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Novel Electrochemical Interfaces Based on Functional Nanomaterials and Their Related Applications

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Abstract: Due to the unique optical, electronic, magnetic and catalytic properties, functional nanomaterials provide new opportunities for the rapid development in a variety of disciplines and show considerable promise in different fields. Specifically, constructions of the novel electrochemical interface using various nanomaterials and exploring their advanced electrochemical properties have received great attention to develop electrochemical devices with potential applications. In this account, we focus on our up-to-date progress in the construction of novel electrochemical interfaces based on nanomaterials, mainly highlighting our research advances on electrochemical sensors, fuel cells and fluorescence spectroelectrochemistry. These novel advanced nanomaterials endow them excellent performances and open the door towards the development of new generation of electrochemical nanodevices. The introduction of them is beneficial to accelerating electron transfer and improving their electrocatalytic efficiency in the field of electrochemical sensors and fuel cells. Searching for and synthesizing proper luminescence materials and electrochromic species with excellent spectrum matching were designed to fabricate novel electroswitching fluorescence nanodevices. In addition, the optimization of the fabrication for multiple stimuli-responsive systems and the realization of their multifunctions were further explored. Finally, future challenges and perspectives toward these research fields mentioned above are described.

Key words: functional nanomaterials; electrochemical sensors; fuel cells; stimuli-responsive materials; fluorescence spectroelectrochemistry

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The boom of nanomaterials provides new opportunities for the rapid development in a variety of disciplines with continuously growing academic and technological impetus. Due to the unique optical, electronic, magnetic and catalytic properties, these functional nanomaterials have shown considerable promise in different fields^[1-3]. Specifically, constructions of the novel electrochemical interface using various nanomaterials and exploring their advanced electrochemical properties have received great attention to develop electrochemical devices with potential applications^[4-8]. The typical example is that the in-

roduction of nanomaterials into electroanalytical chemistry favors the engineering of the electrochemical sensing platform and allows the incorporation of their novel functions into analytical sensing systems, thus resulting in high sensitivity and good selectivity towards different targets^[9-12].

Efforts searching for the functional electrochemical interfaces and thus providing attractive opportunities to develop advanced electrochemical devices lead to the rational design in a variety of nanomaterials. And in turn, the flourish of the synthesis of nanomaterials plays a significant role in the development

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of nanoelectrochemistry, which has already penetrated into different fields. In detail, the improved electrochemical performance at nanomaterial-based electrochemical interface can be ascribed to the following three aspects: (1) Due to small size and high specific surface area, electrochemical interfaces modified with nanomaterials will provide larger electrochemically active areas. Especially with regard to carbon and noble metal nanomaterials, the introduction of them is beneficial to accelerating electron transfer and improving electrochemical performances. (2) By virtue of different properties of nanomaterials, such as electrochemical and spectroscopic attributes, it is of great significance to explore their interactions and further develop novel devices with promising applications. (3) The construction of various multidimensional architectures and functionalization of nanomaterials with specific species could provide fertile opportunities to tailor electrochemical interface and thus effectively enhance electrochemical response. Inspired by these important features, research into nanoelectrochemistry has been flourishing and has made great progress in the past. In this account, we focus on our up-to-date progress in construction of novel electrochemical interface based on nanomaterials, mainly highlighting our research advances on electrochemical sensors, fuel cells and fluorescence spectroelectrochemistry (Fig. 1). The introduction of functional nanomaterials is beneficial to accelerating electron transfer and improving electrocatalytic efficiency in the field of electrochemical sensors and fuel cells. A series of proper luminescence materials and electrochromic species with excellent spectrum matching were synthesized to fabricate novel electroswitching fluorescence nanodevices. Finally, future challenges and perspectives toward these fields are described.

1 Electrochemical Sensors

Sensors constitute an interdisciplinary field that is currently one of the most active areas of research in analytical chemistry. Among them, due to many advantages, such as being easy to operate, economic, sensitive, and suitable for automation, miniaturization

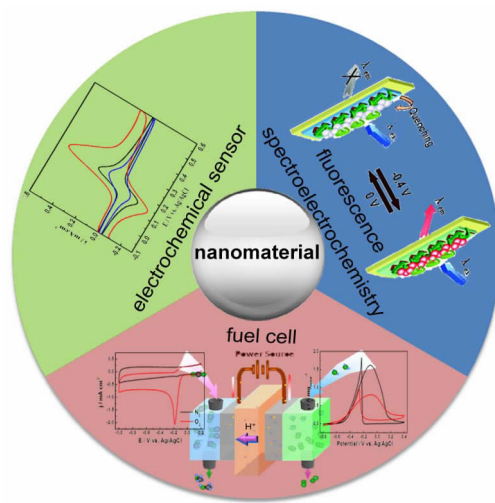


Fig. 1 Representation of novel electrochemical interface based on functional nanomaterials and their applications in electrochemical sensors, fuel cells and fluorescence spectroelectrochemistry

