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Review—Nanostructured Materials for Sensing pH: Evolution, Fabrication and Challenges

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pH sensors with broad applications are in high demand in a variety of fields, including agriculture, healthcare, food processing, textiles, leathers, wet laboratories, and environmental remediation. The majority of pH-related reviews have concentrated on various polymers and metal oxide-based sensing materials, as well as fabrication techniques. However, considerations regarding the context of subsequent pH-sensing platform advancements in terms of materials and technologies with commercial viability must be addressed. Furthermore, the rapid advancement of traditional pH sensors toward nanostructured sensing configurations provides a number of advantages over traditional pH sensors, such as increased sensitivity with larger surface-to-volume ratio, improved stability, faster reaction time, and consistent stability. As a result, we reviewed the evolution of nanostructured pH sensing materials as well as their fabrication methodologies in this paper. Additionally, the inherent challenges and future work required for commercially viable nanostructured pH-sensing platforms are discussed.
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In 1889, the theory of acid proposed by Svante Arrhenius and the postulation of ion concentration proposed by Walther Nernst were combined to pave the way for the evolution of the term pH through the concept of hydrogen ion (H^+) or proton concentration. In 1909, pH was explicated for the first time by Soren Peder Lauritz Sorenson with his novel acid colorimetric analysis, where a hydrogen electrode was integrated with a calomel reference electrode. In this preliminary mechanism, a fixed potential was ensured by the reference electrode (RE), and the hydrogen electrode in solution built up a potential proportional to the H^+ concentration. Notably, pH was originally defined as the negative logarithm base 10 of the H^+ concentration. It was modified to the negative logarithm base 10 of H^+ activity. This update aimed to obstruct inactive ions, which formed due to the deviation of ions from their ideal behavior via reaction between themselves in a solution. Thus, to enhance the purity of analysis, ion activity (or effective ion concentration) was accounted for instead of concentrations.[1,2] Soren's precise assessment for pH analysis was not exoteric due to the supremacy of far cheaper pH paper sensors. However, his contribution has become the unprecedented stuff of modern lexicons. Although there was an effort to popularize electrodes for pH analysis, real groundbreaking development was achieved through the introduction of electrodes with acidometers. In 1920, Duncan McInnes and Malcolm Dole fabricated a glass electrode to detect H^+ ions via a doped glass membrane. Simultaneously, Arnold O. Beckham developed an acidometer to analyze acid strength. Therefore, a combination of these developments opened a new era for the engineering of more accurate pH sensors.[3]

In the present generation of electrochemical glass electrode sensors, pH is measured using two half-cells with glass membranes through the potential difference between two different solutions. pH detection is the prime concern of numerous biosensors and is in high demand in environmental monitoring, biotechnology, analytical chemistry, and industrial production. Despite the reliability and accuracy of a glass-based pH sensor, such as apparatus requires repeated calibration to avoid analysis drifting, exhibits electrolyte leakage and fragility, and is also difficult to miniaturize for in vivo implantations.[4–6] Considering these drawbacks, different review studies have discussed the progress in the research and development of different nanostructured pH sensing platforms to determine potential alternatives to traditional glass electrodes. For example, polyaniline (PANI) nanoparticle-based pH sensors are highlighted due to their stability, fast response, and higher sensitivity than other polymer-based sensors.[4,7] Likewise, Yuqing et al.[8] discussed new pH detection technology. In their work, investigation on ultrasensitive pH analysis platforms were included such as nanowire, nanotip arrays, and nanoscaled ISFET. Recently, Alam et al.[9] considered pH sensor fabrication with polymeric and organic materials for healthcare. In their study, the prospects of inexpensive, compatible, highly sensitive, stable polymers, including PANI and its derivatives, were discussed in conjunction with other materials. Their review also discussed the potential uses of PANI as nanostructured sensing materials, such as nanowires, nanospheres, and nanocomposites. To ensure more versatile applications, Qin et al.[10] highlighted electrochemical pH and chlorine sensors for water analysis. Their research shows that nanostructured metal oxides and polymers have a higher surface-to-volume ratio with additional charge transferability during pH analysis. Kurzweil also investigated metal oxides in terms of ion exchange surfaces for pH analysis, as well as nanoparticle-based pH sensing platforms.[11] Despite the fact that there have been several reviews on pH sensors, discussions are still limited to materials, design, and fabrication. The incorporation of accelerative impacts in the research and development of highly sensitive pH sensors with all their demanding features, such as specificity, flexibility, chemical stability, response time, and rapid functionalization, is insufficient. Furthermore, it is still necessary to focus on the sequential development of various nanostructured materials with compatible fabrication methods to cope with gradually advanced applications and to overcome potential challenges.

As a result, this review of nanostructured pH sensing materials is essential for filling the gaps in previous research. Furthermore, the use of nanoscale materials results in higher sensitivity in conjunction with higher surface-to-volume ratio. In terms of production flexibility, amphoteric reactivity, chemical stability, fast response, low costs, and additional sensitivity for pH analysis, tungsten oxide (WO_3), zinc oxide (ZnO), iridium oxide (IrO_2), and ruthenium oxide (RuO_2) based one-dimensional (1D) nanorods are required rather

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than glass- and polymeric-based sensors.[12–21] However, the total efficiency is heavily dependent on several conditions, such as the aspect ratio, orientation, polydispersity, and volume fraction of nanorods, limiting the overall performance to some extent. Therefore, to evolve toward a more sensitive and versatile material than nanorods, nanotubes have emerged as a potential candidate, with the hollow center of nanotubes allowing solutions to contact twice as much surface area (twofold) as nanorods. The limitations of these 1D nanostructures include a lack of selectivity, longer exposure duration, disturbance by humidity and temperature variation, and irreversible modification via chemisorption.[22,23] Furthermore, nanofilms and nanomaterial arrays with superior sensitivity are introduced, but there are also associated drawbacks such as limited stability and sensor component leaching during analysis.[14,24]

As a result, taking into account all phenomena, this review depicts an in-depth representation of the subsequent development of nanostructured pH sensing materials to overcome individual limitations based on materials chemistry (from polymers to nanotubes), sensing geometry, operating principles, fabrication tactics (from photolithography to spin coating), challenges, and future research. Challenges such as the sensitivity, stability, specificity, reusability, and biocompatibility of nanomaterials for novel electrochemical pH sensors are addressed here. The future prospects of nanoscale material-based pH sensors are also included in this review, where signal stability, dependable earth-abundant materials, and sensing mechanisms for sophisticated applications are primarily highlighted.

Different Nanostructured Sensing Materials

Accurate pH measurement in different applications require good selectivity and sensitivity, fast reaction time, and compatibility of sensing materials. These parameters determine the long term sustainability and commercial feasibility of pH sensing materials and ensure the ultimate intention of field applications.[4] Since 1920 electrochemical based pH sensors are widely used, while glass electrode based sensor is competitive to detect H^+ ion in a solution but also encounter with fragility, repeated calibration and miniaturization challenges for in-vivo and ex-vivo applications. As a result, the development of nanostructured sensing materials is unavoidable in order to overcome limitations and impart synergies in pH analysis over traditional methods. Nanomaterials are materials that have a diameter of 100 nm or less and dimensions (D) ranging from 0 to 3.[25,26] Different nanostructured materials are introduced based on their dimensions, such as nanoparticles (0D); nanorods, nanotubes (1D); nano-films, nano-coatings (2D); and nanofiber arrays (3D).[27] The use of these nanostructures in pH analysis provided a number of advantages, including increased sensitivity with a higher contact surface to volume ratio, lower material costs, and lower power consumptions.[28]

