Research Article

A Comprehensive Evaluation of the Structural Stability of Core-Shell Hybrid Nanostructures for Hybrid Supercapacitor Applications

S.E Umoru[1] iD

[1]Dept. of Natural Science, National Institute for Nigerian Languages, Aba, Nigeria

Corresponding Author: efemenaumoru@gmail.com

Abstract—With a focus on hybrid supercapacitor applications, this thorough study attempts to present an in-depth evaluation of the status of research on the structural stability of core-shell hybrid nanostructures. In order to summarize important discoveries, identify trends, and draw attention to obstacles in the way of improving the structural stability of these nanostructures, the review looks at a broad variety of investigations that have been done in this field of research. Since core-shell hybrid nanostructures combine a functional shell with a stable core material, they present a promising material for enhancing the longevity and performance of hybrid supercapacitors. The review examines the advantages that these nanostructures provide, such as increased electrical conductivity, longer cycle life, and stronger mechanical strength. It also looks at the fundamental of hybrid supercapacitors, classes of core-shell hybrid nanostructures, types of core-shell hybrid nanostructures, factors that affect the structural stability of core-shell hybrid nanostructures, and the strategies for enhancing the structural stability of core-shell hybrid nanostructures. The evaluation does, however, also point out a number of challenges and potential study areas. Understand the long-term stability of core-shell hybrid nanostructures under various operating conditions, such as mechanical stress, humidity, and temperature fluctuations, requires more research. For these nanostructures to be widely used in real-world supercapacitor applications, it is also necessary to address their scalability and cost-effectiveness.

Keywords—Comprehensive evaluation, Structural stability, Core-shell hybrid nanostructures, Durability, cycling stability, Hybrid supercapacitor, Energy storage, Performance.

1. Introduction

The modern world is becoming more and more dependent on efficient and sustainable power sources, which makes the development of energy storage devices crucial [1]. One of the most promising alternatives for energy storage systems is the hybrid supercapacitor, which combines the advantages of batteries with ordinary supercapacitors. The design of the hybrid supercapacitor is crucial since the type of electrode material used determines how effectively the device functions. The development of novel materials and device designs that enhance energy storage and performance has been the main objective of hybrid supercapacitor research. Researchers have looked into a range of materials in an attempt to boost hybrid supercapacitors' capacitance. Metal oxides, conductive polymers, carbon-based compounds, and mesoporous electrode materials are a few of these materials. Graphene, carbon nanotubes, and activated carbon are examples of carbon-based materials with high surface area and electrical conductivity that are widely used as supercapacitor electrode materials [2]. However, their limitations concerning energy density and specific capacitance limit their overall performance in hybrid supercapacitors [3]. Conversely, conductive polymers, like polythiophene, polyaniline, polypyrrole, and polyacetylene, are well known for having a large capacitance in comparison to their high conductivity [4]. However, the reduced cycle stability and mechanical instability of conductive polymers have adversely affected their short-term performance as electrode materials in hybrid supercapacitors [5]. Transition metal oxides, such as ruthenium oxide, manganese dioxide, nickel oxide, and vanadium pentoxide, are used as pseudocapacitive materials in supercapacitor electrodes [6]. Despite having a high specific capacitance, transition metal oxides' poor electrical conductivity and limited cycle stability have an impact on their overall performance in hybrid supercapacitors [7]. The potential of mesoporous materials, including mixed metal oxides, in energy storage applications is being investigated. However, issues with scalability and cost-effectiveness may arise from their synthesis, manufacturing processes, and use in supercapacitor electrodes [8]. Given the shortcomings of these electrode materials for hybrid supercapacitors, scientists are working harder to find alternative materials that may improve hybrid supercapacitors'

functionality. Core-shell hybrid nanostructures are one electrode material that has drawn interest because of its potential to enhance the functionality of hybrid supercapacitors.

Core-shell hybrid nanostructures have great potential, but structural stability is a major problem for them [9]. The issue is that existing core-shell hybrid nanostructures frequently experience structural degradation as a result of recurrent charge/discharge cycles, notwithstanding their efficiency in energy storage and charge/discharge cycles [10]. The hybrid supercapacitors' overall performance and lifespan may be shortened as a result of this structural instability. The restricted implementation of these core-shell hybrid nanostructures in real-world supercapacitor applications stems from the absence of an ideal method for augmenting their structural integrity. This threat must be addressed in order to fully exploit the potential of core-shell hybrid nanostructures and advance the creation of robust and more effective supercapacitors. Thus, a thorough analysis that concentrates on the difficulties related to the structural stability of core-shell hybrid nanostructures in hybrid supercapacitors is required. The objective of this review work is to pinpoint the root causes of structural deterioration and investigate viable approaches to improve stability. By finding a solution to this issue, scientists can progress energy storage technology by designing and creating hybrid supercapcitors that are more resilient and long-lasting. The foundations of hybrid supercapacitors will be covered in detail first, followed by an examination of core-shell technology, structural stability issues, methods for improving structural stability in core-shell hybrid nanostructures, and core-shell hybrid nanostructure processes, all of which will lead to a conclusion.

The rest part of the manuscript is organized as follows, Section 1 contains the introduction of of the study, Section 2 contain the review of related work of the study, section 3 contains some theories used by researchers in studying the structural stability of core-shell hybrid nanostructures, section 4 contains the method used in this review paper. Section **5** brings out the challenges associated with core-shell hybrid nanostructures, section 6 contains the findings on the methods for enhancing the structural stability of core-shell hybrid nanostructures, section 7 contains the conclusion and future scope.

2. Related work

2.1 Fundamental of Hybrid Supercapacitor
One kind of energy storage device that combines the benefits of batteries and supercapacitors is the hybrid supercapacitor. Because of its design, which provides superior power density, energy density (up to 10 times), and an operating voltage of 3.8 V compared to symmetric supercapacitors, it can be used in a wide range of applications. Hybrid supercapacitors are often composed of two primary electrodes: one that functions as a large energy storage battery and the other that functions as a powerful supercapacitor [11]. Hybrid supercapacitors are designed to perform better in terms of cycle life, efficiency, charge/discharge rates, and total energy storage capacity [12].

Double-layer capacitance and pseudocapacitance are the two main ways that hybrid supercapacitors work [13]. When electrical charges are trapped in an electric double layer between the electrode and the electrolyte, double-layer capacitance happens at the interface [14]. This method yields a constrained energy density but a high power density. Conversely, pseudocapacitance enables greater energy storage capacity and is predicated on reversible faradaic redox processes at the electrode-electrolyte interface [15]. The energy and power densities of several electrochemical energy storage systems are displayed in Figure 1.

Hybrid supercapacitors can balance high power and high energy storage by combining these two methods [17]. Maher et al. (2015) [18] demonstrated how to combine active materials with high-voltage electrolytes and logically construct the electrode microstructure to create three-dimensional, high-performance hybrid supercapacitors and microsupercapacitors using graphene and MnO_2
Consequently, hybrid electrodes are generated that have a volumetric capacitance more than 1,100 F/cm^3.
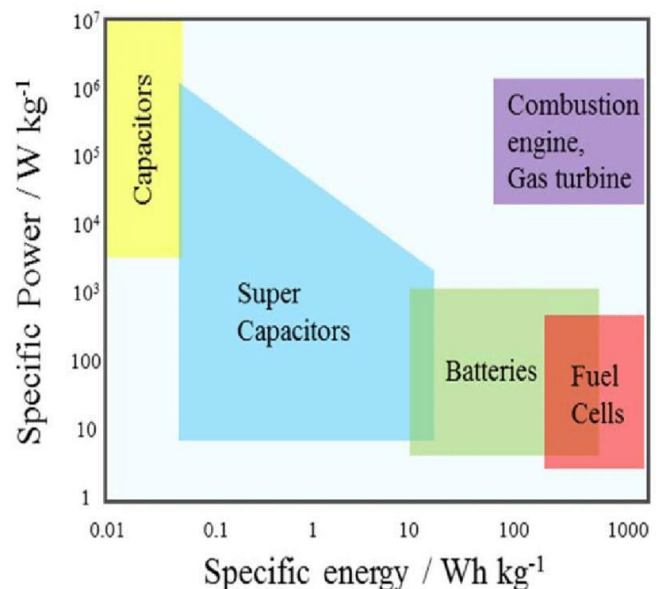

Figure 1: Simplified Ragone plot for the various electrochemical energy conversion systems.[16].

Accordingly, the specific capacitance of the component MnO_2 is 1,145 F/g, very close to the expected value of 1,380 F/g. The overall energy density of the device varies from 22 to 42 Wh/l depending on its setup. This is superior to the energy densities of lithium-ion capacitors, hybrid supercapacitors, double-layer supercapacitors, and commercially available supercapacitors tested under the same conditions. It is comparable to lead acid batteries.

There are three different kinds of hybrid supercapacitors: self-charging supercapacitors, asymmetric supercapacitors, and hybrid batteries/supercapacitors. The first and second variants are a combination of the two techniques that use electrostatic adsorption and Faradaic redox processes to simultaneously obtain high specific energy and specific power. Asymmetric supercapacitors are primarily made up of two different types

of electrodes: electrodes that are similar to batteries and electrodes that are similar to supercapacitors. Battery/supercapacitor hybrids are devices that combine batteries and supercapacitors in series through a variety of techniques. These consist of metal batteries [20], lithium ion batteries [21, 22], lead-acid batteries [19], and lithium sulfur batteries [23]. Moreover, self-charging Supercapacitors allow for the simultaneous harvesting and storing of many energy sources. The three different supercapacitor-based hybrid device types and their hybridization process are depicted in Figure 2. Hybrid supercapacitors have several potential applications in wearable, implantable, and portable electronics in the future energy storage systems.