and field analysis, electrochemical biosensors have received an increasing attention in electrochemical devices^[13-14]. As the key component of electrochemical sensors, the introduction of the nanomaterials could provide more functions for electrochemical sensing, which no doubt allows the high sensitive and selective systems to be fabricated. At present, there has been an explosion of research in the use of carbon nanomaterials, such as carbon nanotubes (CNTs), graphene (GN), mesoporous carbons and carbon nanohorn for constructing high-performance electrochemical devices based on different sensing strategies. On the one hand, these carbon-based nanomaterials have been extensively used in electrochemistry because of their low cost, suitable electrocatalytic activity for a variety of redox reactions, a broad potential window, and relatively inert electrochemistry. On the other hand, several methods have been reported for the functionalization of nanomaterials with biomolecules as specific recognition and/or signal triggering elements, which were beneficial to the excellent selectivity and high sensitivity of biosensing. Our group has carried out extensive and intensive researches for designing a series of electrochemical sensors mainly using CNTs, GN, mesoporous carbons and carbon nanohorn, making them extremely promising for the detection of

different target molecules.

GN, a two dimensional single sp^2 atomic thick carbon, has been greatly pursued since its discovery in 2004^[3, 15]. Remarkably, the emergence of GN induces an explosion of research in the use of GN-based nanomaterials for constructing high-performance electrochemical sensing devices based on different sensing strategies because of the unique electrochemical properties^[16-18]. We synthesized a variety of GN-based nanomaterials and successfully used them in advanced electrochemical sensing platform. Our group for the first time systematically illustrated the advantages of GN in electrochemical bio/sensing applications^[19]. The obtained GN showed high electrosensing ability towards different targets, such as small molecules and biomolecules. Moreover, we reported a green and facile approach to synthesize GN with reducing glucose, which exhibited good electrocatalytic activity toward catecholamines (Fig. 2)^[20]. Significantly, the improved electrochemical response was investigated and could be ascribed to the good conductivity and large specific surface area, the π - π interaction be-

tween analytes and basal planes of GN, hydrogen bonding and electrostatic force. To date, great efforts were made to develop GN-based electrochemical sensors, such as H_2O_2 , N_2H_4 , dopamine (DA), NADH, glucose, DNA, protein and cells^[21-22]. Therefore, GN with favorable electrochemical activity can be very attractive for a wide range of electrochemical bio/sensing applications, which may open up a new challenge and approach to explore the electrochemical behaviors of GN-based nanomaterials for potential applications.

It is established that electrochemical properties of GN could be altered by chemical functionalization. First of all, the chemical functionalization can be considerably favorable for the solubility of GN, making full use of the surface area and providing more reaction sites available for target molecules binding. Furthermore, the introduction of the functional groups allows GN to provide strong specific interaction with the target, which can enhance the electrochemical detection ability of the sensor towards different target molecules^[23]. For example, our group suc-

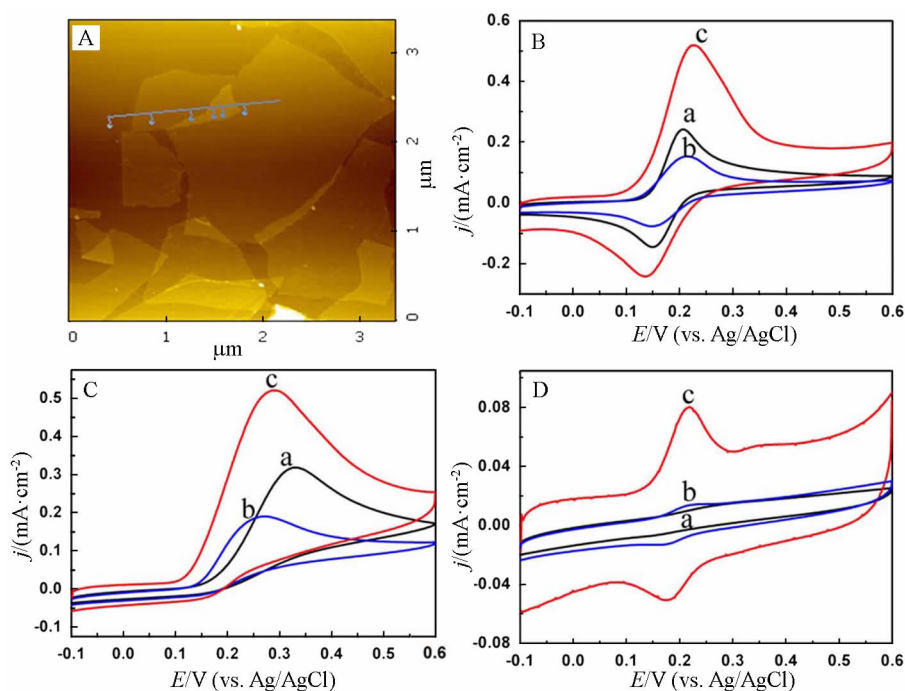


Fig. 2 AFM image of GN nanosheets based on glucose reduction (A). Cyclic voltammograms (CVs) obtained at bare GCE (a), GO/GCE (b), and GNS/GCE (c) in $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS ($\text{pH} = 7.4$) containing $1 \text{ mmol} \cdot \text{L}^{-1}$ DA (B), $1 \text{ mmol} \cdot \text{L}^{-1}$ adrenaline (C), and $0.025 \text{ mmol} \cdot \text{L}^{-1}$ noradrenalin (D). Scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$ (from [20] with permission).

