscript{2} gas, N atoms have also been doped into graphene through other postsynthesis chemical methods.\textsuperscript{[71,72]} Furthermore, other single heteroatoms, such as S, O, P, B, and halogens (e.g., Cl, F, Br, and I), have been doped into carbon materials through other physicochemical techniques. Moreover, codoping of N–S, B–N, N–P, N–F, P–S, and tridoping (e.g., N–P–O, N–P–F) of carbon materials have also been performed to facilitate charge-transfer during electrochemical catalysis.\textsuperscript{[1,2,50,65,66,73]} Although great progress has been achieved on the research and development of C-MFECs within the last 12 years or so, the exact mechanism of doping-induced charge transfer and the nature and location of dopant(s) in heteroatom-doped carbon materials are still not fully understood and controlled. Combined theoretical and experimental studies on the heteroatom-doped active sites and the doping effects on various electrocatalytic reactions could ultimately lead to efficient C-MFECs to replace noble-metal related catalysts in the market place, as demonstrated by various potential applications previously reported\textsuperscript{[1–3]} and to be described in Section 4.

3.2 | Defect-induced charge transfer

Defects in carbon lattice could also promote electron transfer.\textsuperscript{[24]} In particular, the presence of intrinsic topological defects, for example, atomic vacancy, pentagonal-C ring, Stone–Wale defects, and 57/558 grain boundary, in graphene and CNT structures could break the evenness of the charge density distribution by localizing $\pi$ electrons on the nonhexagonal carbon ring or around the grain boundary.\textsuperscript{[42,74]} Moreover, the structural modulation would induce the charge density inhomogeneity at the zigzag edge with respect to the basal plane. As for illustration, a single vacancy locating at the zigzag edge of graphene could enhance the charge density of the neighboring carbon atoms by 0.02 (Mulliken atomic charge)\textsuperscript{[75]} while a 57/558 grain boundary increases the charge density on carbon atoms from the boundary chain even by $\sim$0.1 (Mulliken charge; Table 1).\textsuperscript{[42,75]} The carbon atoms carrying relatively high positive charges can act as potential active sites for electrocatalysis. The defect-induced electron transfer highly depends on the defect (point defect) location and the projection of the nonhexagonal grain boundary. Henceforth, it is conceivable to boost the electrocatalytic activities by analyzing and optimizing the topology and charge density distribution in carbon materials with advanced characterization tools and DFT simulations.

As shown in Figure 4, the transmission across linear defects is well-known to be dependent strongly on their orientation angles.\textsuperscript{[76]} Figure 4A–D present schematic presentations of four different orientations of a 585 extended defect within a graphene ribbon with: $\theta = 0^\circ$, 30°, 60°, and 90° incidence at the defect that indicated different transmission probability as a function of the energy (Figure 4E). This result was attributed to the disruption of particle-hole symmetry due to the defect-induced disruption of the translation symmetry.\textsuperscript{[24]} The stacking of graphene monolayers (such as in bilayer graphene) could also modify the charge and electronic states, as shown in Figure 4F,G.\textsuperscript{[74]} For different energies, there exists a distinct charge wave observed across the interface of the bilayer graphene, along with charge oscillation (charge migration) in between the two layers. Consequently, the related current also oscillates in between those layers. Interestingly, when the charge and current densities in each layer were compared, a distinct imbalance was observed because the electronic charge density and the current density are commonly concentrated on different parts of the graphene bilayer. For the high energy transmission ($E = 0.2$ eV), a clear phase relation with the highest current density spatially overlapping with the highest charge density was observed.\textsuperscript{[74]} It was also reported that a room temperature superconductivity appears when two monolayer graphene sheets are stacked at the magic angle (1.1°).\textsuperscript{[77]} Such observations are sufficient to rationalize the design principles for developing carbon nanomaterials for efficient electrochemical catalysis by modulating their structure, and hence the related electronic and catalytic properties.
| Method          | Structure                   | Charge transfer amount | ORR overpotential (V) | OER overpotential (V) | Distance of donor–acceptor (Å) | Refs.               |
|-----------------|-----------------------------|------------------------|-----------------------|-----------------------|-------------------------------|---------------------|
| Doping          | N-doping                    | 1.24                   | 0.445                 | 0.405                 | 1.41                          | [39,41,117]         |
|                 | P-doping                    | 1.39–1.52              | 0.473                 | 0.382                 | 1.76                          | [39,41]             |
|                 | S-doping                    | 0.28                   | 0.582                 | 0.520                 | 1.78                          | [41,117]            |
| Vacancy-defects | Point defect                | <0.2                   | –                     | –                     | –                             | [42,74]             |
|                 | Stone–Wales                 | <0.2                   | –                     | –                     | –                             | [42,74]             |
|                 | Grain boundary              | <0.22                  | 0.32                  | –                     | –                             | [42,74]             |
|                 | Pentagon-C at zigzag edge   | –                      | 0.74                  | –                     | –                             | [78]                |
| Adsorption      | TCNE on armchair edge       | 0.410                  | 1.874                 | 1.465                 | 3.603                         | [53]                |
|                 | TCNE on armchair edge with defect | 0.498             | 1.248                 | 0.496                 | 3.558                         | [42,53]             |
|                 | TCNE on zigzag edge         | 0.506                  | 0.897                 | 0.457                 | 3.635                         | [42]                |
|                 | TCNE on zigzag edge with defect | 0.484             | 0.657                 | 0.452                 | 3.615                         | [53]                |
|                 | O₂ on graphene at 50–60 K   | 0.812                  | –                     | –                     | –                             | [88]                |
|                 | O₂ in presence of CO₂ on graphene at 50–60 K | 0.752       | –                     | –                     | –                             | [88]                |
|                 | O₂ in presence of N₂ on graphene at 50–60 K | 0.862       | –                     | –                     | –                             | [88]                |
|                 | O₂ in presence of N₂ and H₂O on graphene at 50–60 K | 0.826       | –                     | –                     | –                             | [88]                |
|                 | CO₂ on pyridinic-N          | 0.411                  | –                     | –                     | –                             | [98]                |
|                 | NO₂ on single vacancy of graphene | 0.029 (From graphene) | –                     | –                     | –                             | [102]               |
|                 | NO₂ on divacancy of graphene | 0.017 (From graphene) | –                     | –                     | –                             | [102]               |
|                 | NO₂ on tetravacancy of graphene | 0.012 (To graphene) | –                     | –                     | –                             | [102]               |
|                 | F₄-TCNQ on graphene         | 0.3                    | –                     | –                     | –                             | [118]               |