The design and material selection of hybrid supercapacitors have a significant impact on their performance. In order to enhance the energy storage capacity of hybrid supercapacitors, scientists have investigated various combinations of electrode materials, electrolytes, and device designs. Research has been done on nanoporous designs and composite materials, for example, to increase the surface area and improve ion diffusion within the electrodes. Furthermore, the choice of electrolyte can have a significant effect on the performance of hybrid supercapacitors [24]. Aqueous electrolytes and ionic liquids are often used due to their superior stability and conductivity [25]. The voltage window, power densities, energy densities, and specific capacitance of the three types of hybrid devices—which employed CNT/PANI electrodes as inserting objects—that were previously mentioned are shown in Table 1. The Li-ion hybrid supercapacitor outperforms the others overall, which could make it a key candidate for additional study and advancement.
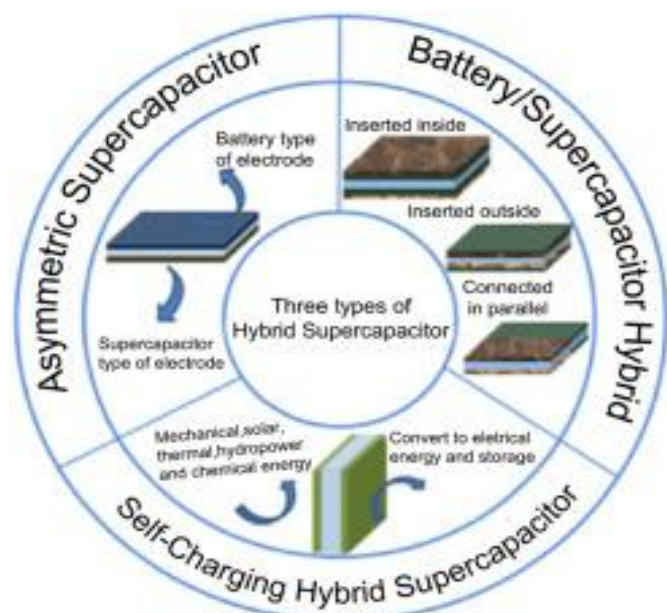
Table 1: lists of the three types of hybrid devices' potential windows, energy densities (Es), power densities (Ps), specific capacitance (Cs), and hybrid technique.

Device	Method of Hybrid	C_s (mA h g^{-1})	E_s (W h kg^{-1})	P_s (kW kg^{-1})	Potential window (V)	**Reference**
Lead-acid hybrid Supercapacitor.	Lead-acid battery and supercapacitor (outside) in series	10 (19% improvement)	19.3 (21% improvement)	20.9 ×10⁻³	1.6-2.6	27
Zn–MnO₂ hybrid Supercapacitor.	Zn–MnO₂ batteries and supercapacitor (inside) in series	33.4 (1.5 times improvement)	47.9 (3.5 times improvement)	14.1	0–1.8	28
Li-ion hybrid Supercapacitor.	Adding a piece of CNT/PANI electrode into the battery	61.1 (18% improvement)	100 (22% improvement)	27.7	2.0-4.1	29

To optimize their electrochemical performance, core-shell hybrid nanostructures are used as the electrode material in hybrid supercapacitors. For example, the core material serves as a framework for the deposition of the active material, while the shell material aids in charge transfer and structural integrity. This design increases the materials' energy-storing capability by optimizing the use of the active materials. Using a simple one-pot synthesis technique based on a water-in-oil microemulsion system, Eunho Lim et al. (2015) [30] create Nb_2O_5@carbon core-shell nanocrystals (Nb_2O_5@C NCs) as high-power anode materials with controllable crystalline phases (orthorhombic (T) and pseudohexagonal (TT)). According to the authors, the T-Nb_2O_5@C NCs show a reversible specific capacity of about 180 mA h g-1 at 0.05 A g-1 (1.1-3.0 V against Li/Li+) with high rate capability, in contrast to TT-Nb_2O_5@C and carbon shell-free Nb_2O_5 NCs. The main reasons for this are (i) T-Nb_2O_5's structural merit and (ii) the conductive carbon shell for high electron mobility working in concert. The maximum power density of 16 528 W kg-1 и energy density of 63 W h kg-1 were achieved at around 5 W h kg-1 densities within the voltage range of 1.0-3.5 V of the HSC using the T-Nb2O5@C anode and MSP-20 cathode. The authors claim that these are impressive results.

2.2 Core-shell Hybrid Nanostructures in hybrid supercapacitors

Core-shell nanostructures combine the properties of both components by encircling a core material ({TiO2 in TiO_2@$Ni(OH)_2$}) with a shell material ($Ni(OH)_2$ in TiO_2@$Ni(OH)_2$). The schematic illustration of the core-shell hybrid nanostructure is shown in Figure 3. Better charge transportation is the core's function in addition to supplying electrocapacitance. Metals, semiconductors, and carbon-based

Figure. 2 : The three different hybrid device types that arise from the hybridization process of supercapacitors. Hybrid supercapacitors have a lot to offer future wearable, implantable, and portable electronics in terms of energy storage systems.[26].

materials make up the three kinds of core materials. Metals and materials based on carbon have higher conductivities than semiconductors. The main function of the carbon and metal cores is to promote charge transmission during the charging and discharging cycles [31]. There are two different configurations in the shell that is growing on the core Making an odd structure, such a layer of nanosheets developing on top of a core of nanowires, is one method. A thin layer forming on top of the core would be an alternative, in which case the morphology of the core would match the structure of the core-shell. The shell's main purposes are to supply a lot of active sites for Faradic redox reactions and a big surface area for charge accumulation [32]. Better charge and ion diffusion are made possible by this combination, which improves electrochemical performance [33].

Core-shell hybrid nanostructures can be fabricated using a variety of materials and techniques and employed in hybrid supercapacitors. For example, Qingqing Ke et al. (2015)[34] synthesize self-supported $TiO_2@Ni(OH)_2$ core-shell nanowire arrays on carbon fiber paper by combining hydrothermal synthesis with chemical bath deposition.
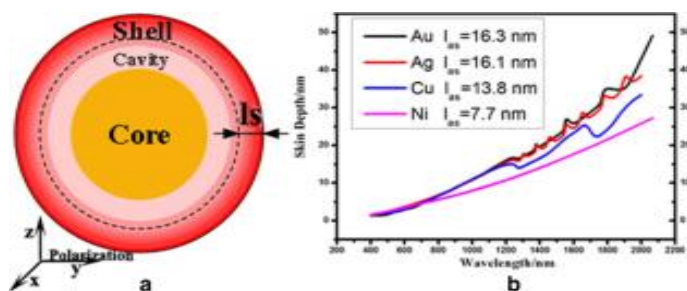

Fig 3 ; (a) Schematic depiction of the core/shell system cross section with the skin depth and x-axis direction perpendicular to each other.(b) The average skin depth for the entire region in the computation, as well as the skin depths for Au, Ag, Cu, and Ni [35].

2.3 Classes of core-shell hybrid nanostructures

Core-shell hybrid nanostructures fall into various groups based on their structure and content. There are several main types of core-shell hybrid nanostructures: Single Core/Shell, Multi-Core/Single Shell, Single Core/Multi-Shell, and Multi-Core/Multi-Shell. The categorization of core-shell hybrid nanostructures is displayed in Figures 4 and 5.
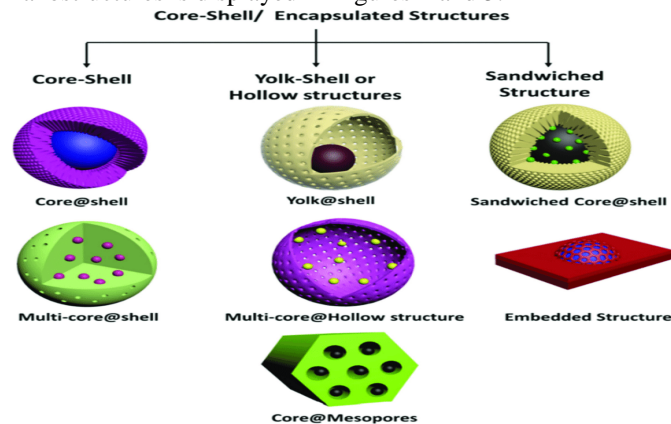

Figure 4; Schematic diagram of different forms of core-shell structure [36]. Reprinted with permission from Ref [36].Copyright @ 1920, Copyright Royal Society of Chemisty .
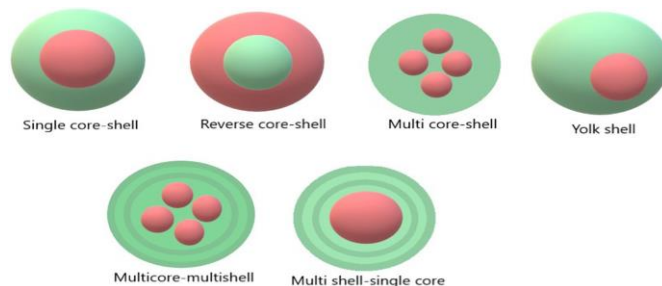

Figure 5: Classification of core-shell nanostructures according to the number of core and shell [37]

2.3.1 Single Core/ single Shell hybrid nanostructure

In order to improve the performance of supercapacitors, a single core/shell hybrid nanostructure for hybrid supercapacitors usually consists of a core material encircled by a shell substance [31]. These structures are perfect for energy storage applications because of their outstanding rate capability, long-term cycling stability, and high specific capacitance [38]. The following are some examples of single core/shell hybrid nanostructures for hybrid supercapacitors: 3D $TiO_2@Ni(OH)_2$ Core-shell Arrays, in which TiO_2 is the core material and $Ni(OH)_2$ is the shell material [34], Binder-free NiO/CuO Hybrid Structure, in which NiO is the core and CuO is the shell [39], $MnCo_2O_4@Ni(OH)_2$ Core-Shell Flowers [40], Nickel Oxide (NiO) Hybrid Core-Shell Nanostructure [41], and NiMoO4@MoS2 Core-Shell Nanorods [42]. The development of a core-shell nanostructure, comprising NiO nanoparticles decorated on polypyrrole nanotube (PNT) via a chitosan (CS) layer (NiO@CS-PNT), is described by Vijeth et al. (2020) [41] as the supercapacitor electrode material. The authors state that a self-degradable soft-template method is used to manufacture PNT. The surface area of polypyrrole (PPy) is increased by the one-dimensional (1D) nanotube framework. By reducing the unavoidable agglomeration of the NiO nanoparticles, CS increases the active material's surface area and improves electrochemical performance.