0D structure.—0D materials have no dimensions (usually nanoparticles) and could be amorphous, single or polycrystalline.[29] Different metal oxide based nanoparticles are studied as pH sensing martials due to the offering of wide advantages such as minimum production costs, compatibility, large surface area, high sensitivity, and availability. Among them ZnO, NiO, and WO_3 nanoparticles are mostly utilized in pH detection.[30–32] Oh et al. reported a novel surface acoustic wave (SAW) based pH sensor without reference electrode, where ZnO nanoparticles are introduced as sensing layer to ensure additional facilities over ZnO film, such as higher surface area, cost-effective and facile fabrication method. In this method, frequency shifting between pH 2–7 was 144 kHz with R^2 value of 0.957.[30] The proposed sensor also ensured analysis stability with chemical resistance. Ibupoto studied nanoporous based NiO nanoparticles that are deposited on gold-coated glass substrate using hydrothermal route with polyvinyl alcohol as a stabilizer. The sensor provided stable potential response of 43.74 ± 0.80 mV pH^{-1} for a pH range from 2–12, with <10 s response time.[31] To add more advantages over these sensors WO_3 nanoparticle based sensor was investigated by Santos et al. and showed sensitivity of 56.7 ± 1.3 mV pH^{-1} with a pH range from 5–9.[32] However, their conformable sensor has narrow linearity range. Another nanoparticle-based pH sensing material based on TiO_2 nanoflower was developed where the sensor showed excellent chemical stability against acid and alkaline media, with lower fabrication cost. The pH detection range was 2–12 and the sensitivity was 46 mV pH^{-1} with a R^2 value of 0.9989.[33] Due to nontoxic in nature, this sensor can be used in vivo. Apart from electrochemical sensor, optical sensor is also noteworthy in terms of evolution of nanostructured pH sensor.[34] Bai et al. fabricated fluorescence-based pH sensor where Ag@SiO_2 core–shell nanoparticle was employed. The author secured the pH detection range from 5–9 and recommended its potential implementation for pH sensing in biological sample.[24] Later, Kauffman et al. fabricated inorganic oxide nanoparticles-based optical pH sensor with the range of 2 to 12.[35] In recent period, Debnath fabricated silver nanoparticle grafted optical pH sensor to measure pH under high temperature as well as elevated pressure media like oil wells.

The ZnO nanoparticle-based pH sensor was also developed to measure the frequency fluctuation in SAW velocity. This oxide-based nanoparticle was employed due to its higher band gap, including large breakdown voltage, minimum electronic noise, and compatible to retain higher electric field. Moreover, the fabrication process was also facile to introduce. However, while the sensor has a high sensitivity, its performance is limited to aqueous media only. To improve competitiveness, the fabrication of NiO nanoparticle-based pH sensors evolved from bulk to micro to nano-size NiO-based sensors. Furthermore, WO_3 was developed to have higher sensitivity at a lower cost than other oxides due to the ease with which its structure and morphology can be controlled during the deposition process (Fig. 1). TiO_2 is primarily used as a semiconductor and is well-known for its chemical stability. As a result, a pH sensor based on TiO_2 nanoparticles was discovered to be one of the most common of its kind. However, there are some limitations in using single metal nanostructured materials for H^+ sensing, such as lower sensitivity and selectivity, as well as being easily poisoned.

To overcome these limitations, researchers included composite metal oxide-based nanoparticles in the fabrication of a pH sensing platform, where multiple metal oxides should be coupled to ensure fabrication feasibility as well as sensing performance.

1D structure.—1D nanostructured materials (i.e. nanorod, nanotube) are usually needle shape.[29] 1D material have gained more attention in research community for pH sensing because of its higher surface area, which is imperative for more sensitive pH analysis (Fig. 2). Different nanorod based sensing materials such as InN, ZnO, $Ir(NO_3)_4$, and WO_3 have been studied.[18,37] With such motivation, Young et al.[38] fabricated ZnO nanorods based wireless pH sensor via hydrothermal route and detect pH in the range of 4–10 with a sensitivity of ∼44 mV pH^{-1}. On the other hand, spin coating was considered for the fabrication of a pH sensor while both electrochemical potential and the site binding methods were considered for sensitivity analysis, which showed a sensitivity of 59 mV pH^{-1} with a pH range of 1–14.[39] InN nanorod as a sensing materials of EGFET based pH sensor was introduced for the first time with a focus to improve pH sensing. However, the obtained voltage was 22.66 mV pH^{-1} within 4 to10 pH limit.[37] The evolution of ZnO-based nanorods is being seriously considered in sensor fabrication due to its higher energy gap and excitation binding energy. Furthermore, ZnO is an amphoteric material that is highly reactive to both H^+ and OH^- ions. Also, ZnO-based nanorods have higher surface area compared to thin film, which reduce diffusion distance between the interactive analyte and the electrode surface. Eventually, it showed more sensitivity and a quick response with high signal-to-noise ratio. However, to enhance the pH sensor sensitivity up to the Super-Nernstian response, combined implementation of electrochemical potential method and site binding model were also considered during pH analysis. In case of nanorod-based

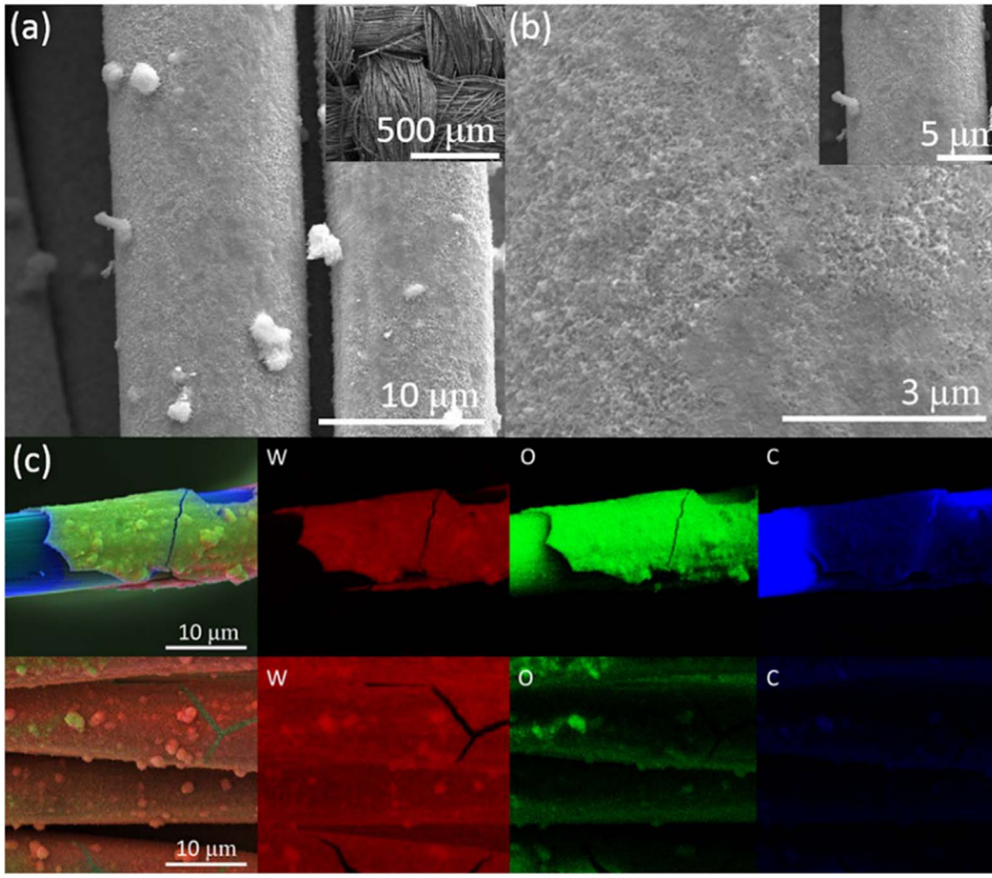

Figure 1. (a), (b) SEM images at different magnifications of WO_3 nanoparticle modified carbon fibre cloth, (c) EDX elemental mapping for W, O and C elements.[36]

EGFET pH sensor, the genesis of InN based nanorod over III–V group materials including AlN, GaN, GaAs was noteworthy because of its potential with high absorption coefficient and high drift velocity. In addition, deposition of InN nanorods on EGFET also imparted more sensitivity and efficiency than thin film based EGFET. Here, it's important to note that experimentation should be carried out to acquire more-qualified crystalline InN nanorods through the utilization of large-area growth methods.