ceeded in synthesizing β -cyclodextrin (β -CD)-modified GN through non-covalent method (Fig. 3) [24-25]. Due to the high supramolecular enrichment capability, the obtained product showed much higher electrochemical performance towards probe molecules (biomolecules and drugs) than unmodified GN and CNTs. Also, due to the high conductivity, chemical and thermal stabilities, and wide electrochemical window, ionic liquid was also combined with GN by covalent approach to synthesize the ionic liquid (IL)-GN hybrids [26-27]. Not only the decreased oxygen defects but also the synergistic effects make these hybrids greatly powerful materials to enhance the electrochemical performance for the detection of trinitrotoluene (TNT). Significantly, the current signals of IL-GNs modified glassy carbon electrode (GCE) towards TNT reduction showed 6.2 and 51.4-folds higher than that of IL-CNTs/GCE and bare GCE, respectively [27]. Chemical doping with foreign atoms is another effective method to modify GN intrinsically, tailor electronic properties, manipulate surface chemistry, and thus enhance the biocompatibility and sensitivity in biosensing applications [28-31]. Lin et al. illus-

trated that N-doped GN displayed high electrocatalytic activity for hydrogen peroxide reduction and fast direct electron transfer kinetics for glucose oxidase. The N-doped GN has further been used for glucose biosensing with concentrations as low as $0.01 \text{ mmol} \cdot \text{L}^{-1}$ in the presence of interferences [30]. Meanwhile, integrations of GN and other inorganic/organic nanomaterials of diverse chemical compositions have attracted extensive interest due to synergistic effects and novel properties via the combination of different nanomaterials [32]. The typical example is that our group synthesized GN-mesoporous silica-gold nanoparticle hybrids (GSGHs) and applied this functional material as an enhanced electrochemical platform to sensitively detect DNA [33], chiral D-vasopressin [34] and adenosine triphosphate [35]. In addition, Pt nanoparticles (NPs) ensemble-on-GN hybrid nanosheets (PNEGHNs) were also constructed through a one-step microwave-assisted heating procedure. In contrast to GN, the electrocatalytic activities of PNEGHNs towards different targets were remarkably increased, providing a kind of more robust and advanced hybrid electrode material with great promise for the design of electrochemi-

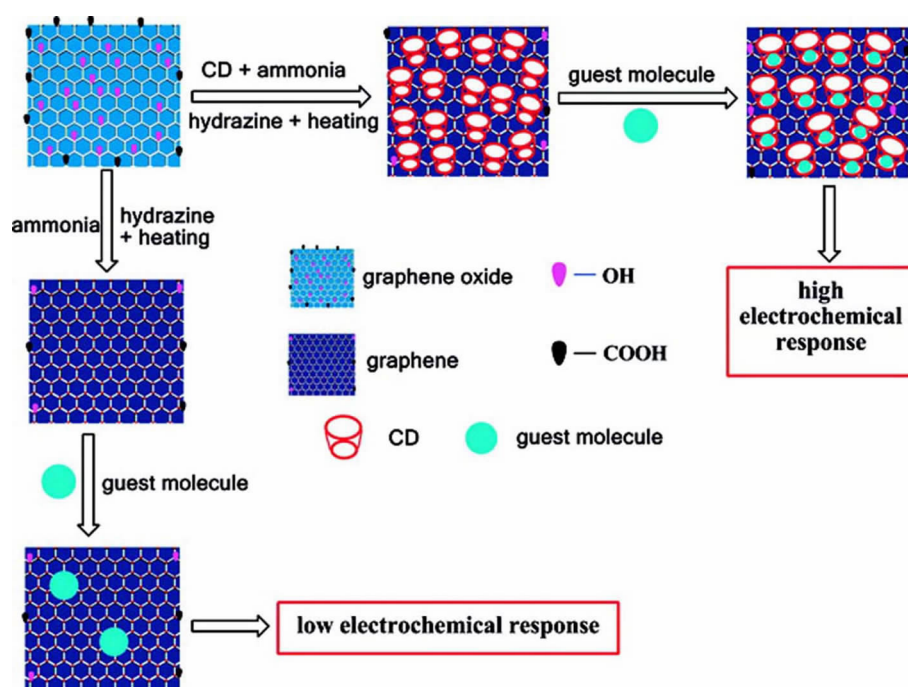


Fig. 3 Illustration of the procedure for preparing CD-GN organic-inorganic hybrid nanosheets and GNs, and sensing the guest molecules by an electrochemical strategy (from [25] with permission).

cal bio/sensors^[36]. Furthermore, 3D GN-based hybrids were also synthesized and utilized as a novel electrochemical sensing platform, providing more porous structure, high surface area and plenty of active sites and, therefore, presenting high sensitivity for different analytes^[37-38].