The NiO/CS-PNT core-shell nanostructure exhibits favorable characteristics such as a high specific capacitance (Csp), low charge transfer resistance (Rct), and a wide surface area when compared to NiO/PNT and pure PNT. An all-solid-state symmetric supercapacitor (SSC) with a high power density (PD) of 4045.69 Wkg-1 and an energy density (ED) of 27.80 Wh Kg-1 was also made using NiO/CS-PNT. Moreover, remarkable cyclic stability was observed, with 84.90% of the capacitance remaining after 10,000 cycles. According to the results, the NiO/CS-PNT core-shell nanostructure makes an excellent electrode material for supercapacitorsThe synthesis of Ni(OH)2@PPy-NTs core-shell nanostructures, which could be employed as supercapacitor electrode materials, is explained by Franciele et al. (2016) [43]. The authors assert that this special Ni(OH)2@PPy-NTs nanoarchitecture improves the electrode's overall electrochemical performance due to the higher electronic/ionic conductivity of 1D nanotubes and the huge surface area provided by 3D nanoflakes. Ni(OH)2@PPy-NTs showed good capacity retention even after 1000 cycles of charge and discharge, with a maximum specific capacitance of 536 F g~1. Not to add, the

low electrochemical series resistance of Ni(OH)2@PPy-NTs was shown by the EIS technique, indicating their potential as a high-performance energy storage medium. In an attempt to enhance supercapacitors' performance, the single core/shell hybrid nanostructure has a core-shell design with programmable nanostructure.

2.3.2 Multi-Core/Single Shell hybrid nanostructure

A multi-core/single shell hybrid nanostructure is a nanoscale material consisting of numerous cores encased in a single shell [44]. These structures are designed to make use of the unique properties of each component to achieve specific goals or functions. Combining numerous cores with a single shell improves the performance of energy storage devices like hybrid supercapacitors [45, 46]. Hybrid nanostructures with several cores and a single shell are engineered to meet certain quality requirements [47]. For example, the inorganic nanocores of the structure can be tailored to promote charge mobility. The performance of the hybrid nanostructure is improved overall by the single shell that surrounds the cores, acting as both a protective and functional layer. One of the many advantages of these hybrid nanostructures is their ability to combine the functions of many elements, leading to improved overall performance and synergistic effects. Furthermore, precise control over the composition and structure of the shell and cores makes customization according to the intended application conceivable [48, 49]. Ni-Co LDH@rGO, where Ni-CoLDH act as the core materials and rGO is the shell material [50], and NiCo2S4@Ni(OH)2/C, where NiCo2S4@Ni(OH)2 is the multi-core and C is the single shell [51], are two examples of multi-core/single-shell hybrid nanostructures in hybrid supercapacitors. Effectively manufactured sandwich-type NiMn2O4@N-C@MnO2 core-shell nanostructures were reported by Chunli Guo et al. (2023) [52]. Microvillous nitrogen-doped carbon (Nsingle bondC), according to the authors, is a highly conductive material that functions as a buffer during repeated charge-discharge cycles, improves electron transport, and increases core-shell nanomaterial conductivity. These properties all contribute to the overall stability of the nanomaterials. The number of active sites in a redox process may rise to some degree with the addition of N. Among all the electrodes that were made, NiMn2O4@N-C@MnO2-2 worked the best. At 10 mA cm−2, the NiMn2O4@N-C@MnO2-2//AC BSH device achieved an energy density of 34.29 W h kg−1, with a power density of 946.75 W kg−1. Moreover, the device retained 96.68% of its initial specific capacitance after 30,000 charge-discharge cycles, which was superior to the bulk of previous published studies on the subject. Because of the device's remarkable electrochemical performance, sandwich-type NiMn2O4@N-C@MnO2 core-shell nanomaterials appear to offer a wide range of potential applications in the development of energy-conversion and storage tools. Xin Jiao et al. (2023)[53] produced Fe3O4@onion-like carbons (OLCs) with few-shelled graphitic coatings that were covalently linked. This was achieved in a size-controllable way using monodispersed Fe3O4@oleic acid ligand nanoparticles that were uniform in size. The study, according to the authors, provides a novel method for creating high-performance Fe3O4/carbon hybrid

structures for use in asymmetric supercapacitors. Compared to the majority of known Fe3O4-based electrode materials, the Fe3O4@OLCs hybrid structure demonstrates a high specific capacitance of 686.1 F g−1 at 1 A g−1 and a high rate capability with 71.3% capacitance retention at 10 A g−1. An asymmetric supercapacitor device built using Fe3O4@ OLCs demonstrates a high energy density of up to 63.1 Wh kg−1, which is sustained at a high power density of 1.49 kW kg−1. The energy density is still as high as 39.1 Wh kg−1. Furthermore, a high cycling stability is achieved, with over 80% of the initial capacitance remaining after 10,000 cycles. Investigations on the multi-core/single-shell hybrid nanostructures' multi-reactive locations indicate that they may play many roles in hybrid supercapacitors. The use of multi-core/single-shell hybrid nanostructures to hybrid supercapacitors is therefore an exciting area of research with the potential to significantly increase the versatility and efficiency of energy storage devices.

2.3.3 Single-Core/Multi-Shell hybrid nanostructure

A single-core/multi-shell hybrid nanostructure is a nanoscale material with a single core, usually composed of a particular material encircled by multiple shells made of different materials. These hybrid nanostructures are quite interesting because of their unique properties and applications in various industries, including electronics and energy storage, among others [54]. A nanostructure having a single core at its center encircled by multiple layers or shells composed of different materials is referred to as "single-core/multi-shell" nanostructure. This design allows for the unique properties of each material to be blended, improving performance and functionality. Hierarchical NiCo2S4@ Ni (OH) 2 Core-Shell Hybrid [56], NiO adorned CNT/ZnO Core-Shell Hybrid [55], and SiC@Co(OH)2/Ni3S2 [56] are a few examples of single-core/multi-shell hybrid nanostructures for hybrid supercapacitors.

Songmin Zhang et al. (2018) [57] created hollow core-shell nanostructures with porous carbon shells encasing T-Nb2O5 nanoparticles. The scientists stated that this construction will enhance the high-rate Li-insertion/extraction capabilities of the nanoparticles. Different silica template precursors can be used to create carbon shells with mesoporous channels or relatively dense structures; both T-Nb2O5@carbon hollow core-shell nanostructures show a significant improvement in rate capability over T-Nb2O5 nanoparticles. In addition, carbon shells with accessible mesopores of around 6 nm may offer a greater specific surface area and bigger Li+ diffusion channels. Therefore, with a capacity of 173 C g−1 at a current density of 50 A g−1, the T-Nb2O5@mesoporous carbon (Nb2O5@MC) hollow core-shell nanostructures show improved high-rate properties. A range of power delivery applications can benefit from the combination of the Nb2O5@MC//MCHS hybrid supercapacitor and mesoporous carbon hollow nanospheres (MCHS) cathode, as it can produce an energy density of 12 Wh kg−1 and an ultrahigh power density of roughly 16 kW kg−1.
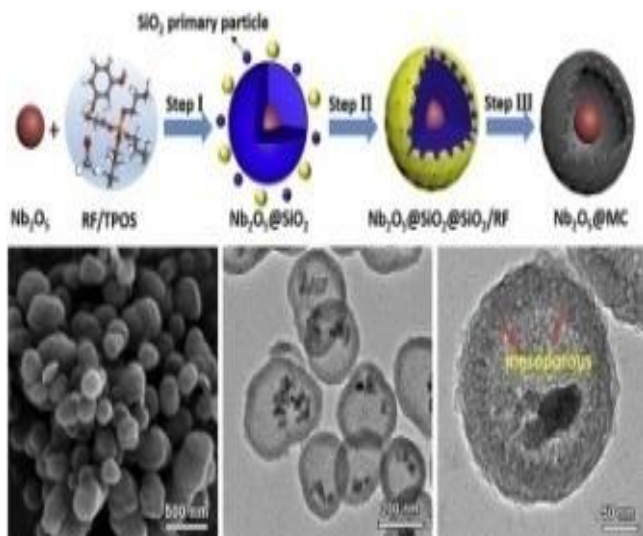
Figure 6: schematic representation of Hollow core-shell nanostructures with porous carbon shells enclosing T-Nb_2O_5 nanoparticles [57]

Miao Du et al. (2023)[58] synthesize self-supported (Ni,Co)Se2/(Ni,Co)Se2 composites on carbon fabric with a simple approach. The generated sugar gourd-like (Ni,Co)Se2/(Ni,Co)Se2/CC nanoarrays preserve 88.9% of their capacity after 5000 cycles, achieving a high areal specific capacity of 1.278 mAh/cm2 (220.34 mAh/g) at 2 mA/cm2, according to the authors. Furthermore, the proposed nanocomposite-based flexible hybrid supercapacitor shows remarkable cycle stability and a high energy density of 0.7051 mWh cm−2 at a power density of 1.6303 mW cm-2. These extraordinary energy storage qualities provide strong evidence for the possibility of the **obtained (Ni,Co)Se2/(Ni,Co)Se2/CC electrode as a** battery-type electrode material for supercapacitor applications.

The application of single-core and multiple-shell hybrid nanostructures in hybrid supercapacitors demonstrates the variety of materials and configurations under investigation to increase the supercapacitor technology's efficiency and potential.

3.1.4 Multi-Core/Multi-Shell hybrid nanostructures
An exciting and cutting edge area of study in energy storage is multi-core/multi-shell hybrid nanostructure research, particularly for the creation of hybrid supercapacitors. These nanostructures show promise for next-generation energy storage devices due to their large specific surface area, enhanced electrical conductivity, and enhanced electrochemical performance [59, 60]. Multi-core/multi-shell hybrid nanostructures are designed with numerous cores and shells built of different materials integrated to maximize the overall performance of the supercapacitor [61]. The combination of these materials at the nanoscale produces synergistic effects that increase the capacity, stability, and efficiency of energy storage [62, 63]. Since carbon-based materials have good mechanical strength and electrical conductivity, using graphene, carbon nanotubes, or carbon nanofibers for the core of a hybrid supercapacitor is a popular way to create multi-core/multi-shell hybrid nanostructures.