Electrochemical pH sensors are gaining popularity due to a variety of features such as flexibility, adequate sensitivity, rapid response and commercial viability in a wide range of application fields. In some cases, the sensor's flexibility is more important for its compatibility with application scopes in a wearable format.[41] Taking this into consideration, a variety of materials have been investigated, with semiconducting metal oxides, such as CuO-based nanorods, being discovered to be more compatible to identify pH with flexibility and associated features. This 1D nanostructured sensor had a sensitivity of 0.64 mV pH^{-1} in the pH range of 5.0–8.5 under various bending conditions with better malleable properties.[42]

In order to improve pH-sensing capabilities, various endeavors were experimented using nanotubes. The presence of a hollow center in nanotube structures allow solutions to come into contact with nearly twice the surface area of a nanorod, resulting in greater sensitivity to the pH. Additionally, better mechanical stability, production feasibility, easy functionalization, and flexible electrical properties make these nanotubes an ideal candidate for pH sensing.[43–46]

In order to utilize these facilities, Bao et al.[47] fabricated a suspended single-walled carbon nanotube (SWCNT) based pH sensor incorporating a low temperature electrophoretic assembly process on a flexible parylene-C substrate. In this process pH value was calculated through measuring the SWCNTs resistance, which decreased with the increase of pH (4–10) of solution. The average sensitivity was 20.63 mV pH^{-1} in 2–11 pH range with R^2 value of 0.99. As a sequence, a SWCNT microfluidic chip as pH sensor was proposed with three fold higher sensitivity of 59.71 mV pH^{-1} (1.5 mV pH^{-1} slandered deviation and 30 s response time) within 3–11 pH range and 0.985 linearity compared to the previous one.[44] With the intension of delivering a flexible, stable, and more sensitive sensor, Qin et al. used functionalized single-wall carbon nanotubes as pH sensitive layers and ensued 48.1 mV pH^{-1} stable sensitivity within 7 s.[43] To facilitate in vivo application, single-walled carbon nanotubes were functionalized by oxygen plasma to develop a flexible sensor that resulted a superior sensitivity of 55.7 mV pH^{-1} with simultaneous R^2 value of 0.9996 within a range of 1–13 pH.[48] At the same time, single wall carbon nanotube functionalized with conductive material like poly (1-aminoanthracene) was proposed. The sensor without reference electrode offered sufficient sensitivity (50 mV pH^{-1}) for pH detection within 3 s and 2–12 pH range.[45]

Researcher also investigated multi-wall carbon nanotubes (MWCNT) for incorporating more efficiency in pH analysis. In consequence, Jung et al.[46] used nickel coated multi-walled carbon nanotube and found stable sensitivity within 30 s of 2–10 pH range. Similarly, highly conductive and chemically durable polyaniline was incorporated with MWCNT and achieved a good R^2 value as mentioned earlier. So, when considering both nanorods and nanotubes, surface area is an important consideration for higher sensing efficiency, with nanotube offering nearly twice the surface area of nanorod and confirming maximum sensitivity in a short period of time.[49] In this case, nanomaterials made up of an inner layer of one material and an outer layer of another material (core–shell structure) can be considered for use in an optical pH sensor.[50] However, Sun et al. constructed lanthanide nanorods-based pH sensor to detect pH

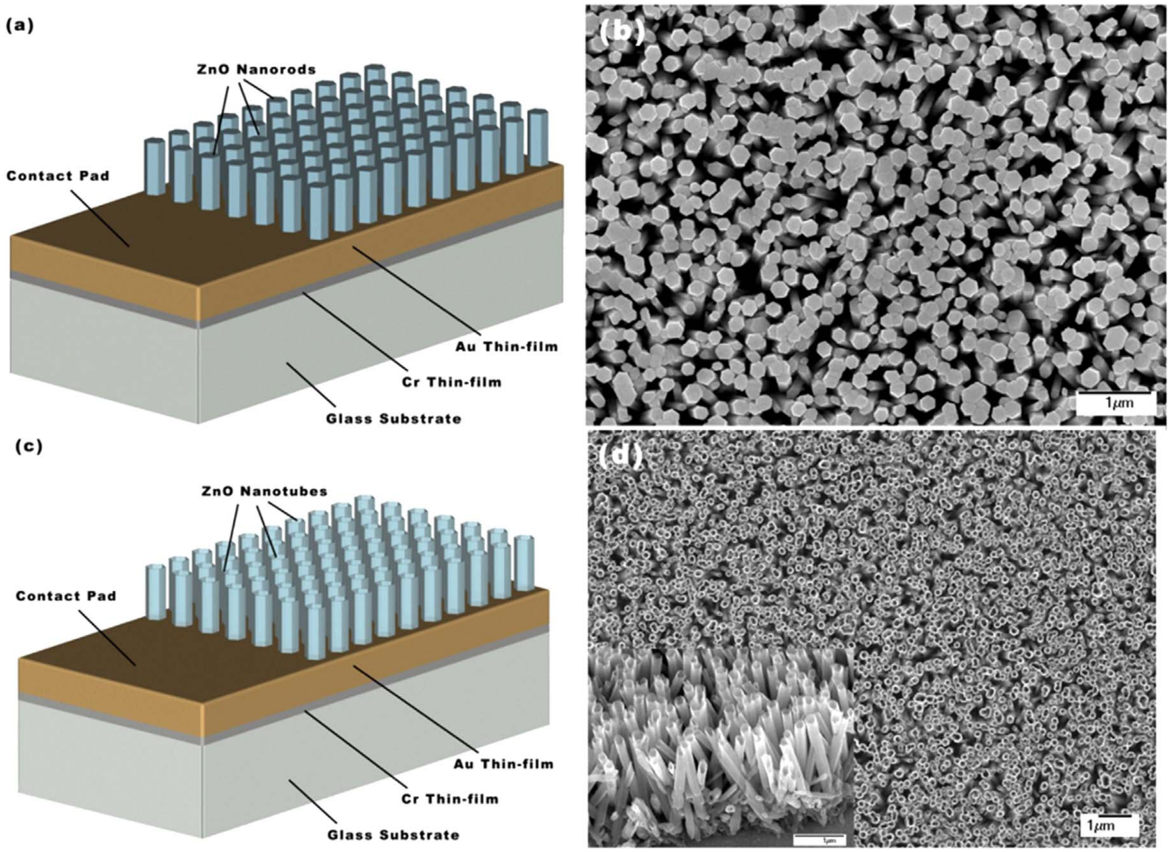

Figure 2. (a) and (c) schematic diagram of ZnO nanorod and nanotube pH sensors, respectively; (b) and (d) SEM images of ZnO nanorods and nanotubes, respectively (insert in image (d) shows tilted cross-sectional view of nanotubes.[40]

with the range of 6–10. The author claimed that such sensor was fabricated for the first time on the principle of up conversion luminescence.[51] Al-Khalqi et al. developed Mg-doped ZnO nanorod based optical pH sensor to sense pH with range of 1–12.[52] Thereby, different 1D nanostructured materials can be integrated simultaneously in both optical and electrochemical pH sensing platforms using a core–shell approach to ensure maximum sensitivity within minimal contact time.

2D structured.—2D structured materials are usually plate shaped and could be formed as nanocoating, nanofilms, and nanolayers. Different 2D conducting oxide layers have been studied in a wide range of applications (Figs. 3, 4). Among them, ZnO nanostructured thin films are more competitive and promising due to a number of advantages, including low cost, ease of fabrication, and a variety of electrical properties that allow them to be used in SAW, conducting electrodes, and a variety of other sensors.[53,40] Batista et al. introduced ZnO nanostructured thin film (thickness 35-–204 nm) to detect pH with 2–12 range and the sensitivity was 38 mV pH^{-1}.[40] To secure more sensitivity, vanadium and tungsten mixed oxide (V_2O_5/WO_3) film was utilized for pH sensing in extended gate field effect transistor (EGFET) device. The sensitivity was 68 mV pH^{-1} in a range of 2–12 pH. A polymeric film (polyethylenimine (PEI)/polypropylenimine based pH sensor was developed for clinical environment with 59 mV/pH sensitivity in 3–10 pH. These data indicate the prospects of EGFET, which is viewed as a potential alternative to ISFET due to its additional benefits, such as light insensitivity, simple packaging, easy to passivate, bio-applicability, reusability, and shape flexibility of extended gate area. Moreover, it is easy to fabricate through the simple combination of MOSFET and sensing structure. It is also worthy to mention that the integration of nanofilm with EGFET is more compatible for pH sensors. Both Pechini method as well as sol-gel method are applied as prospective alternatives of chemical evaporation or sputtering for ion sensitive membrane fabrication. Moreover, these alternative technologies are cheap and easy to operate for film deposition. In the case of a sensing platform, sensitivity is determined by the total number of surface sites per unit area (Ns) of the sensor, and there is a proportional relationship between Ns and pH sensitivity.