Aside from GN-based nanomaterials, we also have made some progress on the design of novel electrochemical sensing platform using CNTs, carbon nanohorns and mesoporous carbons. For example, an excellent electrochemical sensing platform has been designed by combining the high specific surface area of CNTs with the remarkable conductivity of IL. The resulting nanocomposites showed an augmentation on the electrocatalytic activity toward O_2 and NADH^[39]. By virtue of electrostatic interaction, the ultra-high-density metal or hybrid NPs were loaded on the surface of the CNT/silica coaxial nanocable, which could be used as enhanced materials for constructing electrochemical devices with high performance^[40]. Besides, a variety of CNTs-based hybrids, such as Prussian Blue/CNTs^[41], Au/CNTs^[42-43] and CNTs/SnO₂/noble metal NPs^[44] were also reported for the construction of enhanced electrochemical sensors. Recently, a novel concept of sensor devices based on chemical-to-electrochemical energy transformation in biofuel cells (BFCs) element has begun to attract enormous research interest^[45]. On the basis of inhibitive effect, our group demonstrated self-powered biosen-

sors for Hg^{2+} ^[46] (Fig. 4) and acetaldehyde^[47] detections, where the carbon nanohorns and CNTs-IL hybrids were used as an electrode material, respectively. The constructed enzymatic biofuel cell showed the good electrochemical performances. As expected, it is found that the presence of targets would affect the performance of the constructed BFCs and thus novel self-powered biosensors have been developed with wide linear ranges and low detection limits. The highly ordered mesoporous carbons with excellent electrochemical performances were also demonstrated in our previous reports^[48-49].

2 Fuel Cells

Proton exchange membrane fuel cells (PEMFCs) possessing high energy density, low operation temperature, and low environmental impact have been considered as a promising technology to power portable electronic devices and transportation vehicles^[50-51]. Despite their great potential as an efficient device to convert chemical energy into electric energy, challenging issues such as poor anode oxidation kinetics when not using pure hydrogen gas, high electrochemical overpotentials as well as the high cost of Pt-based electrocatalysts are the main obstacles to the commercialization of PEMFCs technology. Therefore, constructing advanced catalysts with enhanced electrocatalytic activity plays a significant role in development of the PEMFCs technology. It is established that accurately controlling the composition allows the

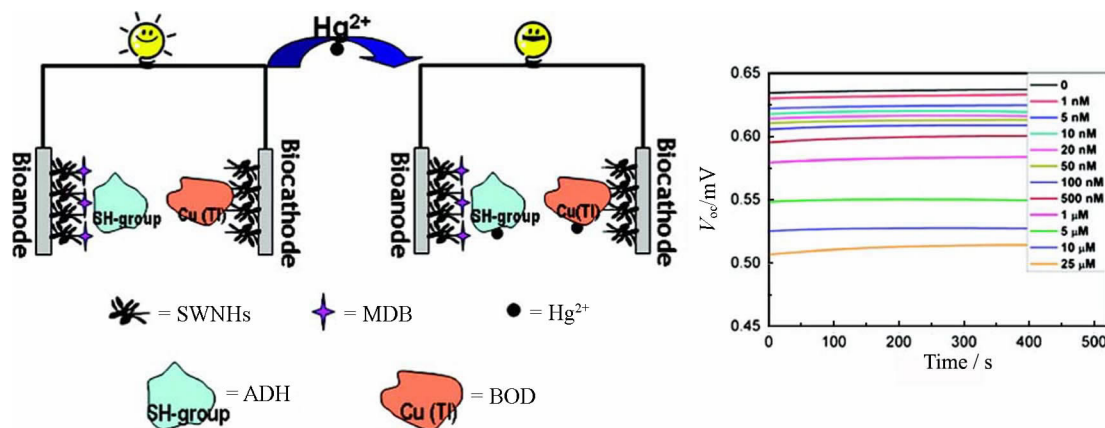


Fig. 4 Configuration of self-powered Hg^{2+} sensor and bioelectrocatalysis mechanism of Hg^{2+} inhibition of the one-compartment miniature alcohol/ O_2 BFC (from [46] with permission).

properties of various noble metals to be varied, and to provide enormous opportunities for tailoring their properties, thus enhancing their electrochemical performance. Compared to single-metal systems, rational design of bimetallic or multimetallic nanostructures can provide more attractive opportunities for further enhancement of their electrocatalytic activity. A great amount of works also stress on the synthesis of metal nanostructures with high-energy facets in which they possessed a high density of atomic steps, ledges, and kinks on their surface which are especially important for improving electrocatalytic activities^[52-54]. Besides, a series of noble metal-based nanoelectrocatalysts with different morphologies and compositions have also been synthesized^[2,55-59]. One-dimensional noble metal nanowires have attracted much attention due to their various potential applications deriving from their unique properties in comparison with their associated 0D morphologies. Our group prepared various 1D noble metal nanowires via wet-chemical strategy. For instance, we developed a facile method for synthesizing the aspect ratio of 1D Pd-based alloy nanowires (ANWs) including PdPt(PdAu)^[60] (Fig. 5A) and AuPtPd^[61] (Fig. 5B), using Te NWs as a sacrificial template and reducing agent. Significantly, the as-prepared Pd-based ANWs exhibited significantly enhanced activity towards ethanol and methanol in alkaline medium. Furthermore, small diameter PtPd bimetallic nanotubes with petal-like surfaces (Fig. 5C)^[62] and ultralong Pt-on-Pd bimetallic dendritic NWs with nanoporous surfaces (Fig. 5D)^[63] based on ultrathin Te NWs were also synthesized by our group, both of which were successfully used as advanced nanoelectrocatalysts for enhancing alcohol oxidation.