Table 2: some reported core-shell hybrid nanostructures and their performance in hybridsuperpacapcitors

Core-shell hybrid nanostructures type	Core-shell hybrid nanastructures	Specific capacitance (Fg⁻¹)	Energy density (Whkg⁻¹)	Power density (Wkg⁻¹)	Cycling stability (%)	Reference
Single Core/shell	$NiCo_2O_4$/$NiMoO_4$	2806	64.2	750	87.7	75
Single Core/shell	MnO_4/N-APC	330	28	560	-	76
Single Core/shell	TiO_2/Ni(OH)$_2$	181	53.54	77.71	70	77
Single Core/shell	Fe-Ni/Fe_2O_3-NiO	1415	27.6	10300	95	78
Singlecore /multishell	Fe-Ni/Fe_2O_3@NiO-HNS	1415.09	11.5	10300	95	79
Single Core/shell	NiO/CS-PNT	337.11	27.80	4045	69	41
Singlecore/Multishell	HCT-2/Co_3O_4@SnS_2	439	40.22	750.22	-	80
Multicore/singleshell hybrid nanostructure	PPy@NPCNFs/MnO_2	595.77	9.36	-	96.2	81
Multicore/singlshell hybrid nanostructure	Ni@CoLDH/rGO	1093	35	3760	-	42
Multicore/singleshell	Fe_2O_3@G@Zn-Ni-Co oxide/$NiMoO_4$	87.5	70	1512	-	82
Multicore/singleshell	C@$NiCo_2S_4$/Ni(OH)$_2$	-	53.3	6420	98.8	51
Multicore/multishell	GO@SnO_2/quantum dot@ppy	928.56	25.6	4098	-	83
Multicore/multishell	FeP-rGO@Ni/ $CuGa_2O_4$@Ni	202.1	63.2	3500	-	84
Multicore/multishell	Ppy@CNT-IL/AuNP@CF	38.49 mF cm⁻²	24.7 μWh cm⁻²	3.52 mW cm⁻²	-	85

These carbon cores are subsequently coated with metal oxides, conductive polymers, or other pseudocapacitive materials to form the shell structure [64, 65, 66].

The multi-core/multi-shell configuration of hybrid supercapacitors offers several noteworthy advantages. The electrochemical performance of the supercapacitor can be improved and ion transport accelerated by combining different materials in the core and shell designs [67, 68]. The

synergistic effects of combining diverse materials also lead to improvements in electron transfer kinetics, cycling stability, and charge storage capacity, among other aspects of overall performance [69, 70]. By carefully selecting the materials for the shell and core components, one may tailor the properties of hybrid nanostructures to meet specific objectives, such as high power density, high energy density, or long cycle life [71, 72, 73]. Multi-core/multi-shell hybrid nanostructures' scalable manufacturing technique and adaptable material selection options allow them to be tuned for a variety of applications and performance metrics. Using a straightforward hydrothermal process, Jing Pan et al. (2022) [74] created a hybrid device with a core-shell nanostructure of NiCo2S4@NiV-LDH/NF-2//BC composite material. With a specific capacity of 1778.8 C g^{-1} (3557.6 F g^{-1}) at 1 A g^{-1}, power density of 749.98 W kg−1, and energy density of 120.81 Wh kg−1, the device exhibits exceptional performance. Table 2 shows some reported core-shell hybrid Nanostructures and their performance in hybrid supercapacitors

2.4 Types of core-shell hybrid nanostructure
2.4.1 Yolk-shell hybrid nanostructure
The result of hybridizing hollow and core-shell structures is a yolk-shell structure with a core@void@-shell configuration. Yolk-shell nanostructures have effective properties such as interstitial hollow spaces, movable cores, and shell functioning, making them valuable for a range of applications [86]. The basic procedure for generating yolk-shell nanostructures is the template-assisted technique, which comprises calcination or solvent encapsulation of the core with dual-shell coatings of different materials to remove the inner shell [87, 88]. It has been reported that the Kirkendall effect, also called the reaction with shell [89, 90], together with a few other techniques [91], can be used to produce yolk-shell structures from core-shell nanoparticles.
Silicon is often used as a disposable layer that is removed to leave a vacancy in yolk-shell structures based on magnetic iron oxide NP (MION) [92, 93, 94].

Hydrolysis-controlling agent L-arginine is employed in the hydrothermal process to produce FeOx@SiO2@C NPs. A silica layer and a polydopamine coating were applied to the a-Fe2O3 NPs simultaneously [95]. Analogously, monodisperse and polyethyleneimine (PEI)-modified yolk-shell nanoparticles were used to create Fe3O4@fmSiO2 NPs utilizing an easy-to-follow procedure (Fig. 6). Zhang and others (2012) [96] Interestingly, the internal functionalities of these foreign species have been enhanced by the range of traits bestowed upon them by encapsulation within hollow colloidal particles. To offer hollow particles new properties, researchers have looked into the idea of employing NPs as movable cores [87].

The qualities of core-shell nanoparticles are said to be influenced by their size, composition of material, and core-shell sequence. A hybrid yolk-shell structure furthermore has a movable core housed inside its hollow shell. There is a core-sacrificial shell and an outer shell that make up the structure. When the sacrificial shell is removed, a void is left behind

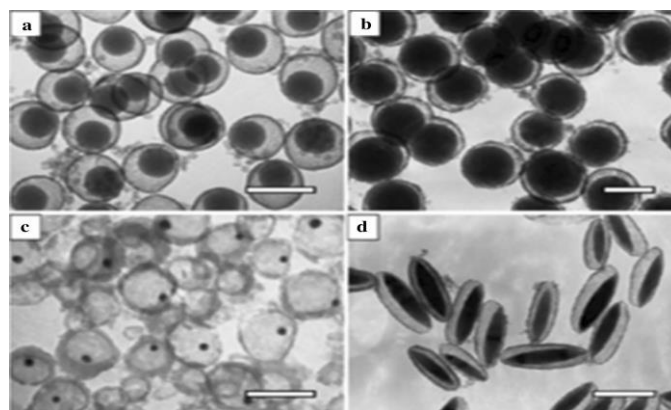that gives the structure its unique properties and multifunctionality**.**

Figure 7: Transmission electron microscopy pictures of yolk/shell structures encasing various NP core types: a) 90 nm SiO$_2$ b) 220 nm SiO$_2$ NPs c) 10 nm Au NPs d) Spindle-shaped Fe$_3$O$_4$ nanostructures [97].

2.4.2 Monodispersed core-shell nanoparticles
The fabrication of monodisperse core-shell nanostructures with magnetic moments that is equivalent to 200emu/g is made possible by a unique method. However, within the range of 2–100 nm, size is controlled by adjusting growth factors. A novel structure was created by Velikov et al. that had a silica (SiO$_2$) shell and a zinc sulfide core, or vice versa. The process of implanted growth was employed to create uniform, well-defined-thickness shells for monodisperse seeds [98]. Cu and Cu@Ag monodisperse nanostructures were produced in a different work. Nevertheless, during synthesizes, three distinct growth mechanisms are at work: metal-assisted growth, galvanic displacement at low temperatures, and overgrowth at high temperatures. Monodisperse core–shell nanostructures can be created using colloidal synthesis [99, 100]. To provide a passivation against Cu oxidation, Cu core Ag shell or Cu@Ag colloids have been created (Fig. 8) [101].
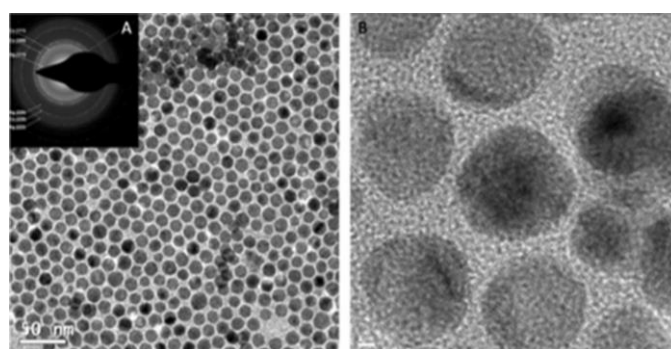
Figure 8: shows TEM pictures of Cu@Ag 4/1 (Cu4@Ag1 Shell produced at T = 25 _C) NPs with HRTEM of polycrystalline Cu@Ag1 NPs and chosen region diffraction bs [101].

2.4.3 Core-shell base on silica nanostructures
Silica is an inorganic material with a variety of applications. Studies have long been conducted on a variety of silica properties, such as its great biocompatibility, stability in acidic environments[102, 103], permeability, etc. [104]. Using the Stober method, tetraethoxysilane (TEOS) is hydrolyzed under simple conditions to create silica

nanoparticles (NPs) [105]. Vinyl groups (-C=C) are added to the silica core in the conventional approach of performance enhancement. This successfully promotes the selective adsorption of target molecules. Due to their distinctive properties, silica metal nanostructures—which are composed of silica cores and metal shells—have recently attracted attention. Furthermore, controlled qualities can be produced by altering the morphology, material, and shape of their shells. It is also possible to contemplate using other metals, such as copper, palladium, nickel, and platinum, as nanoshells in silica metal nanostructures. One such metal is gold. The creation of silica metal nanoparticles through seed-mediated growth provides evidence for the control of surface properties and nanoshell thickness.[106].

The silica NPs are coated thinly with conducting polymers to alter their surface via optical, magnetic, optoelectronic, and catalytic properties. Thus, in these core-shell structures, the conducting polymer shells and the very colloidally durable silica cores show similar features. Due to its low cost, ease of synthesis, chemical and ecological durability, high conductivity, and impressive redox activity, polyaniline (PANI) is the most promising technologically advanced conducting polymer[107, 108].

SiO_2 offers a wide range of advantageous optical applications due to its insulating properties and resistance to high temperatures and liquids. It can be described as "transparent to electromagnetic radiation in the 300–800 nm wavelength range."

On the other hand, silica reacts with boiling hydrogen fluoride or its aqueous solutions, melting Na_2CO_3 and K_2CO_3, concentrated KOH and NAOH, and silica. Hexafluoro silicic acid can be produced through the reaction of hydrofluoric acid (HF) with silica [109]. Not to mention, silica resists coagulation and is neutral in surface redox reactions [110, 111].

2.4.4 Nanoparticles with a magnetic core-shell

In addition to being magnetic, magnetic core-shell nanostructures have special characteristics. Although there are many uses for iron, cobalt, nickel, and their oxidizing materials or alloys, nickel and cobalt are only utilized in a few particular industries [112, 113,114]. Fe3O4 has so piqued interest among these magnetic materials due to its low toxicity, ease of synthesis, and affordability. The separation of magnetic core-shell nanoparticles by an external magnet is an additional advantage over conventional filtering and centrifugation techniques. In light of this, magnetic core-shell nanoparticles have become an attractive material [115]. Wustite/Fe3O4 core-shell nanocubes are synthesized by Pichon and colleagues. Ferrimagnetic Fe3O4 shell coating antiferromagnetic wustite core causes the hysteresis loop to shift below Neel temperature and enhances coercivity, according to Pichon et al. (2011)[116] magnetic measurement. Saturation magnetization is increased by coating, according to research on core-shell NPs employing $Fe_3O_4@c\text{-}Fe_2O_3$ [117] and $a\text{-}Fe_2O_3@Fe_3O_4$ [118]. Using

Fe_3O_4 core–shell nanotubes with a MnZn ferrite shell, magnetic properties are demonstrated [119].