Abbreviations: F₄-TCNQ, 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; TCNE, tetracyanoethylene.
Indeed, recent studies on C-MFECs for efficient ORR in acidic electrolytes have demonstrated the usefulness of the aforementioned defect rationalization for the rational design and development of advanced carbon electrocatalysts.\cite{78–80} Figure 4H,I shows that the pentagonal defects at the edges of HOPG (D-HOPG) hold the lowest work function and the highest onset potential for the ORR in the acidic electrolyte (0.1 M H$_2$SO$_4$) with the highest electrocatalytic current density.\cite{78} DFT simulations revealed that the efficient electron transfer (Table 1) through the D-HOPG sites was the reason for the observed excellent ORR performance.

**Figure 4**: Schematic representation of a linear defect 585 at different orientation angles (A) $0^\circ$, (B) $30^\circ$, (C) $60^\circ$, and (D) $90^\circ$. (E) Transmission probability for each angle. The ribbon has $N = 56$ sites in the width. (F,G) Charge and current density distributions for the nanostructure composed of two graphene (monolayer) ribbons that partially overlapped (AA stacked in the overlap/bilayer region), The two panels stand for two different energies: (F) $E = 0.11$ eV, which corresponds to a low transmission, (G) $E = 0.2$ eV, which corresponds to a maximum of transmission (indicated by the arrows). Reprinted from Ref.,\cite{74} copyright 2015 to American Physical Society. (H) The local work functions were collected from the edge areas of Ar-HOPG, N-HOPG, and D-HOPG. Inset: Scheme of the KPFM test. (I) The LSV curves of Ar-HOPG (red), N-HOPG (blue), and D-HOPG (purple) (for the ORR in 0.1 M H$_2$SO$_4$ solution). Inset: Correlated onset potentials (vs. RHE at 0.05 mA/cm$^2$). Reprinted from Ref.,\cite{78} copyright 2019 to nature.com. Transparent OER catalyst: (J) polarization and (K) stability curves of different transparent graphene/doped graphene films, and (L) OER mechanism through efficient electron modulation and efficient charge transfer in transparent graphene/BN-graphene stacked nanofilm. Reprinted from Ref.,\cite{79} copyright 2020 to American Chemical Society. KPFM, Kelvin probe force microscopy; LSV, linear sweep voltammetry; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; RHE, reversible hydrogen electrode.
3.3 | Adsorption-induced charge transfer

Apart from the heteroatom- or defect-doping assisted charge-transfer mentioned above, efficient charge-transfer can also occur with carbon materials through adsorption of various moieties, such as molecules, ions, and even other carbon allotropes. Depending on the band gap structures, graphitic carbon allotropes can act either as an electron acceptor or donor. For instance, while porphyrins or phthalocyanines are adsorbed on the carbon substrate they acceptor or donor. For instance, while porphyrins or fullerenes or perylene diimide they would donate electrons (Figure 5).[81] Therefore, their electrocatalytic properties could be tuned for a large variety of applications by regulating adsorption-induced charge transfer through either physical or chemical adsorption.