In order to further maximize the activity of noble metal-derived catalysts and minimize the use of various noble metals, it is necessary to load noble metal nanostructures with high activity on the surface of supporting nanomaterials (e.g. CNTs, GN) with low cost, high surface area and good electrical conductivity, which not only maximizes the availability of the catalyst surface area for electron transfer but also provides better mass transport of reactants to the

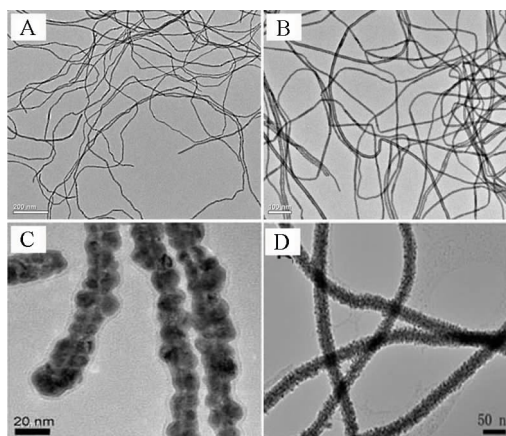


Fig. 5 TEM images of PdPt (A) and PdPtAu (B) alloy nanowires, PtPd bimetallic nanotubes with petal-like surfaces (C) and ultralong Pt-on-Pd bimetallic dendritic nanowires with nanoporous surfaces (D) (from [60-63] with permission)

catalyst^[64-66]. For example, a convenient approach for the synthesis of CNTs/imidazolium-salt-based ionic liquids (IS-ILs)/Pt NPs hybrids using IS-ILs as linkers was described^[67]. The as-prepared three-component CNTs/IS-ILs/Pt NPs hybrids exhibited very high electrocatalytic activity toward methanol oxidation reaction (Fig. 6A, B). GN has been regarded as an ideal supporting material for synthesizing various hybrid nanocomposites. With this point, a wet-chemical approach for the synthesis of high-quality 3D Pt-on-Pd bimetallic nanodendrites supported on GN nanosheets (TPBNGN) was also demonstrated (Fig. 6C, D)^[68]. The as-prepared TP-BNGN exhibited much higher electrocatalytic activity and stability toward methanol oxidation than the commercial E-TEK Pt/C catalyst. Also, polyaniline nanofiber was used as support to load supra-high density Pt NPs. The obtained hybrids exhibited high electrocatalytic activity towards methanol oxidation^[69]. All the contributions mentioned above reveal that the as-obtained hybrids exhibited excellent activities and make them promising electrocatalysts for anode oxidation in fuel cells.

In addition, the cathode catalyst involving the oxygen reduction reaction (ORR) plays a vital role in determining the performance characteristics of electrochemical energy devices. To date, Pt-based nanomaterials with high cost are widely explored as the

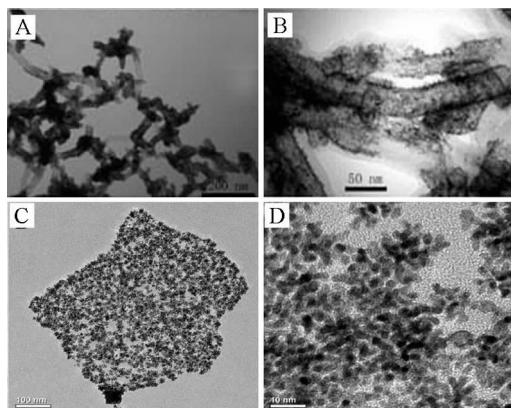


Fig. 6 TEM images of CNTs/IS-ILs/Pt hybrid nanostructures (A, B) and TPBNGN (C, D) (from [67-68] with permission)

cathode catalysts for ORR. Although great contributions have been made to produce high-performance electrocatalysts, two key issues including sluggish ORR kinetics and their susceptibility to time-dependent drift and CO deactivation significantly decrease the cathode potential and reduce fuel efficiency. In this regard, many efforts to seek advanced catalysts alternative to Pt lead to the flourish of the non-noble metal based nanostructures with enhanced electrocatalytic activities. Very recently, in line with the material design and engineering, some recent advances in the development of high-performance electrocatalysts for ORR in electrochemical energy devices were highlighted, indicative of the potential application in this field^[70-72]. Different kinds of nanostructures such as carbon-based nanomaterials^[73-74], metal oxides^[75-76], well-defined Pt nanostructures^[77-78] as well as their hybrids were extensively investigated as promising electrocatalysts in ORR. In comparison to Pt-based catalysts, the prominent feature of cost-efficient metal-free catalysts is their enhanced durability against fuels like CH₃OH and CO, especially in an alkaline medium. In this aspect, our group directed to synthesize several metal free nanomaterials and used them as advanced electrocatalysts in ORR. As shown in Fig. 7A, we also demonstrated a facile method to synthesize nanosheet-like cobalt-nitrogen-GN (Co—N—GN) composites acting as a highly active non precious metal-based catalyst for ORR via *in situ* poly-