2.4.5 Core-shell polymer nanoparticles

Organizing polymeric shell assembly on silicon and gold nanoparticles has been demonstrated in recent work [120, 121]. There exist multiple approaches for depositing magnetite nanoparticles with a controlled thickness of the polymer shell. Particle size is still greater than 130 nm even if there has been development in the "emulsion polymerization of poly (methyl methacrylate) (PMMA) on 10 nm core of mixed-phase iron oxides" [122, 123]. Block co-polymers distributed the oleic acid-coated superparaMIONs in an aqueous medium using iron oxide NPs anchoring block, such as poly (4-n-dodecyl oxybenzalacetal) [124, 125], poly (styrene250-blockacrylic acid13) [126, 127], or PEG-poly (e-caprolactone) [128].

2.4.6 Nanoparticles with a bimetallic core and shell

Novel and state-of-the-art methods have been devised to control the nanoparticle production process. Since ligands prevent particle aggregation, including them during synthesis is the most widely used method for stabilizing particles. Supramolecular contact governs particle stability and assembly, but covalent and metallic bonding also occur (Fig. 9). Serpell et al. (2011) [129] synthesized gold/palladium coreshell nanoparticles via a supramolecular method. Before reduction, they had already created the metal core surface and had bonded the shell metal to it. It has been shown that the produced core-shell NPs may selectively convert chloronitro benzene into the chemical chloroanaline, which is useful in commerce [129]. Gold/palladium bimetallic nanoparticles were created in another study by using the cavitation phenomenon brought on by high-intensity ultrasonic irradiation exposed to the palladium ions and gold aqueous solution. The produced NPs have a palladium shell surrounding a gold core. Adding sodium dodecyl sulphate to the sample solution causes it to act as a stabilizer and reducer. Mizukashi et al. (2000)[130] state that the thickness of the shell and core is indicated by the concentration of both noble metal ions. Using a one-step seeding-growth process, magnetically recyclable Au@Co core-shell nanoparticles were produced in a matter of minutes [131]. In a different study, Zheng et al. (2006)[132] created Au-Pt core-shell NPs using a displacement reaction, avoiding the production of monometallic AuNPs.
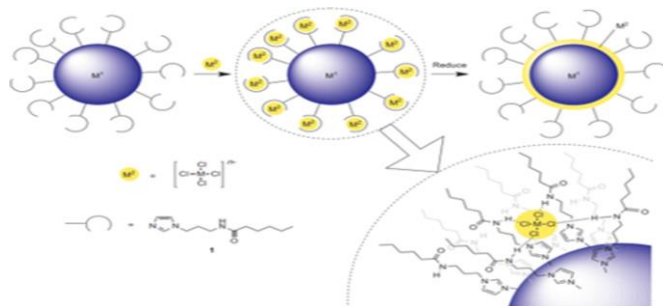

Figure 9: shows a diagrammatic representation of the synthetic anion coordination method for core@shell bimetalllic nanoparticles [129]..

3. Theories/Calculation

Research studies on the structural stability of core-shell hybrid nanostructures for hybrid supercapacitor applications have employed various calculations to evaluate the materials' properties. Some of the calculations used from our findings are presented in the subsection

3.1 Density Functional Theory (DFT) Calculations

DFT calculations are commonly used to investigate the electronic structure, energetics, and stability of materials. Researchers can perform DFT calculations to determine the binding energies, formation energies, and reaction energies of the core-shell hybrid nanostructures. These calculations provide insights into the stability and bonding characteristics of the materials. DFT are supported by some theories which include:

3.1.1 Hohenberg-Kohn Theorems:

The Hohenberg-Kohn theorems form the foundation of DFT. These theorems establish that the electron density uniquely determines the ground-state energy and potential of a system. They provide the theoretical basis for using the electron density as the fundamental variable in DFT calculations. The theorems are stated in equation (1) and (2)

$$E_{HK}(n) = T[n(r)] + V_{int}[n(r)] + \int n(r)\, v_{ext}(r)\, d^3r \qquad (1)$$

$E = E_{HK}$, the exact energy of the system

$T[n]$

where V_{int} is the internal potential for electron-electron interaction,

$T(n)$ is the energy of electron that are in motion,

and $v_{ext}(r)$ is the outside potential at position r for the function for nuclear-electron iiteration

$$\langle \Psi' | H | \Psi' \rangle = E' + \int [V_{ext}(r) - V'_{ext}(r)] n_0(r) d^3r \qquad (2)$$

3.1.2 Kohn-Sham Equations:

The Kohn-Sham equations are a set of equations derived from the Hohenberg-Kohn theorems. These equations reformulate the many-body problem of interacting electrons into an equivalent single-particle problem. Solving the Kohn-Sham equations allows for the determination of the electron density and the total energy of the system. The Kohn-Sham equation is presented in equation 3

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(r)\right)\psi_i = \varepsilon_i \psi_i(r) \qquad (3)$$

Where the effective potential $V_{eff}[n(r)]$ is given by

$$V_{eff}[n(\mathbf{r})] = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{EXC}(\mathbf{r}) \qquad (4)$$

3.1.3 Exchange-Correlation Functional

The exchange-correlation functional is a key component of DFT calculations. It accounts for the effects of electron exchange and electron correlation, which are crucial for accurately describing the electronic structure and energetics of materials. Various approximations and functionals have been developed to approximate the exchange-correlation energy.

3.1.4 Local Density Approximation (LDA)

LDA is an approximation to the exchange-correlation functional that assumes the exchange-correlation energy depends only on the local electron density at each point in space. LDA provides a computationally efficient approach for DFT calculations but may not capture certain non-local effects accurately.

3.1.5 Generalized Gradient Approximation (GGA):

GGA is an extension of LDA that includes the gradient of the electron density in the exchange-correlation functional. GGA improves upon LDA by incorporating additional information about the electron density distribution, leading to more accurate results for many systems.

3.1.6 Hybrid Functionals

Hybrid functionals combine the exchange-correlation functionals of DFT with a fraction of exact exchange from Hartree-Fock theory. These functionals provide a balance between accuracy and computational efficiency, making them suitable for a wide range of materials and properties.

These theories and approximations support the use of DFT in materials science and quantum chemistry, enabling researchers to calculate electronic structures, energetics, and other properties of materials accurately and efficiently.

3.2 Molecular Dynamics (MD) Simulations

MD simulations are employed to study the dynamic behavior and stability of materials at finite temperatures. Researchers can use MD simulations to analyze the structural changes, thermal stability, and mechanical properties of core-shell hybrid nanostructures. These simulations provide information about the materials' stability under different environmental conditions.

3.3 Monte Carlo Simulations:
Monte Carlo simulations are utilized to explore the thermodynamic properties and phase transitions of core-shell hybrid nanostructures. Researchers can use Monte Carlo simulations to investigate the stability of the system, including the formation of defects, phase separation, and ordering of the materials.

3.4 Finite Element Analysis (FEA)

FEA is a numerical method used to analyze the mechanical behavior and structural stability of materials. Researchers can apply FEA to study the stress distribution, deformation, and failure mechanisms of core-shell hybrid nanostructures under different loading conditions. FEA helps assess the mechanical robustness and reliability of the materials for practical applications.

These calculations and simulations enable researchers to comprehensively evaluate the structural stability of core-shell hybrid nanostructures for hybrid supercapacitor applications. By analyzing the materials' properties and behavior, researchers can optimize the design and performance of these nanostructures for efficient energy storage.

4. Methodology

Systematic review method was applied in this paper because it involved a systematic and a transparent approach in order to identify, select, appraise, and analyze relevant studies so that evidence-base conclusion can be provided. A systematic

research is conducted to identify all relevant studies that address the research objectives. Therefore, this paper was conducted across multiple database, providing problems associated with core-shell hybrid nanortsures when put into use in hybrid supercapacitors. solutions were also provided from the findings and a coherent conclusion were drawn from the fingings.

5. Structural Stability Challenges of Core-Shell Hybrid Nanostructures in Hybrid Supercapacitors

5.1 Interface stability challenges
Making sure the core-shell interface is stable is one of the most important factors to take into account when using core-shell hybrid nanostructures in hybrid supercapacitors. Geometric structure, atomic disorder, and surface stress are some of the aspects that affect the interface problems of core-shell hybrid nanostructures [133]. To preserve the structural integrity of the nanostructure, the interface between the materials that make up the core and shell should be robust and resistant to deterioration. Preserving structural stability and averting delamination or shell material separation from the core necessitates optimal interface compatibility between the core and shell materials. A range of tactics have been utilized to improve the stability of the core-shell interface, including surface modification techniques, utilizing appropriate materials with compactible qualities, and fine-tuning the synthesis conditions [134]. The instability of core-shell nanostructures is attributed to surface stress and the interplay between chemical ordering pattern and geometric structure, as noted by Schmidt et al. (2008) [135] and Bochichio et al. (2013) [136]. According to Mangel et al. (2016) [137], atomic disorder at the core-shell interface may be a more important contributor in interface instability than lattice mismatch, which is the conventional theory. In the synthesis of core-shell nanostructures, Wang et al. (2013) [138] highlight the significance of decreasing core-shell interfacial tension and the possibility of utilizing core-shell synergy to address interface instability issues.

5,2 Mechanical stability challenges
The mechanical toughness of the core-shell hybrid nanostructures is an additional factor contributing to their structural stability. When various materials are integrated into core-shell systems, mechanical stress and strain may result from these cycles of charge and discharge. This could eventually lead to structural deterioration and decreased performance. For a nanostructure to function well in applications involving mechanical stress or strain, its mechanical characteristics—such as its strength, flexibility, and resistance to deformation are essential [138]. In order to increase the mechanical stability of core-shell hybrid nanostructures, researchers have looked into a variety of strategies, including creating hierarchical structures, adding reinforcing materials, and enhancing the composition and shape of the nanostructure [139,140]. When it comes to the mechanical stability of core-shell hybrid nanostructures in hybrid supercapacitors, the flexibility attribute is essential.