So, the evolution was noticed in terms of material structure in deposited film. More precisely, evolvement of amorphous materials from crystalline structure have noted because of Ns enhancement and sol-gel method is more rational to deal with. However, till now, most of the experiments were conducted with crystalline sensing film. So, it is important to investigate the fabrication of 2D nanostructure with amorphous material in order to have maximum Ns and ultimate sensitivity with super-Nernst response.

3D structured.—3D nanostructured materials are usually composed of nanocrystalline structure, bulk powders, nanoparticle dispersion, and array of nanorods, nanotubes, and nanowires as well as multi-nanolayers.[29] 3D nanofiber array-based polyaniline (PANI) sensing material was implemented to fabricate pH sensor for food processing industry. Here, due to its rough morphology, high surface area and extreme sensitivity to H_3O^+ ions, this 3D structured pH sensor provided a maximum sensitivity of 62.4 mV pH^{-1}, with R^2 value of 0.9982 and response time of 12.8 s.[57] In addition, Abu-Thabit et al. introduced flexible polyaniline (PANI) and polysulfone (PSU) based optical pH sensor to detect pH with range of 4–12. The thickness range of the fabricated sensor was between 100–200 nm. The sensor response time and sigmoidal response were <4 s and $R^2 = 0.997$ respectively.[58]

Due to the amphoteric material and reactivity with both OH^- and H^+ ions of solutions through surface adsorptions by forming surface bonds or oriented dipoles, ZnO nanorods (ZnO-NRs) array has great potential as 3D nanostructured pH sensing material.[59] A resistance

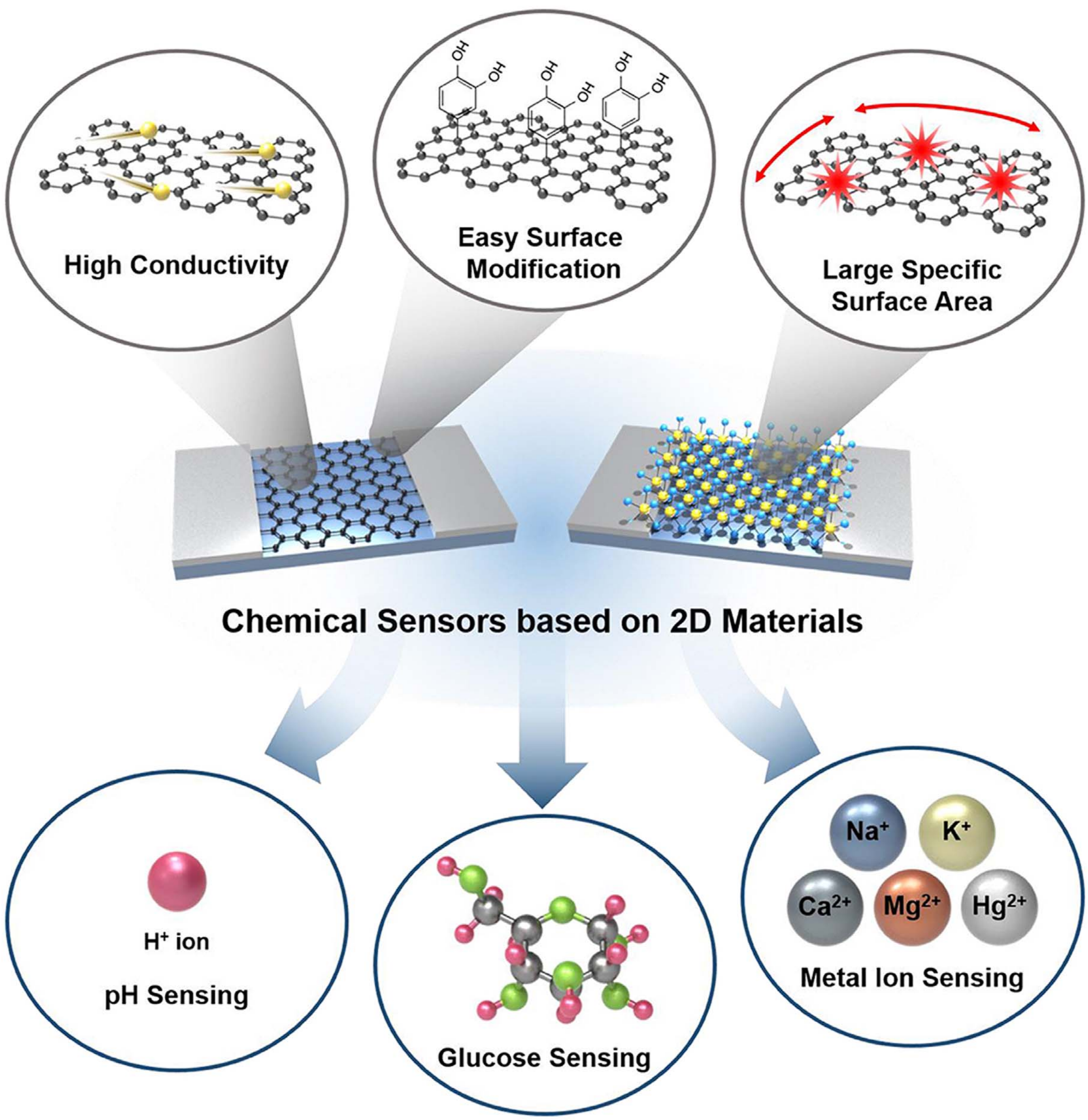

Figure 3. Schematic illustration of chemical sensors based on 2D materials with advantages of 2D materials and their application into ion/molecule sensing.[54]

based ZnO-NR array was implemented for pH detection and found plausible change in varying pH within 10 s.[60] At the same time Qi et al. utilized ZnO-NRs array to analyze pH with 45 mV pH^{-1} sensitivity, 6–7 s reaction time within a pH limit of 4–12.[61] A series of studies was also conducted on ZnO-NRs arrays integrated with AlGaN/GaN heterostructures for use in ion-sensitive field-effect transistors (ISFET).

Three consecutive methods were employed to fabricate the highly reactive sensor including photo electrochemical (PEC) etching method, PEC passivation, and PEC oxidation method. Basically, applied PEC passivated ZnO array increased the sensing surface area with inhibition of Fermi level pinning effect through the passivation of dangling bonds on the sidewall surface of arrays to inhibit the band alignment of electrolytes.[18] Later in 2017, Janczak et al. used graphene nanoplatelets (GNP) and submicron RuO_2 powder for fabricating flexible pH sensor. In this work, GNP were considered because of its higher selectivity towards H_3O^+ ions and lower cost than RuO_2. In addition, RuO_2/GNP composite based pH sensor offered flexibility at minimum production costs, easy optimization, and construction simplicity. In pH analysis, the newly developed sensor exhibited 53.65 mV pH^{-1} sensitivity in a pH range of 2.18–6.82.[62]

Here the inception of PANI based nano-array with screen printing technology was noted due to the more cost effectiveness over variety of metal oxides and printing technologies as well. In addition, flexibility, sensitivity and repeatability of PANI based pH sensor were also higher and more feasible to use in food processing industries. So due to its higher sensitivity, study should be carried out to apply 3D nanostructured PANI based pH sensor to monitor human health, water quality, and bio-reactions. On the other hand, GNP based flexible pH sensor also emerged to partially reduce the utilization of expensive Ruthenium (IV) oxide (RuO_2) for ultimate sensor costing as well to ensure higher sensitivity. But still, investigation should be conducted to check the influence of UV-Irradiation on RuO_2 to optimize the sensor performance. Also, this kind of irradiation exposure should be considered regarding other earth abandoned metal oxides for pH sensing platforms. From the Table I, it is evident that the sequence of nanostructured pH sensing materials with fabrication technologies regarding sensing performance within wide pH range can be noted as $1D > 2D > 3D > 0D$.