merization of polypyrrole and followed by annealing heat treatment. The as-synthesized Co—N—GN composites exhibited an extraordinary electrocatalytic performance towards ORR comparable to commercial Pt/C, for instance, high onset potential, superior methanol tolerance, and excellent stability in alkaline medium, making them the state-of-the-art non-precious metal ORR electrocatalysts for electrochemical energy applications (Fig. 7B, C)^[79]. With regard to other carbon materials, we synthesized bifunctional fluorescent carbon nanodots derived from soy milk through a facile and green approach, which not only showed favorable photoluminescent properties, but also exhibited good electrocatalytic activity towards ORR due to the nitrogen doping^[80]. Using the cobalt porphyrins/iron phthalocyanine functionalized CNTs as the precursor to prepare the Co/Fe/N/CNTs based ORR nanocatalyst through high-temperature pyrolysis was also reported^[81]. It is worth mentioning that the high electrocatalytic activity and good stability made the product as a better candidate for the efficient cathode material in microbial fuel cells compared to commercial Pt/C electrocatalysts. However, further enhancing their electrocatalytic activity is highly pursued and remains to be great challenge.

3 Fluorescence Spectroelectrochemistry

Designing multifunctional stimuli-responsive fluorescence systems are one of the most attractive candidates for the rational fabrication of novel luminescence switches because of their promising applications in various fields^[82-83]. Fluorescence spectroelectrochemistry involving the combination of an electrochemical method with the fluorescence spectroscopic technique can provide information on both the electrochemical response and optical phenomena during the redox process^[84]. Significantly, electrical stimuli have attracted an increasing attention as they can be applied rapidly, remotely, reversibly, and locally (at an electrode surface instead of throughout the bulk), while maintaining the mild conditions amenable to biological systems^[85]. So far, many electrochemically controlled fluorescence response systems have been

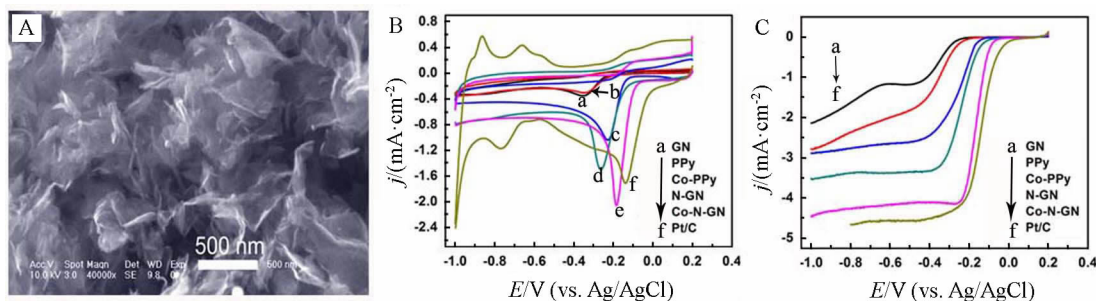


Fig. 7 A. SEM image of the obtained Co—N—GN composite. B. CV curves of ORR on the GN, PPy, PPy-Co, N—GN, Co—N—GN and Pt/C electrodes in an O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1}$ KOH solution at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. C. RDE voltammograms of GN, PPy, PPy-Co, N—GN, Co—N—GN and Pt/C electrodes at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$, electrode rotating rate: $1600 \text{ r} \cdot \text{min}^{-1}$ (from [79] with permission).

reported^[86-87]. However, most of these built systems usually lack good reversibility as well as high contrast of fluorescence response upon application of long-term electrical stimuli. Therefore, developing more perfect electroswitching fluorescence systems is greatly demanded for the future practical applications. Our group constructed a series of electricity-dependent luminescence-controllable systems based on different luminescence materials and electrochromic species, expanding the application of the fluorescence spectroelectrochemical technology in fluorescence response systems. Noting that the conversion of absorbance of the electrochromic component is responsible for the modulating the emission of luminescence materials. Our researches focused on the followings: (1) Searching for and synthesizing proper luminescence materials and electrochromic species with excellent spectrum matching. Once these materials were applied in electricity-dependent luminescence-controllable systems, good reversibility, high contrast of fluorescence response, rapid spectral response as well as long-term electrical stimuli stability could be realized. (2) On this basis, multifunctional stimuli-responsive materials containing luminescence materials and electrochromic species simultaneously were greatly pursued to simplify the preparation of the electrochemical devices. (3) Exploring multiple stimuli-responsive systems, e. g., light, electricity and chemical, and investigating them in bio/sensors, logic gate and other fields are of remarkable importance.

(4) The mechanism for the electricity-dependent luminescence switching systems is still be elusive and needs to be deeply explored, which no doubt in turn promote the development of fluorescence spectro-electrochemistry.