3.3.1 | Physical-adsorption-induced charge transfer

Generally speaking, van der Waals force having strength in between 0.4 and 4 kJ/mol acts in physical adsorption. When an adatom or a molecule is adsorbed on a carbon surface, a transient shift (with respect to the nucleus) in electronic density occurs. Consequently, a transient charge separation is generated for which the nearby carbon atom can either be attracted or repelled. In general, when the interatomic distance of two atoms remains greater than 0.6 nm the force does not become strong enough to be observed, however, the force becomes repulsive for a distance below 0.4 nm.[82,83]

The ultimate influence also depends on the type of adsorbate. It is worth noting that, for electrocatalytic reactions the adsorption of chemical molecules or ions and related charge transfer are crucial, such as O2 adsorption for ORR, OH− anion adsorption for oxygen evolution reaction (OER), CO2 adsorption for carbon dioxide reduction reaction (CO2RR), and N2 adsorption for nitrogen reduction reaction (NRR). For example, BN-codoped graphene is demonstrated to induce efficient OER in graphene layer through interfacial charge transfer while stacked together to form a transparent electrocatalyst, as shown in Figure 4J-L.[79]

For organic molecules (e.g., tetracyanoethylene, TCNE) being adsorbed on graphene, DFT calculations show that there is ~0.44e transferred from graphene to TCNE molecule.[52] Therefore, the neighboring carbon atoms on the graphene plane accumulate relatively high positive charge density, imparting the catalytic activity for electrocatalysis. Similar charge transfer can also occur when a heteroatom-containing graphene layer is adsorbed onto undoped graphene surface. On hybrid C3N4@N-graphene structure, for example, the transferred electrons (0.15e per CN4@N-graphene unit cell) lead to an electron-rich region on the g-C3N4 layer and a hole-rich region on the N-graphene layer. The related electron mobility was significantly increased, which could further promote electrocatalytic hydrogen evolution reaction (HER).[84] It was also revealed by the DFT calculation that amine-based organic molecules promote an n-type doping influence on graphene owing to the decrease in the work function of graphene due to the formation of a graphene–organic complex.[85] However, the adsorption of amine-based molecules onto graphene do not alter its mobility. So far, various polymers (e.g., n-methyl-2-pyrrolidone, hexamethyldisilazane),[66] copolymer (epichlorohydrin-dimethylamine copolymer)[67] and organic and inorganic molecules (e.g., O2, NO, NO2, H2O, CO, CH4, CH3OH, C6H5NO2)[51,88–93] have been adsorbed onto carbon nanomaterials, which, along with carbon–carbon hybrids (e.g., CNT–C60) and carbon–phosphorus hybrid materials, have been used for various potential electrocatalytic applications.[53,94]

Adsorption of chemical molecules is influenced by the presence of defects, edges, and/or heteroatoms on the surface of carbon nanomaterials. Specifically, the edges of nanoporous carbon materials exert dominant interactions with polar molecules (e.g., nitrobenzene).[92] Moreover, micropores played the most important role in the adsorption of nitrobenzene at a low concentration, but meso- and macropores became more important at higher nitrobenzene concentrations.[92] The chirality (e.g., armchair, zigzag) of graphene edges was also reported to influence their ultimate adsorption characteristics (see Table 1).[95] For adsorption on heteroatom-doped carbon materials, CO2 adsorption on N-graphene,[96] polysulfide adsorption on...
C₃N₄, [97] and acetone on N-doped porous graphene have been studied. [54] DFT calculations have demonstrated that pyridinic-N is the most favorable site for CO₂ adsorption with the highest charge transfer of 0.041e to CO₂ molecule. [86] However, Figure 6A,B show that pyrrolic-N configurations on graphene lattice are the only thermodynamically favorable adsorption sites for CO₂ molecules. It was theoretically predicted that O₂ adsorption on graphene at a low temperature (50–60 K) was influenced by the presence of CO₂, N₂, and H₂O molecules adsorbed at the graphene edges. [88] The charge transfer of O₂ (0.812e) was enhanced in the presence of certain coadsorbents (e.g., N₂ [0.862e], N₂ and H₂O [0.826e]), but decreased in the presence of CO₂ (0.752e) adsorbed at the graphene edges attributable to the modulation of magnetic moments (Table 1). [88]

The organic semiconducting molecule of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) was reported to form a continuous and highly ordered PTCDA monolayer on epitaxial graphene in the well-known herringbone arrangement, as evidenced by STM images in Figure 6C. [99] Such herringbone structure of the PTCDA layer is quadrupolar and generally stabilized by hydrogen bonding. The interactions between the PTCDA molecules are thus much stronger than the π-π* interfacial interaction between PTCDA and graphene. [8,99] Moreover, molecular adsorption can also exfoliate graphite into graphene sheets, as indicated in Figure 6D. [100] Besides, C₆₀ molecules adsorbed on single-walled CNT (SWCNT) walls were demonstrated to be efficient C-MFECs for pH universal ORR, OER, and HER while polyelectrolyte adsorbed on the inside wall of multiwalled CNTs (MWCNTs) was effective for ORR in alkaline medium. [94,101] If the adsorption-induced intermolecular charge transfer is coupled with the heteroatom-/defect-doping induced intramolecular charge transfer, the resultant carbon nanomaterials could become highly efficient C-MFECs. [1,2,84]