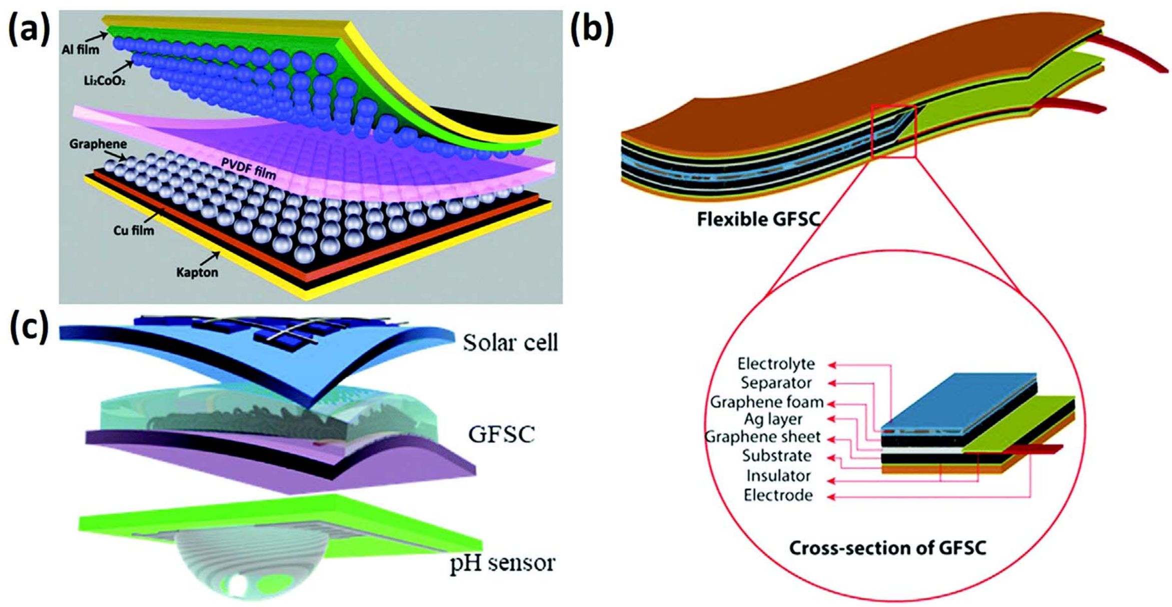

Figure 4. (a) Schematic showing the design of a flexible SCPC. Graphene nanosheets composited Cu foil used as anode; a layer of polarized PVDF film performs as separator; a LCO based mixture on Al foil is used as cathode; Kapton boards are used as shell. (b) Schematic of a flexible GFSC full cell consisting of two electrodes and its cross-sectional structure. (c) Schematic of a WBED consisting of a PV, a GFSC and a pH sensor for solar-self-powered pH sensing.[55,56]

Specifically, several parameters are considered to compare in same prospects between different materials with associated methods, such as 1D materials have significant sensitivity in a wider pH range, with maximum surface area, high electro-diffusion rate, optimum inter-material distance, and controlled stability; while 2D nanofilms have maximum pH sensitivity with limited pH range. Moreover, PANI based 3D nanostructured materials confirmed super-Nernstian response and sensitive within a certain pH sensing range. Finally, because of the lower sensitivity when compared to other nanostructured materials, 0D nanoparticles are considered a poor choice as pH sensing platforms.

Fabrication

The evolution of fabrication methods for highly sensitive pH sensing platforms have been noticed along with different nanostructured materials in recent years. During the application of pH sensors, several basic parameters have to be ensured while the ultimate considerations are maximum sensitivity, more operational life time, biocompatibility, fast response in large pH range, commercial feasibility and portability. But the prime motivation for this successive development of sensing platforms are to minimize fabrication cost with wide scale applicability. Evolution can be observed in two ways based on manufacturing costs. The first is the introduction of entirely new materials or processes in order to reduce overall costs. Although the initial development of any material is expensive, the total cost can be reduced in the long run through process optimization. Another is the use of existing technologies, such as more readily available materials and widely used processes with well-established equipment. As a result, research community is following either of the path for gradual development of sensing mechanism. Moreover, by considering the wide scale applicability of pH sensors, traditional one such as glass electrode is engaging in different fields but also encountering with analysis instability or drifting and required frequent recalibration. It is also offering limited span of utilization in pH detection specifically in rough surface and wearable media with lower sensitivity, and fragility.[74] To overcome these drawbacks, researches are heading towards carbon based nanostructured materials along with different metal oxides due to their stable electrical conductivity, low cost, suitability, wide availability, selectivity, and high surface area. Thus, in order to integrate more sensitive materials, different ways are launched to construct electrochemical based platforms with ease and success both. Screen printing, inkjet printing, spraying, wax printing, photolithography, radio frequency sputtering, electro-deposition, sol-gel, dip coating, hydrothermal method, spin coating, and ISFET are among them.[21,75–90] The comparative developments regarding the facilities of different fabrication methods with a variety of compatible materials are incorporated here so that maximum limitations can be overcome to ensure simple use of pH sensor with high performance.

***Photolithography.*—**Over the last decade, nanofabrication research has focused on developing ultra-miniaturized sensing platforms for a variety of applications. Because of the successful size reduction, the sensor can be fabricated with low material costs, light weight, and requires less power to perform during analysis. In this case, traditional photolithography is crucial for creating miniaturized sensitive sensors.[78,91] This method is used in the fabrication of nanostructured electrochemical sensors, where light is used to impose a geometrical pattern through a photo mask to a light sensitive chemical photoresist on the materials. Through this patterning process, it is very much possible to construct precise nanostructure with major control upon geometry, uniformity and sensitivity. At this point, the nanostructured circular electrode provided higher surface area (due to higher aspect ratio and packing density) than the planner pattern electrode. With such view point, electrochemical sensors with ultimate intension of biomedical implantation (i.e. glucose and DNA sensing) via top-down lithography and etching silicon and CMOS substrate over conventional planer sensor has been constructed. These investigations mentioned that such kind of patterning tactics is more compatible in case of limited casting area for sensor construction with higher sensitivity. Muaz et al. also demonstrated the photolithography technique via aluminum based interdigitated electrode fabrication with expected sensitivity and surface topology for pH 4–10 measurement.[78]

***Screen printing.*—**In the field of paper based electrochemical sensor construction, screen printing was the first and extensively used fabrication method. Initially it was intended for textile industry to ensure quick designing on outfits, but later in Colorado State University, Henry et al. utilized this method for the first time to construct electrochemical sensor. In this method, ink is used upon a

Table I. Representation of different nanostructured sensing materials with fabrication methods.

Structure	Sensing materials	Fabrication method	Sensitivity (mV/pH)	pH range	Response time (s)	References
	NiO	Spin coating	144 (kHz)	2–7	—	30
0D nanoparticle	WO_3	Hydrothermal method	43.74 ± 0.80	2–12	< 10	31
	ZnO	Hydrothermal method	56.70 ± 1.30	5–9	23–28	32
	WO_3	Hydrothermal method Hydrothermal method	41.38	3–10	150	36
	TiO_2	Electrodeposition	46.00	3–8	—	63
	MnO_2		57.05	1.5–12.5	20–60	64
	InN	Molecular beam epitaxy	22.66	4–10	—	37
	ZnO	Hydrothermal method	44	4–10	—	38
1D nanorod	ZnO	Spin coating	59	1–14	—	39
	CuO	Hydrothermal method	0.64 μF pH^{-1}	5.0–8.5	—	42
	ZnO	Spin coating	50.1	4.3–9.2	—	65
	SnO_2	Hydrothermal method	55.18	1–13	—	66
1D nanotube	SWCNT	Inkjet printing	48.1	3–11	7	43
	SWCNT	Photolithography	59.7	3–11	30	44
	SWCNT/PAA	Electropolymerization	50.0	2–12	3	45
	MWCNT/Ni	Electrodeposition	—	2–10	30	46
	MWCNT	Spraying	55.7	1–13	—	48
	MWCNT/PANi	Screen printing	20.6	2–11	—	49
	ZnO	Chemical growth	45.9	2–12	<100	67
	TiO_2	Anodization	59	4–10	—	68
	ZnO	Sol-gel method	38	2–12	—	40
	V_2O_5/WO_3	Sol-gel method	68	2–12	300	69
2D nanofilm	PEI/PPI	Electrodeposition	59	3–10	<15	70
	IrO_2	Electrodeposition	72.9 ± 0.9	3–11	—	71
	SnO_2	RF sputtering	58.1	2–12		72
	PANI	Screen printing	62.4	4–10	12.8	57
3D nanoarrays	ZnO-NRs	Hydrothermal method	45	4–12	6–7	61
	TiO_2	Anodization	59	2–12	<30	73
3D nanoplatelet	ZnO-NRs/AlGaN/GaN	Photoelectrochemical oxidation	57.66	4–10	—	18
	RuO_2/GNP	Screen printing	53.65	2.18–6.82	—	62

desired template with constant pressure through the squeezer to ensure uniform spreading of the ink on material surface. Here, the template have to be fabricated at the very beginning of the process via CAD software and specialized equipment based on the design complexity.[92]