In our early work, for the first time, the change of the photoluminescence property of CdTe quantum dot (QD) assembled multilayers along with applied potential has been systematically investigated in aqueous solution^[88]. It is found that when the sample was under nitrogen or exposed to air, the luminescence of QDs bore quenching by adding positive potentials. On the contrary, while applying negative potentials, the luminescence of QDs was weakened only in the air condition. According to the detailed analysis, it is indicative of that the variation of surface structure of QDs accounted for the photoluminescence (PL) property of CdTe QDs significantly. Thereafter, diverse electrochromic species were introduced to electricity-dependent stimuli-responsive systems. Typical example is that electrochromic materials, poly(methylene blue) (PMB), and CdTe QDs, were adopted to compose hybrid system (Fig. 8)^[85]. It is found that reversible electroswitching of QDs luminescence was achieved in aqueous solution by modulating the potentials between 0.4 and 0 V. It is clear fluorescence quenching via either inner filter effect or energy transfer effect between PMB and QDs plays a significant role in modulating the emission of QDs effectively. The switching operation exhibited good r

versibility and cyclic stability. As an innovation, Liu et al. recently reported the multi-colored PL switching system by controlling the organization of crown-type polyoxometalates (POMs) and CdSe@CdS core-shell QDs into the layer-by-layer nanostructures. The PL of this system can be switched on and off reversibly upon application of step potentials for different redox states, owing to the energy transfer between reduced POMs and QDs. In addition to a quick response, high on/off contrast ($\sim 91\%$), good cycling performance, the reversible four-state fluorescence switching could also be realized by integrating different-sized QDs in one multifunctional system^[89]. Besides, organic-inorganic hybrid systems including poly (3,4-ethylenedioxythiophene)/pyronin Y-doped silica nanoparticles^[90], polyoxometalates/organic dye-doped silica nanoparticles^[91] and prussian blue (PB)/Au clusters^[92] were also reported to fabricate electroswitching fluorescence hybrid film structures.

Very recently, we synthesized a novel multi-stimuli luminescence switching device based on pyronin Y-doped silica NPs (PYDS) and Na-POMs core-shell nanostructures^[93]. Several features of such a device make it particularly attractive: (1) core-shell structures integrating luminescence “donor” (PYDS) with “acceptor” (Na-POMs) as an entirety not only improved stability of the system and minimized the organic dye leaching, but also enhanced the fluorescence quenching rate and simplified the preparation process of the device. (2) Reversible three-state fluorescence switches triggered by light, electricity and chemical inputs could be facile realized via the related luminescence quenching effect. (3) An implication logic gate was fabricated based on fluorescence output signals activated by potential and chemical inputs, and linear detection towards H_2O_2 was realized simultaneously. Similarly, multifunctional polyoxometalates-modified lanthanide doped upconversion nanoparticles were also demonstrated for electrically controlled fluorescence switches^[94]. Under an electricity trigger, Na-POMs transformed between oxidation and reduction states, resulting in reversible and high contrast upon conversion fluorescence switching

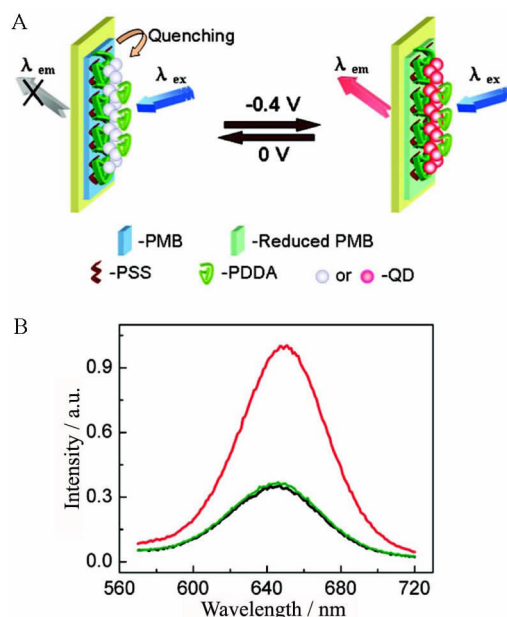


Fig. 8 A. Schematic representation of luminescence modulation by applied potential on the PMB/PSS/PDDA/QDs/PDDA hybrid films. In the open circuit, the QDs emission is reduced owing to the quenching effect from PMB. When a more negative potential was applied, the electrochromic PM was converted to its reduced form, which then recovers the QDs emission. B. Luminescence switching of the hybrid thin film from an open circuit (green line) to an applied potential of -0.4 V (red line) and an oxidized potential of 0 V (black line). The experiments were performed in N_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1}$ phosphate buffer solution (PBS, pH = 7) ($\lambda_{ex} = 390 \text{ nm}$) (from [85] with permission).

between “on” and “off”. Furthermore, by taking advantage of the highly sensitive redox reaction of Na-POMs and the target glutathione, the sensitively monitoring of antioxidant levels in aqueous solution was successfully illustrated. These findings are thought to be of great importance not only for constructing novel electrochemical devices but also providing the ideal platform to extend their potential applications in sensors and other fields.