**Figure 6** Bidirectional Examination of selective adsorption of CO₂ over N₂ by functionalized surface. (A) ΔE_{ads} of CO₂ and N₂ gas molecules, and (B) ratio and difference of adsorption energies. Reproduced with permission from Ref., [98] copyright 2016 to American Chemical Society. (C) The organic semiconductor, 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecules and scanning tunneling microscope images of PTCDA on epitaxial graphene/SiC. Adopted with permission from Ref., [99] copyright 2009 to Nature.com. (D) Interaction between 1-pyrenecarboxylic acid (PCA) adsorbed on graphene. Adapted from Ref., [100] copyright 2010 to American Chemical Society.
The atomic vacancy on carbon lattice is also reported to influence the adsorption properties. When NO₂ molecules interact with the graphene lattice, the oxygen atoms in NO₂ intermingle with carbon atoms in the graphene. When the graphene possesses vacancy defects, however, the electron density gathered on the unsaturated carbon atoms adjacent to the vacancy defect attracts the unpaired electrons in the nitrogen head of NO₂, promoting further the charge-separated region on the defect. In fact, the vacancies generated through the removal of odd-numbered carbon atoms are found to be more favorable for the NO₂-graphene surface interactions than the even atomic numbered carbon vacancies. The carbon atom adjacent to a single vacancy onto graphene lattice provides a strong attractive force to the NO₂ gas molecules with a charge transfer value of 0.029e (from graphene to NO₂) and with a reported magnetic moment of 0.88 μB. Divacant (charge transfer: 0.017e to NO₂) and tetravacant (charge transfer: 0.012e to graphene) graphene systems can be good choices as they facilitate NO₂ gas adsorption with lower binding energies. In addition, the adsorption strength for this system is not as high as that for the monovacant and trivacant graphene, suggesting a promising recovery rate for sensing and electrocatalytic applications. Therefore, controlled manipulation of the vacancy defect type and its density is essential for electrocatalytic applications.

3.3.2 Chemical-adsorption-induced charge transfer

Chemical adsorption or chemisorption occurs with higher binding energy than physisorption on carbon surfaces. A covalent or ionic bond is often created in chemisorption, leading to the formation of a covalent bond between the carbon nanostructure and chemisorbed molecules or ions. Due to the fact that the adsorbed molecules are associated with the surface by valence bonds, they usually possess particular adsorption sites on the carbon lattice and only chemisorbed monolayer is developed. Recently, it has been reported that NO₂ adsorbed chemically onto CNTs can significantly increase the electrical conductance of CNTs due, most probably, to the electron donation to NO₂ associated with fluctuation-induced tunneling of electrons. The CNT conductivity change induced by chemisorption was not recovered even after stopping the NO₂ supply while chemisorption also introduced considerable structural modulation in carbon nanomaterials around the adsorption sites and such corrugated structure was not easily recovered either. Nevertheless, chemisorption has been widely utilized for energy conversion/storage and many other applications, such as chemical sensors and optical switches.

Charge transfer could also occur by covalently bonding amine-functionalized porphyrins (Por-NH₂) to GO via amide formation to yield donor-acceptor hybrid structures, followed by photoexcitation of singlet Por onto the graphene unit, as observed by fluorescence quenching. To increase the adsorption of CO₂, phenylenediamine was covalently grafted onto MWCNTs, as schematically shown in Figure 7A–C. As a result, 0.59 mmol/g of CO₂ was reported to be accumulated by aminated MWCNTs at 303.15 K temperature and 200 kPa pressure, when only 0.17 mmol/g of adsorption capacity was attained under the same conditions on the raw materials. Tetraethylenepentamine-modified CNTs were also reported to increase CO₂ adsorption considerably (3.87 mmol/g). Such modified MWCNTs with the enhanced CO₂ adsorption efficiency can be utilized for electrocatalytic CO₂RR, along with other electrocatalysis because the charged carbon atoms in the covalently functionalized carbon nanomaterials may also provide electrocatalytic active sites for various energy conversion processes.

As shown in Figure 7D, the nitrobenzene group was chemically adsorbed through the formation of a covalent bond onto the graphene sheet. Nitrobenzene acted as a p-type dopant and induced charge transfer onto the graphene lattice, as demonstrated by modulation in Raman spectra. On the other hand, the electrochemical analysis showed that nitrobenzene adsorbed graphene (NB-graphene in Figure 7E,F) demonstrated a higher ORR activity than that of the pure graphene in regard to the onset potential and the limited current density. Furthermore, such adsorption excelled fuel selectivity and durability in graphene as comparable to the commercially available Pt/C catalysts. Graphite-conjugated catalysts produced by conjugating N-doped molecular fragments on the surface of graphitic carbons have exhibited excellent ORR activities and the covalent molecule is reported to be electrocatalytically active for the ORR. Combined DFT calculations and experimental results have revealed that the alpha electrophilic carbon atoms near the pyridinium-N moiety acted as active sites for O₂ adsorption and ORR electrocatalysis. Besides, chemisorption of polysulfides on a carbon fiber paper containing oxygen functional groups has been used for lithium–sulfur batteries.