Screen printing has some advantages over other techniques, such as reliability, high performance, flexibility, low cost, miniaturized structure, and fewer shoulder joints. This method is more suitable for commercially producing nanostructured thick film electrodes with optimized arrangement, shape, and integrated design.[93,94] To date, a variety of materials including RuO_2, SnO_2, PbO_2, PtO_2, WO_3, SnO_2, Co_2O_3, IrO_2, and OsO_2 are being used with this patterning method to fabricate pH sensors with excellent sensitivity, a large pH scale, and a broader range of application areas.[11,95,96] But among those oxides, RuO_2 is found to be more compatible over other oxides as H^+ sensing materials. However, due to cost, it is important to prepare composites of RuO_2 with other appropriate metal oxides without compromising its actual performance. So with such point, research has been carried out on Pt-doped RuO_2 nanostructured sensors to monitor water quality.[97,98] TiO_2 is also suitable for printing RuO_2-TiO_2 working electrode for sensing pH. Furthermore, the use of TiO_2 introduced antifouling properties in working electrodes in harsh working environment, as well as protecting RuO_2 from corrosion. To take advantage of all of these benefits, Manjakkal et al. investigated the RuO_2-TiO_2 sensing property and ensured sufficient reactivity (near the Nernstian response) over a wide pH range.[98] Other research groups have also worked with this metal oxide (RuO_2) and PANI and discovered the maximum sensitivity within a short reaction time.[57,96,99] As a result, it is safe to say that paper-based screen printing is a simple, low-cost fabrication method. The architecture and production process are also simple and do not necessitate a high level of skill to carry out. However, despite its numerous benefits, this method has a number of drawbacks, including the requirement for a large volume of materials during the fabrication process. Furthermore, this method employs the use of a stencil to design the electrode, which limits the working resolution and makes it difficult to eliminate the use of the stencil, indicating that a problem exists. Furthermore, the squeezer's pressure increases the likelihood of clogging the paper pores and impeding fluid flow during paper-based patterning.[79]

Inkjet printing.—Inkjet printing technology is used as a deposition method in both domestic and commercial level. So, the popularity towards this technology is gradually uprising over screen printing to manufacture electrochemical based pH sensor. Because the stencil is not required for printing purpose and the pattern can easily be designed in CAD software along with the direct transfer to the printer to impose ink droplets row by row to create various shapes. Due to the deposition facility, it allowed more precise control on pattern than screen printing. As a result, many research teams are working with this method for the fabrication of pH sensor. Maattanen et al. fabricated sensing electrode with the composition of Ag and Au while AgCl is deposited upon the surface of silver stripe to form reference electrode (Ag/AgCl). Considerable sensitivity was achieved for pH analysis through this method.[100] So in case of low cost fabrication, conventional office printer could be modified to fabricate paper based sensors. On the other hand, for high quality and more precision, sophisticated printer can also be used to control ink volume, speed and spacing.

Moya et al. used inkjet printing to construct iridium oxide based electrochemical sensor with the intention of both pH and dissolved

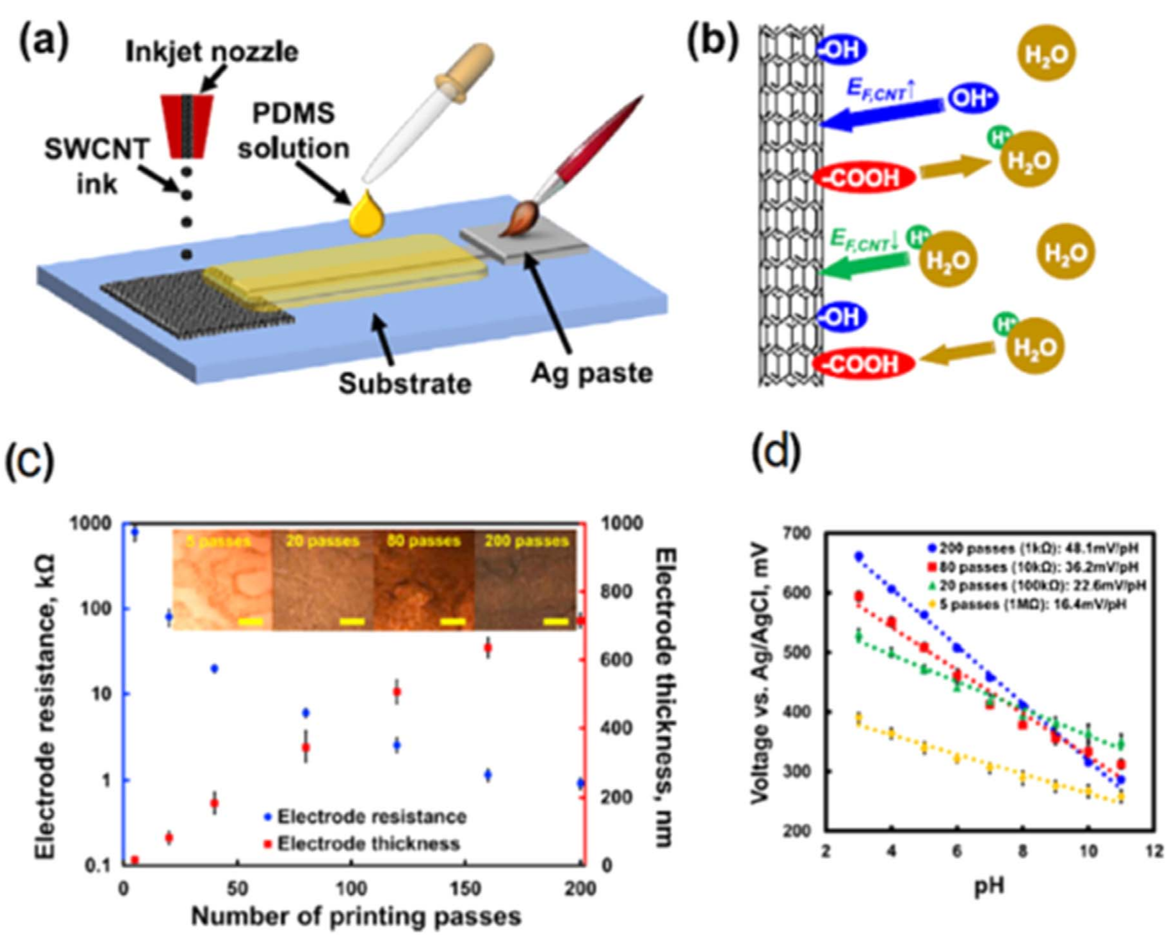

Figure 5. Schematic of fabrication process (a) SWCNT-based pH sensing electrode, (b) pH sensing mechanism for SWCNT-COOH (c) electrode resistance and thickness as a function of the number of printing passes. Inset: optical microscope images of SWCNT films printed using different number of passes (scale bar: 100 mm, 200 passes); (d) calibration curves of SWCNT pH sensing electrodes on glass (different numbers of printing passes).[104]

oxygen detection. Greater sensitivity was achieved with super-Nernstian level (65 mV pH^{-1}) within the pH range of 3 to 10.[101] Da Costa et al. executed a electrochemical sensing platform by this method while carbon ink based MWCNTs are constructed by utilizing sodium dodecyl sulfate as an ionic surfactant.[102] Shamkhalichenar et al. developed electrochemical based sensor via carbon nanotube and silver nanoparticles. Hu et al. developed highly sensitive nanostructured gold electrode arrays through the utilization of domestic photo printer (Epson R230) without modifying paper substrate.[103] In recent period Eshkalak et al highlighted the modification of SWCNT with oxygen containing functional group to have more pH sensing capacity (Fig. 5).