These nanostructures are crucial parts of flexible supercapacitors since they are made to perform both mechanically and electrochemically [141]. The entire flexibility and durability of the supercapacitor device depend on the mechanical flexibility of these core-shell hybrid nanostructures. These nanostructures' flexibility helps the supercapacitor maintain its electrochemical performance by allowing it to adjust to various mechanical circumstances without losing functionality [142]. Flexibility is an essential component of mechanical stability, as was previously mentioned, when designing core-shell hybrid nanostructures for usage in hybrid supercapacitors. This property is important, as shown by the studies of Qu et al. (2020) [143] and Sekhar et al. (2019) [135], who show the excellent electrochemical performance and stability of moss-like nickel-cobalt phosphide nanostructures, and Sekhar et al. (2019) [135] who show the high capacity and long-term cycling durability of core-shell-like copper hydroxide nanotube arrays grafted with nickel aluminum layered double hydroxide nanosheets. Veerasubramani et al. (2017) [144], who used a binderless cobalt hydroxide-cobalt molybdate core-shell structure, further highlight the importance of flexibility in liquid electrolyte mediated flexible pouch-type hybrid supercapacitors. Last but not least, Zheng et al. (2013) [145] report TiO2@C core-shell nanowires for flexible and high-performing solid-state supercapacitors, highlighting the significance of flexibility for these nanostructures' mechanical stability.

Strength is the nanostructures' capacity to retain their structural integrity and fend off deformation or failure in the face of mechanical stress or strain in the context of the mechanical stability of core-shell hybrid nanostructures in hybrid supercapacitors. These nanostructures' mechanical strength plays a critical role in how well supercapacitors function since it directly affects their long-term stability and endurance, particularly in applications that need frequent cycles of charging and discharging. Research by Liang et al. (2018) [146] and Sekhar et al. (2019) [147] emphasizes how crucial this feature is to obtaining high capacity and long-term cycle durability. Superior cycle stability is demonstrated by the crystalline/amorphous Co3S4 core-shell heterostructure in Liang's work and the core-shell-like nanoarchitectures in Sekhar et al.'s work, highlighting the importance of mechanical stability in their functionality. The importance of core-shell nanostructures in enhancing structural mechanical stability is further emphasized by Jiang et al. (2016) [45], as this is crucial for the long-term performance of supercapacitors. Finally, Wang et al. (2017) [148] emphasize that the mechanical stability of the core-shell FeOF/Ni(OH)2 hierarchical nanostructure plays a crucial role in attaining high performance, as do the unique microstructure and synergistic effects. In the context of hybrid supercapacitors, where core-shell nanostructures significantly improve the overall performance and dependability of the energy storage devices, the idea of strength is very crucial.

5.3 Electrochemical stability challenges
The combination of various materials and their features in core-shell hybrid nanostructures creates significant obstacles

for electrochemical stability in hybrid supercapacitors. In hybrid supercapacitors, these difficulties may affect the longevity and functionality of these nanostructures. Material compatibility, oxidation and corrosion, electrochemical reactivity, and structural integrity are the main causes of the electrochemical stability problems with core-shell hybrid nanostructures [149, 150]. Combining several materials, such as metals and biomolecules, so that one serves as the shell and the other as the core, is a common technique used in core-shell hybrid nanostructures. Maintaining stability and preventing degradation can be difficult when these materials are not compatible with the electrochemical environment [151]. A potential field of study is the construction of core-shell hybrid nanostructures for electrochemical applications, with an emphasis on improving stability and performance.According to Jiang et al. (2016) [109] and Feng et al. (2018) [152], these structures have a lot of potential for electrochemical energy storage, especially in Li-ion batteries and supercapacitors. They talk about how different materials can be used, such as metal-phosphide and carbon-based core-shell nanostructures, and they stress how crucial stability and compatibility are to these designs. The usage of polymer nanofibre membranes with a core-shell structure in gel polymer electrolytes is further explored by Bi et al. (2014) [153], who show that these membranes have high ionic conductivities and stability. A particular example of a core-shell nanostructure is the Fe@FeP/CNT material, which shows remarkable catalytic activity in the hydrogen evolution reaction, as reported by Li et al. (2017) [154]. The compatibility of electrolytes and core-shell nanostructures plays a significant role in hybrid supercapacitor design. In order to achieve high ionic conductivities and stability, Bi et al. emphasize the significance of the microstructure and the affinity between the electrolyte and the core-shell structure. Core-epitaxial shell nanocrystals are a unique way of stabilizing battery electrode/electrolyte interfaces that Kim et al. (2015) [155] introduces and that may be able to solve some of the compatibility issues. The cumulative findings of these investigations highlight the promise of core-shell hybrid nanostructures in electrochemical settings as well as the necessity for additional study to maximize their functionality and design. These difficulties demonstrate the necessity of more study and advancement in this field.

When different materials are present in core-shell nanostructures, oxidation and corrosion problems may arise, particularly in electrochemical settings. This results from the asymmetric paths for corrosion as well as the possibility of nanoparticle migration and coalescence during catalytic reactions [156, 157]. Over time, this can have an impact on the nanostructures' performance and stability. On the other hand, these problems can be lessened by using porous shells that let chemical species in freely and regulate how various parts of the nanostructure interact with one another [158]. By combining metallic, porous metal oxide, and carbon nanoparticles into polymeric matrix, hybrid nanostructured coatings can also protect base metals from corrosion. This allows for the creation of multifunctional coatings. [159] Structural stability in electrochemical processes may be hampered by the reactivity of core-shell materials. For

instance, it might be challenging to regulate the development of passivating layers on the electrode surface of Li-ion batteries, which can result in undesirable reactions and decreased durability [160]. Comparably, despite their excellent power delivery and long-term cycling stability, core-shell nanostructures' special qualities in electrochemical capacitors can make it difficult to maintain structural stability [106]. In order to overcome these obstacles, [161] and [162] suggest methods for enhancing the structural stability of core-shell materials. These methods include the use of atomically thin Pt shells to shield the core from oxidation and dissolution and the use of core-shell nanocomposites to counteract negative surface effects and stabilize the materials. The overall stability of the nanostructures can be affected by the interaction between the core and shell materials when electrolytes or other electrochemically active chemicals are present.

The ability of core-shell hybrid nanostructures to preserve their physical and chemical integrity during the supercapacitor's operating conditions is referred to as structural integrity in the context of hybrid supercapacitors. A key component of the performance and longevity of hybrid supercapacitors is the structural integrity of their core-shell hybrid nanostructures. Research has indicated that the electrochemical performance and stability of supercapacitors can be greatly improved by employing core-shell-like nanoarchitectures, such as hierarchical $CuCo_2S_4@NiMn$-layered double hydroxide core-shell hybrid arrays [249], hierarchical polyaniline-coated $NiCo_2S_4$ nanowires [248], and copper hydroxide nanotube arrays grafted with nickel aluminum layered double hydroxide nanosheets [116]. With their high electron diffusion efficiency, plenty of readily available electroactive sites, and enhanced structural stability, these architectures produce large specific capacitance, strong rate capability, and extended cycle lifetimes.
The performance of supercapacitors may also be enhanced by the application of core-shell nanostructures, such as single-wall carbon nanotubes covered with covalent organic frameworks [162]. To address the particular problems with structural integrity in these hybrid nanostructures, more investigation is necessary.

5.4 Cycling stability challenges
The ability of core-shell hybrid nanostructures to retain their structural and functional integrity across multiple cycles of use, especially in the face of changing environmental conditions or external stimuli, is referred to as cycling stability. This characteristic is essential for the real-world uses of core-shell hybrid nanostructures in hybrid supercapacitors. The long-term performance and dependability of core-shell hybrid nanostructures are significantly influenced by cycling stability [116, 132]. For instance, good cycle stability in hybrid supercapacitors was established by the core-shell-like copper hydroxide nanotube arrays grafted nickel aluminum layered double hydroxide nanosheets in the work of Sekher et al (2019)[116]. Comparably, Liang et al. (2018)[132] revealed that a crystalline/amorphous Co_3S_4 core–shell heterostructure exhibited higher cycling stability in aqueous hybrid supercapacitors. Excellent cycling performance was

also facilitated by the creation of self-supported yolk-shell nanocolloids with high surface area and structural stability, as reported by Zhu et al. (2015)[163]. It has an immediate effect on how suitable they are for real-world uses, particularly in situations where frequent usage or exposure to various environments is anticipated. The significance of the stabilizing agent in preserving the macroscopic characteristics of hybrid nanomaterials is emphasized by Spataro et al. (2020)[164]. Bowles et al. (1988)[253] and Razak et al. (2019)[165] both highlight how thermal cycling affects the physical properties and dimensional stability of hybrid composites, with Bowles et al. highlighting the enhanced stability of specific hybrid laminates. Yao et al. (2012)[166] highlight the importance of cycling stability in real-world applications by showing how conductive polymer coatings can greatly improve silicon nanowire anode cycling stability. Together, these investigations highlight how important cycling stability is in deciding whether hybrid nanostructures are suitable for real-world applications.

Numerous factors affect the core-shell hybrid nanostructures' cycle stability. The thermal behavior and thermodynamic stability of yolk-shell nanoclusters can be influenced by the size of the shell, core, and void space [156]. Another important factor is where the core is located within the shell; in Ni-Au core-shell nanoparticles, decentralized cores promote greater stability [167]. In addition, the thermoresponsiveness and colloidal stability of nanoparticles can be affected by the kind of polymer topology in the shell, such as cyclic versus linear [168]. These results emphasize how crucial it is to take into account a variety of structural elements when designing and refining core-shell hybrid nanostructures in order to maximize cycling stability.

Core-shell hybrid nanostructures have been shown to have the potential to improve cycling stability in a variety of applications. For example, Wang et al. (2016) [169] designed highly cross-linked Cu/a-Si core-shell nanowires for use in lithium batteries, achieving ultra-long cycle life and high rate performance. Jiang et al. (2016) [109] reviewed the use of core-shell nanostructures in electrochemical capacitors, highlighting their ability to provide high power delivery and long-term cycling stability. Recent research has shown just how beneficial core-shell hybrid nanostructures can be in a variety of applications. Zhu et al. (2015) proposed self-supported yolk-shell nanocolloids, exhibiting high capacitance and outstanding cycling behavior, for use in pseudocapacitors. All of these investigations highlight how core-shell hybrid nanostructures can improve cycling stability for a variety of energy storage uses.

5.5 Material Degradation:
The structural stability of core-shell hybrid nanostructures in hybrid supercapacitor applications is seriously threatened by material deterioration [170]. By offering a wide surface area and excellent conductivity, core-shell nanostructures are intended to improve the electrocapacitive performance of supercapacitors [171]. Nevertheless, these nanostructures are susceptible to degradation with time, which could impair their overall performance and structural stability [172].

Exposure to extreme working conditions, such as high temperatures, humidity, and chemical reactions, is one of the primary causes of material degradation in core-shell hybrid nanostructures [173]. These circumstances may cause the materials in the core and shell to deteriorate, resulting in structural damage and decreased functionality.