Undoubtedly, efficient C-MFECs can be produced through intermolecular and interfacial charge transfers. Through proper design to ensure efficient intramolecular, intermolecular, and/or interfacial charge transfers, various C-MFECs have been developed so far to show fruitful ORR, OER, HER, and CO₂RR electrocatalytic activities. However, further research in both experimental and theoretical frontiers are needed, and it is very
crucial to cost-effectively develop advanced carbon-based metal-free electrodes through physical or chemical adsorption to replace noble-metal-based electrocatalysts of practical significance.

### 3.3.3 | Photo-induced charge transfer

Light-assisted electron/charge transfer is another effective way to impart efficient electrocatalytic activities to carbon nanomaterials for various catalysis applications. For efficient light absorption, however, the electronic configurations of carbon nanomaterials need to be modified either by covalent (or chemical) or noncovalent (physical) functionalization. A notable setback of the covalent functionalization relates to the disturbance of the ballistic long-range electron-transport characteristics in carbon nanomaterials. Henceforth, enormous research studies have been performed to develop thermodynamically stable and noncovalently functionalized CNTs, graphene, carbon dots, and their hybrids through van der Waals, hydrophilic–hydrophobic, charge transfer, and/or π–π stacking interactions.\(^{[55,114,115]}\) In principle, some binding motifs for creating hybrids with SWCNTs are shown in Figure 8.\(^{[55]}\)

Preliminary investigation has revealed that small polycyclic aromatic hydrocarbons, for example, pyrenes, are suitable anchors for SWCNT functionalization because of their strong π-stacking abilities. As such, direct stacking of various photosensitizers with an extended π-system helped in the formation of useful charge-transfer hybrid materials.

Very recently, the excited state charge-transfer interactions between SWCNTs and a variety of phenyl, 4-bromophenyl, and thiophene substituted diketopyrrolopyrroles (DPPs) were reported to show about 81% transfer efficiencies for the one-electron oxidization of DPPs.\(^{[114]}\) A similar strategy can be adapted for hybrid porous carbon nanostructures for efficient electrochemical energy conversion and storage devices and integrated energy systems.\(^{[55,114–118]}\)

### 4 | POTENTIAL APPLICATIONS OF CHARGE TRANSFERRED CARBON CATALYSTS

Before advanced applications of C-MFECs will be realized, it is important to identify and understand their active sites and related reaction mechanisms. As
discussed above, doping of heteroatoms into carbon lattice could break down the π conjugated symmetry and the doping-induced charge transfer would lower the activation energy for a catalytic reaction. Apart from the doping-induced charge transfer, the corresponding spin-momentum redistribution also has considerable influence in the catalytic activity.\textsuperscript{[1,38,60]} In fact, DFT calculations have recently revealed that the intrinsic electrocatalytic performance and the ORR mechanism depend strong on triple effects: the charge density, spin density, and coordination state (i.e., ligand effect) of the active sites.\textsuperscript{[119]} These effects act together to increase binding energies of *OOH or *OH in the following order: negative charge effect < positive charge effect < low-spin effect < ligand effect < high-spin effect. For metal-free single heteroatom-doped graphene, such triple effects generate active carbon sites around the doped heteroatom. On each single carbon active site, only the end-on adsorption of *OOH is normally preferred, leading to the ORR following the associative mechanism with an intrinsic limitation in its overpotential of 0.44 V.\textsuperscript{[38,42]} Interestingly, for dual-heteroatom-doped graphene, the aforementioned triple effects are reported to activate double carbon sites and lead the ORR to follow the dissociative mechanism, which rules out the activity limitation in the associative mechanism and further enhances the electrocatalytic ORR activity.\textsuperscript{[119]} Figure 9A–F shows the Bader charge and spin density distribution for B–N, P–N, and S–B codoped-graphene frameworks and the corresponding energy diagrams for ORR following the oxygen dissociation mechanism. Heteroatom-doping-induced active sites have been shown to perform efficient ORR, OER, HER, CO\textsubscript{2}RR, and NRR.\textsuperscript{[1–3]} Figure 9G summarizes various electrocatalytic reactions using C-MFECs, which are often comparable or even superior to their metal counterparts.\textsuperscript{[120]}

Now, graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is very well known for efficient HER.\textsuperscript{[1–3,33]} DFT calculations revealed that the reported high HER activity in N-doped graphene-supported g-C\textsubscript{3}N\textsubscript{4} could be attributable to the electron-transfer-induced strain.\textsuperscript{[84]} Therefore, by tuning small strain (2%–3.5%) in g-C\textsubscript{3}N\textsubscript{4}, Gibb’s free energy for hydrogen adsorption, and hence the hydrogen coverage, can be modified to desirable values, leading to the efficient charge transfer to maximize the HER performance for g-C\textsubscript{3}N\textsubscript{4}.\textsuperscript{[121]} In addition, heteroatom-induced charge transfer has also been reported to generate considerable magnetic momentums to induce spin redistribution in carbon lattice.\textsuperscript{[122,123]} However, graphitic N cannot generate a magnetic moment because of the lack of non-bonding electrons. While pyrrolic and pyridinic N in a graphitic carbon lattice possess a nonbonding electron