Although this method is offering variety of opportunities, but at the same time suffering from problems including insufficient accuracy of material deposition, lack of printing resolution, absence of precise control for sophisticated sensor fabrication etc As a result, research should be conducted to modify commonly used photo printers for better sensor fabrication, develop advanced inkjet printers for increased commercial productivity, ensure the availability of compatible ink to print highly sensitive and selective electrodes with maximum resolution, and establish a base mark standard for selecting pretreated convenient paper to ease this patterning process.

Wax printing.—Wax printing is an easy, cost-effective, and well-established method for producing large volume (hundreds to thousands) of sensors due to its fewer manufacturing steps. This process is mostly used among different patterning methods (screen printing, photolithography, and inkjet printing) to fabricate microfluidic paper-based analytic devices (μPADs) for diagnostics and in other field of applications. Le et al. evaluated laser heating wax printing method for the development of user friendly, sensitive and affordable sensor for pH analysis.[105] Authors found that in comparison to other patterning methods, wax printing requires less special equipment, possess higher heat resistance, and do not use of poisonous reagents. Need to mention that photolithography process demands sophisticated machineries, along with well-furnished clean room.[106] However, wax technology can be implemented both as pattern printing upon the paper surface and also as melting the wax by hot plate into the paper to construct hydrophobic barriers.[107] Despite having more advantages over remaining printing method, wax printing also has some problems and need to overcome. During the process, wax is mainly used to keep the printing liquid within printing zone by preventing the liquid flow in all direction. But in case of biological fluid, which may have lower surface tension could flow over the hydrophobic barriers. It is because, wax decreases the surface energy of the paper instead of filling the pores of cellulose fibers.[108]

Spraying.—The determination of hydroxyl ion in aqueous media is a critical parameter to monitor. As a result, the measurement of pH is an ultimate challenge in different field of applications. In this situation, the genesis of 1D nanostructured based carbon nanotube technology could be a potential solution with accuracy and precision. The unique structure of this material can be used as a link between biomolecules and solid state devices to transduce a measurable signal for information extraction.[109] Kwon et al. for the first-time construct SWCNTs based highly sensitive pH sensor with spraying method. The sensor showed an optimized sensitivity as well as selectivity with a wide pH range.[80] Extensive research has been carried out including single semiconductor CNT[110] or random networks of SWCNTs to fabricate pH sensing platforms in FET (Field Effect Transistor).[111] However, these processes have some drawbacks like more complicated and limited controllability and thus very difficult to construct high density nanostructured sensors.[112] Thus, SWCNTs fabrication by ultra-precision spray is introduced due to its simplicity and user friendliness. In addition, spraying can be carried out to deposit suspended SWCNTs on catalyzed substrate as well as arbitrary substrate with precise controlling of geometric structures.[113]

Radio frequency sputtering.—As an alternative to glass electrode, metal oxide based electrochemical pH sensors are more competitive and prospective with several advantages.[21] RuO_2 is a popular sensing material and screen printing is a convenient method to fabricate pH sensor platform with this oxide. But recent analysis claimed the accuracy of material deposition is lower than standard and impractical in case of thin film development. So radio frequency sputtering have gained more concern to fabricate pH sensors in conjunction of Ag/AgCl RE. Compared to the patterning technique, this fabrication method is imparting several unique features including maintenance of stoichiometry of the target by adding oxygen with argon gas, precise controlling of film thickness and geometry at nano level via optimized deposition rates, and unique morphology of the surface due to the molecule-by-molecule sputtering. In consequence, all of these additional features allow this method to ensure super-Nernstian sensitivity within nominal reaction time.[21] Sardarinejad et al. checked the influence of different Ar/O_2 ratio during radio frequency sputtering of RuO_2 working electrode for pH sensing. The performance of fabricated sensor was analyzed regarding hysteresis, sensitivity, stability, response time, and reversibility. Super-Nernstian response (64.33–73.83 mV pH^{-1}) was observed with Ar/O_2 gas ratio 8/2 in 3 s of reaction time.[21] Yin et al. fabricated ion sensitive SnO_2/ITO glass EGFET structure as a pH sensor via RF sputtering. During the study variety of sensing gate structures were studied, like ITO glass, SnO_2/ITO glass, SnO_2/Al/Corning glass, ITO/micro slide glass, and SnO_2/Al/micro slide glass. Among them, SnO_2/ITO glass based sensing gate structure of EGFET was observed to provide nominal drifting and hysteresis effect with high sensitivity of 57 mV pH^{-1}. Other research group also continued investigation of pH sensing platform fabrication with metal oxide via RF sputtering. Ta_2O_5, SnO_2/ITO, SnO_2, and WO_3 have been studied as pH sensing materials and their ability to impart sensitivity up to Nernstian response level in a short time and over a wide pH range has been demonstrated.[72,114–116]

Electrodeposition.—The electrodeposition term is referring either to electrophoretic deposition (EPD) or electroplating. The electroplating is based on ionic solution (mainly water based) while EPD works in the suspension of colloidal particles. Metal oxide electrodes frequently provide lucrative properties as a pH sensing platform, such as sensitivity over a wide pH range, stable conductivity, and a lower tendency for dissolution. Among the variety of metal oxides, iridium oxide is the compatible one for electrodeposition and Yamanaka was the first member to introduce this. During the investigation, iridium was used in the fabrication of electrochromic display devices.[117] With such motivation, Marzouk et al. proposed iridium oxide based electrodeposited pH sensor with super-Nernstian response (63.5 ± 2.2 mV pH^{-1}) in the pH range of 2–10.[118] Later Marzouk again used electrodeposition method to fabricate iridium-based pH sensor in conjunction of etched titanium substrates. Because this method is offering additional advantages over frequently used depositional methods like sputtering. It also required low temperature, and have superior control on the versatility of sensor geometry. During analysis, 73.7 ± 1.2 mV pH^{-1} (super-Nernstian sensitivity) was achieved for 1.5–11.5 pH range.[81] IrO_2 based micro-electrochemical transistor was also constructed by Kreider et al. for pH sensing and the sensor showed the 65 mV pH^{-1} sensitivity in pH range of 1.8–12, within 40 s response time.[119] Besides iridium, other metal oxides like PbO_2, WO_3, MnO_2/GPLE are also engaged with this film deposition method and provided sufficient sensitivity during pH detection.[64,120]

Sol-gel method.—The sol-gel fabrication is a low temperature material synthesis method based on the hydrolysis and condensation reaction of organometallic compounds in alcoholic solutions. This method is more feasible than other deposition methods for the construction of pH sensors due to its simplicity, which require less expensive setup.

For example, well established sputter deposition, and thermal oxidation are extensively studied as effective film synthesis manner and at the same time encountered with several limitations. These methods are expensive due to the utilization of highly pure targets and sophisticated deposition systems in vacuum media. Moreover, thermal issues during sensor fabrication on flexible polymer substrates is also an additional burden.[121] In this case, sol-gel method was emerged with some favors during coating fabrication like, efficient control of solution stoichiometry, simple compositional modification, functionalization of sensing elements with ease, lower annealing temperature, high chance to ensure coating deposition on higher surface area of the substrate, and cost effective fabrication methods.[87] To utilize all the advantages of sol-gel method, Nguyen et al. fabricated pH sensor array by using iridium oxide. After completing, the developed sensor array was experimented and exhibited Nernstian response with 57.0–63.4 mV pH^{-1}. Chemical stability, process repeatability, and lower hysteresis impact of pH sensor were also identified.[122] Batista et al. considered the construction of SnO_2 based EGFET pH sensing platform by simple and cost effective sol-gel pechini method.[123] Moreover, Liao et al. analyzed the pH sensing performance of TiO_2 coated thin film following sol-gel method. Here, TiO_2 film was immobilized through the addition of phosphotungstic acid and polyvinyl chloride with the intension of procaine drug sensor development. Hence, thin film of TiO_2 was performed as a membrane substrate for drug sensing. Higher sensitivity of the sensor near to Nernstian response (55.03 mV pH^{-1} within 16 s) with low drifting tendency were noticed.[87]

Dip coating.—This is a simple, low-cost, and stable technique for depositing a liquid film on a substrate by immersing it in a solution containing hydrolysable metal compounds. As a result of the withdrawal from solution, a homogeneous liquid film is deposited on the surface of the substrate at room temperature. This method is similar to the wet chemical method, except that the drying time is reduced due to the use of solvents.[124]

So in the recent years, this method has become very popular as an inexpensive and sensible thin film deposition technique compared to other vacuum based deposition methods.[84] Nishio et al. used dip coating process for the development of IrO_2 thin film.[125] Based on this work, Huang et al. considered dip coating for the fabrication of iridium oxide based flexible pH sensor. Despite the availability of a variety of fabrication methods such as sputtering deposition, electrochemical deposition, thermal oxidation, and sol-gel processes, the dip coating process was used to provide additional benefits for pH sensors such as low cost, less drifting, fast response, and repeatability.