Material deterioration can also be facilitated by the supercapacitor's cycle of charging and discharging [174]. Every cycle puts stress on the core-shell nanostructures, which can result in mechanical fatigue and the development of flaws or fissures. These flaws have the potential to worsen the nanostructures' structural stability and hasten the process of deterioration.

Furthermore, material deterioration may also be facilitated by contaminants or other impurities in the core-shell materials [175]. The materials may react with these contaminants, triggering chemical reactions that hasten the deterioration process. To reduce the chance of deterioration, it is essential to guarantee the purity of the materials employed in core-shell hybrid nanostructures [175].

Researchers are looking into a number of approaches to lessen the difficulties caused by material degradation. To shield the core-shell nanostructures from challenging working circumstances and stop degradation, one strategy is to create protective coatings or encapsulation approaches. Mitigating the degradation of core-shell hybrid nanostructures in hybrid supercapacitors is a critical function of protective coatings. Since the electrodes are the most crucial parts of a supercapacitor cell, these coatings are intended to improve their functionality and longevity of the material during operations. Using protective coatings, a layer of material is applied to the core-shell nanostructures' surface to act as a barrier of defense. The stability and durability of the nanostructures can be improved by designing these coatings with specific properties. These coatings are often made of polymers, epoxies, polyurethanes, and metals like aluminum and zinc. For instance, for all-solid-state flexible supercapacitors, K. Qi et al. (2018)[176] created a core-shell tubular structured graphene nanoflake-coated polypyrrole nanotube (GNF/PNT) hybrid. The GNF coating does not only function as an effective surface protector but aslo an electron transport channel, while a precisely calibrated coating quantity maximizes the composite's overall capacitance, according to the authors. Thus, the GNF/PNT hybrid exhibits a stable cycle behavior, a large capacitance, and a high capacitance retention. Encapsulation techniques entail the encasement of core-shell nanostructures in a matrix or protective shell. The nanostructures are physically protected from outside influences by this encapsulation. For example, a work by Kavinkumar et al. (2021) [177] described a class of electrodes that are core-shell type and are encapsulated in a homogeneous outer nanolayer. With a model electrode consisting of a $NiCo_2O_4/MoO_2$ core-shell encased by an atomic layer-deposited NiO nanolayer, the authors proved the effectiveness of the kind of electrodes. Based on DFT calculations and experimental investigation, the authors assert that the electrical modulation at the interface formed by the outer nanolayer offers a significant increase in capacity more than 450 C g^{-1} for the model electrode. . After 20,000 cycles

of charge and discharge for the model electrode, the flexibility provided by the thin nanolayer helps maintain the physical integrity of the encapsulated inner structure, lowering the loss in capacity to less than 3% from more than 10%. To increase the stability and endurance of the nanostructures, another tactic is to optimize the synthesis techniques and material compositions. For example, using a one-step hydrothermal process, Lingli Cheng et al. (2018) [178] effectively designed and synthesized size-t3nable hierarchical hollow core/shell submicrospheres based on nickel sulfide, in which Ni3S2/NiS hollow submicrosphere functions as a core and Ni3S4 nanoflakes as shells. The authors assert that these hybrids have better electrochemical performance because of the complementary effects of different phases of nickel sulfide. To sum up, in hybrid supercapacitor's applications, material degradation presents a major barrier to the structural integrity of core-shell hybrid nanostructures. To solve these issues and enhance the durability and performance of core-shell hybrid nanostructures in supercapacitors, researchers are currently working on creating safeguards and refining synthesis techniques.

6. Results and Discussions

6.1 Strategies for Enhancing Structural Stability in Core-Shell hybrid Nanostructures

6.1.1 Protective Coating or Encapsulating Technique

Protective coating or encapsulating is a method used to address the problem of structural stability in core-shell hybrid nanostructures for hybrid supercapacitor applications [269]. This method involves applying a protective layer or shell around the core of the nanostructure to enhance its stability and prevent degradation or structural damage [179].

The use of protective coatings in hybrid supercapacitors can improve the structural integrity of the core-shell nanostructures, enhance their mechanical strength, and protect them from external factors such as moisture, temperature variations, and chemical reactions [180]. One common material used for encapsulating core-shell nanostructures is silica due to its excellent colloidal stability, controllability in synthesis, chemical inertness, controlled porosity, high processability, and optical transparency [181]. By encapsulating the core nanomaterials with silica, the exterior surface properties can be modified, and colloidal stability can be enhanced [181].

The encapsulation process involves depositing a shell layer, such as silica, onto the core of the nanostructure. This shell layer encapsulates the entire core, providing a protective barrier. The protective coating of core-shell hybrid nanostructures in hybrid supercapacitors is crucial for maintaining their structural stability and ensuring long-term performance. It allows for the efficient storage of electrochemical energy and helps optimize the power and energy density of the supercapacitors. K. Qi et al. (2018)[182] created a core-shell tubular structured graphene nanoflake-coated polypyrrole nanotube (GNF/PNT) hybrid. The GNF coating does not only function as an effective surface

protector but aslo an electron transport channel, while a precisely calibrated coating quantity maximizes the composite's overall capacitance, according to the authors. Thus, the GNF/PNT hybrid exhibits a stable cycle behavior, a large capacitance, and a high capacitance retention. A work by Kavinkumar et al. (2021) [183] described a class of electrodes that are core-shell type and are encapsulated in a homogeneous outer nanolayer. With a model electrode consisting of a $NiCo_2O_4/MoO_2$ core-shell encased by an atomic layer-deposited NiO nanolayer, the authors proved the effectiveness of the kind of electrodes.

In summary, protective coating is a method used to enhance the structural stability of core-shell hybrid nanostructures in hybrid supercapacitors

6.1..2 Surface Functionalization Techniques

Surface functionalization techniques are used to address the problem of structural instability in core-shell hybrid nanostructures in hybrid supercapacitor applications [184]. Through these methods, the stability and functionality of the nanostructures are improved by altering their surface. Supercapacitors can greatly increase their specific and volumetric storage capacity by carefully controlling the surface characteristics of the electrode materials. Surface functionalization provides more surface area for ion adsorption, increasing the amount of ions that may be stored. It shortens the nanostructures' ion diffusion lengths, facilitating quicker ion transport and improving electrochemical performance all around [183,184]. Some common approaches include: Chemical Modification, Coating, Doping, and Hybridization.

In order to change the surface chemistry and reactivity of core-shell hybrid nanostructures, functional groups or particular molecules are added to their surface [185]. Samia et al.(2011) [185] presented a review on the use of diazonium salts as a new class of surface modifiers and coupling agents for attaching artificial polymers, biomacromolecules, and nanoparticles to surfaces. Surface functionalization can be achieved using a variety of techniques, such as covalent and non-covalent attachment of functional groups or molecules to the surface of the core-shell hybrid nanostructure. Covalent functionalization is the process by which molecules or functional groups attach themselves to the surface of a core-shell hybrid nanostructure by forming strong chemical interactions. Depending on the type of functional groups to be attached, covalent attachment can be accomplished by a variety of chemical processes, including diazonium coupling, thiolation, and silanization [186]. In the case of silanization, for example, the surface hydroxyl groups of nanostructures react with silane coupling agents, resulting in the covalent attachment of functional groups, like aryl or alkyl moieties, to the surface [187]. Zhenghu et al. (2017)[188] described the construction of a one-dimensional coaxial CNT@microporous carbon composite (CNT@micro-C) using surface-confined cross-linking generated by covalent bonds. The precursor for microporous carbon chosen by the authors is octaphenyl polyhedral oligomeric silsesquioxane (Ph-POSS), which is made up of eight phenyls and a $-Si_8O_{12}$ cage. The authors harvested CNT@micro-C, which consists

of a microporous carbon shell and a CNT core, after etching and carbonizing $-Si_8O_{12}$ cages. This process involved layer-by-layer cross-linking of phenyl anchored Ph-POSS on the surface of CNT. According to the authors, the surface area of CNT@micro-C can reach 1306 m^2 g^{-1}, and the thickness of the microporous carbon shell can be precisely controlled between 6.0 and 20.0 nm. With a wide surface area, high electrical conductivity, quick ion transfer speed, and short ion transfer distance, CNT@micro-C combines the structural benefits of carbon nanotubes and microporous carbon. In a related development, Neha et al.(2023)[189] employed aryl diazonium salts as a fascinating element to alter the surfaces of $NiFe_2O_4$ nanoparticles. This was achieved through a radical pathway that formed strong covalent links, resulting in stable interfaces at the NP-organic molecules. The authors claim that in order to guarantee NP production and covalent surface functionalization, this complimentary surface analysis is used. Non-covalent surface functionalization is a method for modifying the surfaces of core-shell hybrid nanostructures without forming strong covalent bonds [190]. Using weak intermolecular forces such as hydrogen bonding, π-π interactions, van der Waals forces, electrostatic interactions, and hydrophobic effects, non-covalent functionalization allows molecules to be attached to the surface of the core-shell nanostructures [191]. This technique does not cause any harm to the original structure of the material [192]. This is essential to preserving the nanostructure's stability in the face of the mechanical strain and electrochemical cycling seen in supercapacitor applications. Self-healing properties are made possible by the weak and reversible nature of non-covalent bonding [193]. The functional layer has the ability to self-assemble if it is broken or separated, preserving the structural integrity over time. Doping is a surface functionalization procedure whereby impurities are added to a nanostructure's surface to modify its electrical properties [194]. Through modifications to the surface chemistry or an increase in conductivity, this can improve specific functionality.

6.1.3 Optimization of Synthesis Methods

One effective tactic for improving the structural stability of core-shell hybrid nanostructures is synthesis techniques optimization. By improving the synthesis process, the resulting nanostructures' robustness and durability can be raised. The search results lead to the following conclusions.

Optimizing the synthesis process involves controlling the nucleation and growth processes. Temperature, reaction time, and precursor concentrations can all be carefully controlled to gain more control over the nucleation and growth of the core and shell components [195]. By reducing flaws and guaranteeing nanostructure homogeneity, this control can result in increased structural stability. Elena et al. (2003)[195] investigated how $CoPt_3$ nanocrystal size is controlled by nucleation rate. In order to understand the mechanisms controlling the creation of the metal alloy nanocrystals, many experimental parameters (such as reaction temperature, stabilizing agent concentration, cobalt to platinum precursor ratio, etc.) were examined in their work. The authors demonstrate that $CoPt_3$ nanocrystals nucleate and develop to their full size early in the synthesis process, and that additional heating does not cause Ostwald ripening. In this

instance, controlling the size of the nanocrystals requires striking the right balance between their rates of nucleation and development from molecular precursors. As a result, the authors concluded that $CoPt_3$ nanocrystals' size can be accurately adjusted in a predictable and repeatable manner between 3 and 18 nm.