These studies mentioned above mainly concentrated on seeking luminescence materials and electrochromic species with excellent spectrum matching and thus fabricating the functional response systems via different methods. To extend the applications of

this field, we made a great exploration from the viewpoint of novel electrical signal supply as well as their multifunction. As a new kind of green energy-conversion technology, biofuel cells (BFCs) extract bio-energy from biochemical reactions to produce electricity and exhibit many advantages in moderate conditions. With the help of this special function, BFCs are expected to be designed as self-powered electrical signal supply to control some fluorescence switch operation effectively. As shown in Fig. 9, our group initially presented an integrated self-powered fluorescence switch system based on biofuel cells. With the aid of the electroactive material PB as the controller of fluorescence change and the biocatalysis, the fluorescence switch and electricity generation could be achieved in one BFCs. Due to its excellent electrochromic property and suitable redox potential, PB acts as the electrochromic component to switch the fluorescence from $\text{Ru}(\text{bpy})_3^{2+}$ -doped silica nanoparticles with excellent reversibility and reproducibility. Moreover, the introduction of PB can also construct membraneless and mediatorless BFCs through connecting with the bioelectrode, demonstrating the potential of independent and sustainable electronics to harvest energy from the environment^[95]. We believe that this fluorescence spectroelectrochemistry system combining with electrochemical energy, photoelectric technology and other electrical signal supply methods will hold great promise in the development of and new generation of electrochemical nanodevices.

4 Conclusion and Outlook

In this account, we highlighted our up-to-date progress in the construction of novel electrochemical interface based on functional nanomaterials in the field of electrochemical sensors, fuel cells and fluorescence spectroelectrochemistry. Many new exciting research contributions were presented to improve the applied performance. First, new nanomaterials such as GN were actively explored and developed to use as advanced materials for electrochemical applications. Moreover, tuning electronic properties of GN via chemical functionalization and hybridization

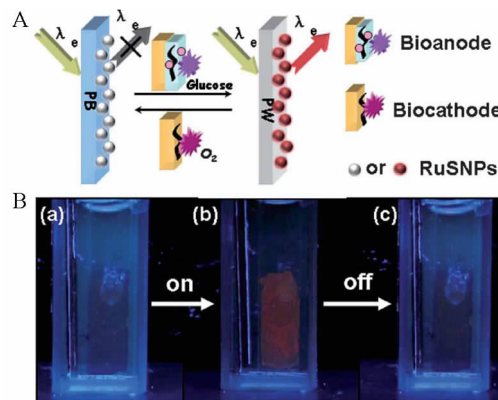


Fig. 9 A. Schematic diagram of luminescence modulation by the bioanode/biocathode on the hybrid film. B. The fluorescence images of the hybrid film: (a) in the open circuit; (b) connection with the bioanode; (c) connection with the biocathode. The fluorescence was excited by a hand-held UV lamp (365 nm). (from [95] with permission).

could provide more opportunities for enhancing electrochemical performance. The effects of the sizes, morphologies and compositions of the metal nanomaterials on the electrocatalysis in fuel cells were also stressed. Finally, stimuli-responsive materials-based novel electricity-dependent luminescence-controllable systems as the research frontiers were demonstrated with great interests in the future applications. Despite a great deal of success above, some important challenges remain for future development of functional nanomaterials. One of the most important challenges is the development of facile and effective approaches to prepare advanced functional nanomaterials with favorable parameters at low cost. Significantly, the requirement of highly active catalysts for electrochemical sensors and fuel cells has drawn tremendous interests in accurately controlling the synthesis of nanomaterials with specific size, composition as well as morphology. Secondly, it is generally accepted that interactions among the nanomaterials involving in the electrochemical interface play a critical role in the development of high-performance novel devices and this intriguing issue needs to be explored thoroughly. For example, the synergistic effect

between electroactive catalysts and supporting materials can no doubt contribute to the enhanced electrocatalytic activities in the field of electrochemical sensors and fuel cells. In the electricity-dependent luminescence-controllable systems, the interaction between luminescence materials and electrochromic species directly determines the response time, on/off contrast and good cycling performances. Furthermore, the exploration of novel interface engineering and the creation of new fabrication concepts or methods merit further attention.

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基于功能性纳米材料的新型电化学界面的构筑以及相关应用

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摘要: 由于独特的光、电、磁以及催化性质, 功能性纳米材料的研究已经渗透到各个学科并在不同领域展示出潜在的应用前景, 尤其是利用纳米材料构建功能性电极界面、研究其电化学行为并发展新颖的电化学纳米器件引起了人们的广泛关注. 本篇综述主要介绍作者研究小组在以功能性纳米材料构建新颖的电化学界面的最新进展, 集中关注其在电化学传感器、燃料电池以及光谱电化学中的应用. 这些纳米材料的应用极大地增强了电子转移、提高了电化学传感器的灵敏度以及燃料电池的催化效率. 作者也通过合成一些光谱匹配的荧光以及电致变色纳米材料构建新颖的荧光光谱电化学器件, 同时在材料的合成组装、多重刺激响应体系以及多功能化进行探索. 最后, 作者对这类基于纳米材料的电化学器件的发展和应用予以展望.

关键词: 功能纳米材料; 电化学传感器; 燃料电池; 响应性材料; 荧光光谱电化学