\[ \text{FIGURE 8} \quad \text{Single-walled carbon nanotube (in black color) and molecular structures of representative photosensitizers based on phthalocyanines (ZnPc) (in green color), p-extended TTFs (exTTF) (in yellow color), and rylene (in pink and purple colors). Adapted with permission from Ref., [55], copyright 2016 to Elsevier Inc.} \]
FIGURE 9  Bader charge and spin density distribution of the doped-graphene (G) frameworks: (A) N, B–G and N, P–G and (D) S, B–G. For the charge distribution, the color of the balls represents the value of the Bader charge, which increases gradually from blue to red. For the spin density distribution, yellow and blue isosurfaces correspond to positive and negative spin density, respectively, and the isosurface levels are 0.0005 eÅ−3. The energy profile of O₂ dissociation on such doped-G surfaces: (B) N, B–G and N, P–G and (E) S, B–G. Free energy diagram of the ORR dissociative mechanism on the carbon atoms circled in (A) and (D) at the equilibrium potential UNHE = 0.455 V versus NHE: (C) N, B–G and N, P–G, and (F) S, B–G. Reprinted from Ref. [119] licensed under creative commons attribution, Copyright 2018 to The Royal Society of Chemistry. (G) Electrocatalytic activities of carbon-based metal-free electrocatalysts. Adapted with permission from Ref., [120] copyright 2019 to Wiley. ORR, oxygen reduction reaction
pair, however, only pyrrolic N can form π and π* states, which can lead to electronic spin polarization. Henceforth, pyrrolic N can create strong magnetic moments in carbon nanomaterials, whereas pyridinic N has a weak magnetic moment effect. More specifically, it has been found from the theoretical investigation that each pyrrolic N doped at the edge sites of graphene nanoribbons could generate a magnetic moment of 0.95 μB while pyridinic N at the edges created a magnetic moment of only 0.32 μB.\[123\] Besides their applications in spintronics, such magnetic moments could also be useful in manipulating electrocatalytic activities of C-MFECs at the atomic level. Therefore, the fundamental understanding discussed above underpins the potential applications of C-MFECs.

Owing to the simplicity in fabricating the electrodes and attractive performance, physical adsorption-induced charge transfer in carbon nanomaterials has been applied for various electrocatalytic reactions for energy conversion and storage.\[84,94,101,124,125\] including polyelectrolyte (poly(diallyl dimethyl ammonium chloride) [PDDA]) functionalized CNTs for efficient ORR.\[101\] As shown in Figure 10A, the polyelectrolyte chain with positively charged nitrogen (N+) moieties can generate a sustainable network of positive charge on the surface of nitrogen-free CNTs through intermolecular charge transfer, as confirmed by the negative shift of N1s X-ray photoelectron spectroscopy peak to lower binding energy by ~0.5 eV in PDDA-CNTs compared with pure PDDA.\[101\] As a result, the ORR electrocatalytic activity of PDDA-functionalized CNTs was significantly improved compared to that of the pristine CNTs. Recently, PDDA-functionalized CNTs were demonstrated to perform efficient water oxidation reaction (WOR),\[124\] yielding a remarkably lower WOR overpotential of 370 mV at 10.0 mA/cm² with a much smaller Tafel slope of 76 mV/dec with respect to pure CNTs (4520 mV, 166 mV/dec), and even comparable to the benchmark RuO\textsubscript{2} catalyst (360 mV, 137 mV/dec) in 0.1 M KOH. The intermolecular charge transfer between CNTs (donor) and PDDA can not only promote the reaction kinetics and generate active sites but also motivate the reactants (OH\textsuperscript{−}) by electrostatic interaction to act as a buffer layer during the electrochemical reaction.\[124\] In addition, a desirable four-electron reaction pathway for WOR occurred at PDDA-functionalized CNTs with 97% Faradaic efficiency, suggesting the high selectivity towards water oxidation.