Adjusting the ratio and mix of core and shell components is another tactic. The structural stability of the core-shell hybrid nanostructures can be improved by choosing suitable materials with complementary qualities [196].. A thorough understanding of the materials, synthesis methods, and desired properties of the nanostructures is necessary for the difficult process of optimizing the synthesis method for structural stability augmentation. To evaluate the efficacy of the optimization procedures, experimental validation and characterization approaches are necessary.

To sum up, one effective tactic for improving the structural stability of core-shell hybrid nanostructures is synthesis technique optimization. The overall structural integrity and durability of these nanostructures can be enhanced by regulating the nucleation and growth process, adjusting the ratio and composition of core and shell materials, and using post-synthesis treatments.

6.1.4 Optimization of Materials Composition

Optimizing the composition of materials used in the synthesis of core-shell hybrid nanostructures is a valuable strategy for enhancing their structural stability [197]. By carefully selecting and designing the materials, it is possible to improve the overall stability and durability of the nanostructures.

One approach to optimizing materials composition is through multi-material designs [198]. This involves using multiple materials with complementary properties in the core-shell nanostructure [199]. By selecting materials with similar thermal expansion coefficients and mechanical properties, it is possible to reduce stress at the interface and enhance the overall stability of the nanostructures [200]

Another technique is topology optimization, which aims to find the optimal distribution of materials within the nanostructure to maximize stiffness and minimize mass. Topology optimization considers the arrangement of materials at a macroscopic level, allowing for the identification of material layouts that enhance structural stability [201]. This technique can be particularly useful when dealing with complex parts carrying multiple loads, as it helps identify material layouts that maximize stiffness and minimize mass. In addition to topology optimization, size, shape, and free-shape optimization can be employed to fine-tune the formation of structural product concepts. These optimization techniques help identify optimal solutions for key product characteristics such as cross-sectional thickness, material choice, and areas with high stress concentration. By refining these areas, the risk of product failure can be reduced, leading to improved structural stability

Furthermore, introducing vacancy engineering, substitution/gap doping, object modification, and combination engineering can optimize the cycle stability and structural

stability of cathode materials for various applications, such as aqueous zinc ion batteries [202]. These strategies aim to inhibit material dissolution, improve reaction reversibility, and enhance the overall structural stability of the cathode materials.

It is important to note that the optimization of materials composition for structural stability enhancement of core-shell hybrid nanostructures is a complex process that requires a deep understanding of the core-shell materials and their properties. Experimental validation and characterization techniques are essential to assess the effectiveness of the optimization strategies.

In conclusion, optimizing the composition of materials used in the synthesis of core-shell hybrid nanostructures is a valuable strategy for enhancing their structural stability. By carefully selecting materials, employing multi-material designs, utilizing topology optimization, and considering vacancy engineering and doping techniques, it is possible to improve the overall stability and durability of these nanostructures.

6.1.5   Designing Hierarchical Structures

Designing hierarchical structures is a powerful strategy for enhancing the structural stability of core-shell hybrid nanostructures. Hierarchical structures, which incorporate multiple levels of organization, can improve the mechanical properties and overall stability of these nanostructures. By carefully designing the hierarchical architecture, it is possible to distribute stress, enhance load-bearing capacity, and minimize the risk of structural failure. Here, the concept of designing hierarchical structures as a strategy for structural stability enhancement specifically for core-shell hybrid nanostructures is explored.

One approach to designing hierarchical structures is through architectural design. By organizing the core and shell materials in specific patterns or arrangements at different length scales, it is possible to optimize their interaction and enhance structural stability [203]. For example, incorporating a hierarchical arrangement of core-shell layers, with progressively changing shell thicknesses or material compositions, can distribute stress and strain more effectively, improving the overall stability of the nanostructure [204]. Matthew et al.(2016)[203] presented three methods of organizing hierarchical structures which include: ligands placed on the surface of nanostructures, atoms organized into crystalline nanostructures, and nanostrsuctures organized into crystalline superlattices

Another strategy is hierarchical reinforcement [205]**.** This involves incorporating reinforcing elements at multiple length scales within the core-shell hybrid nanostructure. By introducing nanofillers, such as nanoparticles or nanotubes, into the core or shell materials, it is possible to enhance their mechanical properties and reinforce the structure. The addition of these reinforcements at different length scales can improve strength, toughness, and resistance to deformation, leading to enhanced structural stability.

Additionally, self-assembly techniques can be employed to create hierarchical structures within core-shell hybrid nanostructures. Self-assembly processes, such as molecular self-assembly or electrostatic self-assembly, allow the materials to organize themselves into ordered structures spontaneously. By utilizing self-assembly, it is possible to create complex hierarchical architectures with precise control over their organization and arrangement. This can lead to improved load distribution, stress transfer, and overall structural stability of the core-shell hybrid nanostructures. For instance, Qiannam et al.(2015)[206] presented a two-step self-assembly techniques for hierarchical-ordered nanostructures: Two-step self-assembly carrying out two discontinuous processes and two-step self-assembly finished in one pot involving two continuous processes. According to the authors, the two-step self-assembly strategy, in contrast to the traditional one-step method, enables the fusion of several synthetic processes and the creation of intricate nanostructures with hierarchically-ordered multiscale structures. Furthermore, this strategy makes it possible for heterostructures or hybrid nanomaterials to self-assemble economically. It is anticipated that the broad use of two-step self-assembly would open up new avenues for the fabrication of multifunctional nanostructures with purposeful morphologies. Multiple-step self-assembly is the extension of the two-step self-assembly idea to syntheses that involve more than two chemical or physical reaction steps.

Furthermore, surface engineering plays a crucial role in designing hierarchical structures at the nanoscale [207]. By modifying the surface properties of the core-shell nanostructures, such as through nanostructuring or introducing coatings, it is possible to enhance adhesion, reduce stress concentrations, and improve interfacial compatibility between the core and shell materials [208, 209]. These surface modifications can contribute to the overall stability and durability of the nanostructures.

In conclusion, designing hierarchical structures is an effective strategy for enhancing the structural stability of core-shell hybrid nanostructures. This approach allows for the development of more robust and durable core-shell hybrid nanostructures, expanding their potential applications in various fields.

6.1.6 Utilization of Appropriate Materials With Compactible Qualities

Utilizing appropriate materials with compatible qualities is indeed a strategy for enhancing the structural stability of core-shell hybrid nanostructures [210]. By carefully selecting materials that have compatible properties, it is possible to improve the overall stability and durability of the nanostructures. Here are some insights based on the search results:

One important consideration is the lattice matching between the core and shell materials [211]. In some cases, lattice mismatches between the core and shell can lead to structural instabilities [212]. However, Jia & Jiatao (2020)[213] has reported a synthetic route that achieves nanoscale heterostructures with substantial lattice mismatches between the core and monocrystalline semiconductor shell . This is

achieved by controlling soft acid-base coordination reactions between molecular complexes and colloidal nanostructures, allowing for the growth of a semiconductor shell with an incommensurates lattice structure with that of the core.

Another aspect to consider is the compatibility of materials at the interface. When the core and shell materials have different thermal expansion coefficients or mechanical properties, stress concentrations can occur at the interface, leading to structural deformations or failures [214]. By selecting materials with similar properties, such as thermal expansion coefficients and mechanical strength, it is possible to reduce stress at the interface and enhance the overall structural stability of the core-shell hybrid nanostructures.

Furthermore, the choice of materials with appropriate surface properties can also contribute to structural stability [215, 216]. Surface engineering techniques, such as nanostructuring or introducing coatings, can improve adhesion, reduce stress concentrations, and enhance interfacial compatibility between different materials. These surface modifications can enhance the overall stability and durability of the nanostructures [217, 218].

In conclusion, utilizing appropriate materials with compatible qualities is a valuable strategy for enhancing the structural stability of core-shell hybrid nanostructures. By considering factors such as lattice matching, compatibility at the interface, and surface properties, it is possible to improve the overall stability and durability of these nanostructures.

7. Conclusion and Future Scope

An in-depth understanding of the current status of research in this subject has been made possible by this extensive review on the structural stability of core-shell hybrid nanostructures for hybrid supercapacitor applications. This review has consolidated important discoveries and highlighted significant trends and problems in the quest to improve the structural stability of these nanostructures by looking at a wide range of studies.

The research findings demonstrated that core-shell hybrid nanostructures have enormous potential for improving the longevity and efficiency of hybrid supercapacitors. Improved mechanical strength, increased electrical conductivity, and extended cycle life are just a few advantages of the novel design, which combines a stable core material with a functioning shell. These properties are essential to supercapacitors' effective and dependable performance in a variety of applications, such as portable electronics, renewable energy systems, and electric vehicle energy storage.

Furthermore, the thorough analysis has provided significant new information on the factors affecting the structural stability of core-shell hybrid nanostructures. Overall stability and performance of these nanostructures have been found to be significantly influenced by a number of parameters, including the synthesis method, the interface between the shell and core, mechanical toughness of the core-shell materials when in operation, electrochemical reactivity of the core-shell material, cycling stability of the core-shell materials in the face of changing environmental condition, and the choice of materials for the core and shell. Designing and refining core-shell hybrid nanostructures to maximize stability and performance in supercapacitor applications requires an understanding of these variables. Through protective coating or encapsulation, surface functionalization, optimization of synthesis methods, optimization of materials composition, designing hierarchical structures, and utilization of appropriate materials with compactible qualities, researchers have made significant progress in improving the electrochemical performance and durability of these nanostructures

This review has also pointed out a number of issues and directions for further investigation. For example, more research is required to determine the long-term stability of core-shell hybrid nanostructures under various operating conditions, such as mechanical stress, humidity, and temperature fluctuations. To enable their broad use in useful supercapacitor devices, it is also necessary to address the scalability and cost effectiveness of these nanostructures.

This extensive review has shown how core-shell hybrid nanostructures can significantly improve the structural stability of hybrid supercapacitors.

For future research and development projects aiming at enhancing the functionality, durability, and commercial feasibility of these nanostructures, the conclusions and insights offered in this evaluation offer a strong foundation. Core-shell hybrid nanostructures has the potential to transform the field of energy storage and aid in the development of efficient and sustainable energy systems, provided that material synthesis, characterization methods, and device engineering advances further.

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