Apart from the PDDA-adsorbed CNTs, PDDA adsorbed reduced graphene oxide (rGO) has also been used for ORR in 0.1 M KOH electrolyte.\[126\] Furthermore, poly (3, 4 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) adsorbed rGO was also demonstrated to perform efficient ORR in an alkaline medium.\[127\] In addition, the electron transfer number for ORR at the above polymer adsorbed graphene electrode (PDDA-rGO, PEDOT:PSS/rGO) is always higher than that on the pure graphene electrode and favors a four-electron pathway, which could be attributed to the synergy between the polymer adsorption-induced charge transfer as well as the existing defects in the rGO lattice. Physically adsorbed fullerenes (C\textsubscript{60}) onto SWCNTs have also been demonstrated to act as an excellent electron acceptor to induce intermolecular charge transfer from the SWCNTs. Such efficient intermolecular charge transfer made the metal-free and heteroatom-free C\textsubscript{60}-SWCNT an efficient trifunctional electrocatalyst for ORR, OER, and HER over a wide pH range. Figure 10B schematically shows the mechanism for charge transfer between C\textsubscript{60} and SWCNT.\[94\] The CV and linear sweep voltammetry curves of C\textsubscript{60}-SWCNT in an O\textsubscript{2} and N\textsubscript{2}-saturated KOH solution (0.1 M) are shown in Figure 10C,D. The onset potential of 0.91 V (vs. reversible hydrogen electrode) for ORR is very close to that of the commercial Pt/C catalyst. Figure 10E–I shows the OER and HER performance in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution. As can be seen, C\textsubscript{60}-SWCNT shows about 1.26 V OER onset potential (overpotential of ~420 mV and Tafel slope = 38.4 mV/dec)—overperformed the commercial RuO\textsubscript{2} (~1.28 V onset potential, overpotential = 430 mV, and Tafel slope = 37.4 mV/dec). Moreover, the OER stability of C\textsubscript{60}-SWCNT is also similar (5% change in current density) to that of the RuO\textsubscript{2} catalyst (5.4% change) after 1.5 h in 0.5 M H\textsubscript{2}SO\textsubscript{4}.\[94\] The OER stability in an acidic medium is very challenging in electrocatalysis due to a related high overpotential. In this respect, the OER performance of C\textsubscript{60}-SWCNT is very attractive. No doubt, more research efforts along this direction will further advance the C-MFECs for efficient OER electrocatalysis and beyond.

As mentioned earlier, the combination of heteroatom-doping and adsorption-induced charge transfer can be used to significantly enhance the electrocatalytic performance for C-MFECs. This is clearly illustrated by poly-ethylenimine (PEI)-adsorbed nitrogen-doped CNTs (N-CNTs) for CO\textsubscript{2} reduction reaction.\[125\] In CO\textsubscript{2}-saturated aqueous KH\textsubscript{2}CO\textsubscript{3} electrolytes, it has been demonstrated that the CO\textsubscript{2} reduction products differed significantly for different heteroatom doped C-MFECs, and N-CNT exhibited significantly higher Faradaic efficiencies for formate (59%) than either oxygen-doped CNT (7%) or pure CNT (5%). Furthermore, after PEI adsorption, based on the heteroatom-doping and adsorption-induced charge transfer, PEI/N-CNT electrocatalyst achieved the highest Faradaic efficiency of 87% for formate production with a current density of 9.5 mA/cm². Figure 10J shows the detailed CO\textsubscript{2}RR mechanism for the PEI/N-CNT electrocatalyst, in
which CO₂ adsorption is important and PEI acts perfectly as a CO₂ adsorbent owing to its high adsorption capacity and selectivity.\textsuperscript{[125]} The nitrogen atoms doped into the CNT structure and the associated charge transfer between PEI and N-CNTs are also crucial for efficient CO₂RR. DFT calculations have revealed that CO₂ adsorption on the N-doped carbon lattice is not thermodynamically favored at normal conditions, except for the pyrrolic-N defects.\textsuperscript{[96]}

FIGURE 10 (A) The illustration of the charge transfer process in physically adsorbed PDDA decorated CNT. Reproduced with permission from Ref. \textsuperscript{[101]} Copyright 2011 to American Chemical Society. (B) Illustration of the charge transfer process and ORR/OER/HER on C₆₀-SWCNTs, (C) CVs of C₆₀-SWCNT in an O₂ and N₂-saturated KOH solution (0.1 M), (D) LSVs of ORR for pure C₆₀, SWCNTs, C₆₀-SWCNT, and Pt/C. (E) LSVs of OER for pure C₆₀, SWCNTs, C₆₀-SWCNT, and RuO₂ in 0.5 M H₂SO₄ solution. (F) The corresponding Tafel plots. (G) I-t curve at 1.7 V versus RHE. Inset shows polarization curves before and after 1.5 h I-t curve. (H) LSVs of HER for pure C₆₀, SWCNTs, C₆₀-SWCNT15, and Pt/C in 0.5 M H₂SO₄ solution. (I) The corresponding Tafel plots. Reproduced with permission from Ref., \textsuperscript{[94]} copyright 2019 to American Chemical Society. (J) The proposed CO₂ reduction reaction process mechanism with PEIF functionalized, nitrogen-doped CNT as the electrocatalyst. Reproduced with permission from Ref., \textsuperscript{[125]} copyright 2014 to American Chemical Society. CNT, carbon nanotube; HER, hydrogen evolution reaction; LSV, linear sweep voltammetry; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; PDDA, poly(diallyl dimethyl ammonium chloride; RHE, reversible hydrogen electrode; SWCNT, single-walled CNT.
Therefore, for utilization of N-functionalized carbon nanomaterials for CO₂RR, most of the N content must be in pyrrolic configuration. However, it has also been reported that pyridinic-N can transfer the highest charge onto adsorbed CO₂ molecule. [98] Therefore, the combination of heteroatom-doing-induced intramolecular change and adsorption-induced intermolecular charge transfer can be helpful not only for CO₂RR but also for other reactions with C-MFECs.

So far, heteroatom-doped carbon-based electrocatalysts have been utilized for electrodes in fuel cells (ORR), metal-air batteries (ORR and OER), water splitting electrolyzer (OER and HER), and other emerging energy conversion and storage technologies, along with the chemical conversion of CO₂ into useful fuels (e.g., CO₂RR:CO₂ to CH₃OH or other hydrocarbon products) and production of commodity chemicals (e.g., NRR:N₂ to NH₃). [1-3,33] However, much more progress needs to be achieved for the commercial success of C-MFECs in renewable energy and environmental protection technologies. [1-3]

5 | COMPARISON AMONG DIFFERENT CHARGE TRANSFER METHODS IN CARBON-BASED MATERIALS

As summarized in Table 1 (the charge transfer amounts are either in multiple of electronic charge or Mulliken atomic charge), the N and P doping into graphitic carbon lattice promote the highest amount of charge transfer (1.24e for N and 1.39–1.52e for P). However, for S doping only 0.28e charge is transferred within carbon lattice might be due to its small size but this charge transfer amount is a little higher than the defect-induced charge transfers (<0.2–0.22e). On the other hand, the charge transfer amount related to the adsorbed diatomic gas molecules (e.g., O₂) or other chemical molecules (e.g., TCNE) onto graphitic carbon lattice is moderate, ranging from 0.41e to 0.86e as summarized in Table 1. However, triatomic compound gas molecular adsorption (e.g., NO₂) onto the vacancy defects in carbon lattice induces a very low amount of charge transfer (about 0.012–0.029e). NO₂ adsorption on the single vacancy (0.029e) and divacancy (0.017e) acts as electron acceptor whereas on trivacancy it becomes electron donor (0.012e) which might be related to the electronic spin interaction effects. This could also be related to the variance in the diameter of the vacancy defects (or pores) onto graphene lattice and the related modification in the charge transfer resistance. Therefore, the modulation of topological defects onto graphitic carbon lattice can effectively alter the quantity and quality of charge transfer between adsorbed molecules and carbon lattice which could bring insightful prosperity in this field.

Interestingly, CO₂ adsorption onto the pyridinic-N doped within carbon lattice transfers around 0.41e charge which could be beneficial for efficient metal-free CO₂RR electrocatalysis. TCNQ molecule with its high electron-accepting characteristics takes about 0.3e charge from the graphene lattice offering p-type doping effect (Table 1). While it is difficult to directly conclude on the strategy for achieving the highest charge transfer that is beneficial for electrochemical catalysis, however, more systematic and detailed research efforts are needed to elucidate this critical issue. From Table 1, it can be at least suggested that N-doping into carbon lattice with high charge transfer is beneficial for both ORR and OER electrocatalysis with low-related overpotential which could be correlated to the proper size of N atoms and modulated charge transport characteristics of N-doped graphitic carbon lattice. However, more research efforts in essential to comment exclusively on this.

For electrocatalytic energy conversion applications, the grain boundary-induced vacancy defect in carbon lattice demonstrated the lowest ORR overpotential (0.32 V) as compared to heteroatom(s) doped and chemical/gas adsorbed carbon catalysts (Table 1). For OER, however, P-doped carbon-based electrocatalyst showed comparatively lowest overpotential of about 0.382 V which is little lower than that for N-doped carbon catalysts (0.405 V) and TCNE adsorbed on defective graphene topological edges (Table 1). Therefore, a combined and in-depth theoretical and experimental rationalization efforts must be performed to achieve suitable charge transfer in carbon-based metal-free electrodes for promoting particular electrocatalytic reactions for gaining the highest energy conversion efficiency in energy devices and integrated systems.

6 | CONCLUSIONS AND OUTLOOK

Efficient charge transfer is crucial for generating and/or activating electrocatalytic active sites in carbon-based metal-free materials. Heteroatom-doping or codoping has been extensively used to introduce intramolecular charge separation and to create partially positive or even negatively charged carbon sites depending on the electronegativity difference between the heteroatom(s) and carbon atom. Moreover, it has been observed that atomic vacancy and edges can also introduce charge redistribution within the graphitic carbon lattice. In particular, the edge functionalized graphene sheets are found to be catalytically more active than their homogenously doped counterparts. Therefore, it is very important to explore and tune the active sites for optimizing the electrocatalytic performance of C-MFECs.

On the other hand, physical adsorption-induced charge transfer has also been utilized for many electrocatalytic
reactions. Interestingly, proper combination of the heteroatom-/defect-doping induced intramolecular charge-transfer with the molecular-adsorption-induced intermolecular electron transfer was reported to produce highly efficient electrocatalysts for ORR, OER, HER, CO2RR, and other reactions. Thus, a combination of intramolecular and intermolecular charge-transfer effects would be an attractive option for uplifting C-MFECs towards commercialization success. Such efforts would witness a revolution in efficient electrocatalysis with cost-efficient and earth-abundant C-MFECs to replace expensive precious metal electrocatalysts. Furthermore, carbon-based materials are promising electrocatalysts for large-scale applications because of its economic benefits and earth abundance. Therefore, the efficient charge transfer induced by structural and compositional modifications is a key factor for altering the electrochemical properties of carbon materials towards efficient and cost-effective energy applications.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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