On the other hand, different metal oxide sputtering can provide unique film structure with good quality and precision, but it is a costly method specially target costs. Moreover, the oxygen and argon ratios, positioning of target, deposition rates, and RF power flow during fabrication affects the pH sensing parameters including redox interferences and analysis drifting. In case of thermal oxidation and electro-deposition, quality of the deposited film may require high annealing temperature (500 °C–800 °C) and precise power supply system respectively. Film fabricated at high-temperature has a tendency to crack, which is responsible for poor sensing performance during pH analysis.

Moreover, high temperature treatment is also limiting the use of some sensing material like polymers. In spite of having flexibility on dip-coating, the major challenge is still remained the controlling of coating thickness uniformity. Here, focus should be considered upon several factors during nanostructured pH sensor fabrication including solvent evaporation rate, nature as well as concentration of the solvent, the angle at which the substrate is immersed into the solution, and compatible viscosity as well as optimum concentration of the solutions.

Hydrothermal method.—In recent years, successive research and development have been observed as a result of the evolution toward more sustainable pH sensor fabrication. Wang et al. and Slewa et al. focused feasibility on the improvement of Ir/IrO_2 pH sensing electrode and nanorod synthesis via the hydrothermal method, respectively.[86,126] Because the method is the simplest, synthesis is carried out in a steel pressure vessel known as an autoclave.

Actually, a variety of construction methods have been introduced up to this point, but these methods are also constrained by limitations. For example, most popular metal oxide based nanostructured thin film fabrication methods are electrodeposition, reactive sputtering, and thermal oxidation. With variety of advantages, these methods are used to construct sensors for food, biology and for other extreme environments. But the formation of dry film with high temperature via all of these methods are responsible for defects and surface cracks of sensing film. It is also leading to significant aging effect and ultimately resulting potential drifting in pH analysis. To minimize this, immersion of fabricated film into the deionized water is a general practice which required weeks or even months for sufficient hydration of the sensing platforms to ensure detection stability. So, it can be said that hydration is a key functional factor for analysis drifting. Thus, electrode hydration should be more optimized to suppress electrode thermal stress, internal surface defects, potential deviation, and mitigation of potential drifting in terms of longer sustainability. In addition, electrode surface crystalline integrity with grain size and interplanar spacing of material crystallinity should also be tuned by optimizing electrode hydration during the hydrothermal method.[121,127,128]

Spin coating.—In order to ensure more uniformity via precise controlling of modulable nano-topography and homogeneous chemistry of film surface, spin coating is the best option over any other method. Spin coating is a process to deposit thin films uniformly upon the surface of flat substrates. However, required amount of coating material is applied on the center of the substrate, which is either spinning at low speed or not spinning at all. During this process, the centrifugal force play the crucial role to spread the coating materials uniformly. In consequence, Liao et al. fabricated the TiO_2 based pH sensing membrane with spin coating while solution was prepared via sol-gel method. About 58.73 mV pH^{-1} sensitivity was obtained during experimentation. Later on-trend, Kumar et al. experimented ZnO nanorods, fabricated on the surface of SiO_2/Si and confirmed pH sensitivity of 50.1 mV pH^{-1}. Basically, during the analysis, intended solution with material species are deposited with a volatile solvent on the substrate surface and at last spun around its normal axis, uniformly spreading the excess of precursor solution due to the centrifugal force. At the same time the film thickness is also reduced till the reaching of equilibrium condition or until solvent vaporization of the solution. As, the method is potential to fabricate ultrathin film with the scale of 1 to 200 nm, so it's noteworthy that, influence of different factors into this process should be further optimized for the construction of nanostructured pH sensing platform including concentration of polymer, compatibility between the viscous and centrifugal force, volatility of solvent, associated environmental parameters (relative humidity, system temperature, pressure), and spinning speed.

ISFET.—The ISFETs were first manufactured in 1970 as an alternative to electrochemical glass electrodes. The metal gate was replaced in the structure of an ISFET by an ion-selective membrane, electrolyte, and a reference electrode drain. As a result of this modification, the ISFET became sensitive to changes in pH level and could thus be used as a pH sensor.[129] The working principle of an ISFET is based on the fact that the drain current is an indicator of pH in the solution when the ISFET is immersed in it. It is a low-cost, glass-free device with a smaller size than a glass electrode. These devices are used to measure the pH of a wide range of solutions, from basic to acidic, and both Si_3N_4 and Al_2O_3 are used as gate insulators.

Thu-Hong et al. developed a simple, and fast fabrication method with stable response via spraying of SWCNT. Here, the conductance and the typical amperometric respond of SWCNT were successfully demonstrated in different hydroxyl ion concentrations at room temperature. Here, sprayed SWCNT bundle are easily produced either by direct growth on a catalyzed or by deposition upon an arbitrary substrate from a solution of suspended SWCNT. For measuring the changes of SWCNT electrical properties, a pair of those Cr electrodes was used between the two electrodes.[130]

On the other hand, extended gate field-effect transistor (EGFET) structure also reveals many advantages over the conventional ISFET including low cost, simple passivation and package, sensitivity against temperature and light, flexibility of gate structure, and long-term working stability. It's important to note that surface ion adsorption mechanisms of pH sensitive membranes in both ISFET and EGFET are same. Hence, the basic principle distinction between pH-ISFET and pH-EGFET is the impedance of sensing films. Insulating membranes like SiO_2, Si_3N_4, and Al_2O_3, were commonly used for the fabrication of ISFET and presented very low sensitivities when applied in EGFET. So, the extended gate of EGFET must be constructed with a conductive material for easy transmission of sensing signals.

Recently, Wang et al. fabricated a highly sensitive and stable EGFET on the basis of aluminum doped ZnO (AZO) for pH sensing. The AZO nanostructures with different Al concentrations were synthesized on AZO/glass substrate via hydrothermal method. Then AZO nanostructures as sensing platform was connected with the metal-oxide-semiconductor field-effect transistor (MOSFET) and ensured higher sensitivity about 57.95 mV pH^{-1}, with 0.9998 linearity, lower drifting rate, and wide pH sensing range (1–13).[131]

After going through the critical analysis of the evolution of nanostructured pH sensor, some salient points can be incorporated (Fig. 6). Till now patterning technique for sensor fabrication is mostly popular while screen printing is the leading one. Simultaneously it has drawbacks like sophisticated machinery requirement for stencil preparation to print sensors. So, in order to minimize this complexity, researchers are gradually heading for more patterning method but deposition accuracy regarding nanostructured senor fabrication is still questionable. Then the introduction of RF sputtering, thermal oxidation, and electrodeposition improved process accuracy and precision. But at the same time ageing effect was infused with pH sensor due to higher annealing temperature and ultimately responsible for analysis drifting. After that, sol-gel, dip coating, and hydrothermal method were introduced by focusing with lower annealing temperature, more flexibility, lowest drifting, and easiest manufacturing process. Here, hydrothermal method is more prospective and potential to minimize thermal stress and internal surface defects of fabricated pH sensor and ensued more accuracy with stability. Emergence of spin coating is a remarkable evolution in the research field of pH analysis. This method is mostly effective for ultrathin (1 to 200 nm), uniform and tunable nano-topography of sensor structure. At the same time, the method is cost effective with easy going manner. ISFET is also a groundbreaking development where the concept of FET is utilized and the metal gate is replaced by an ion-selective membrane, electrolyte and a reference electrode drain to ensure flexibility with long term stability of pH sensor. As a result, it is clear that the evolution of nanostructured pH sensing materials and fabrication methods is primarily due to the assurance of higher sensitivity, process flexibility, greater stability, faster response, lowest production cost, material compatibility, minimum manufacturing complexity, avoidance of complex machineries, and compliance with updated field of pH analysis.

Application

The evolution of nanostructured sensing materials and fabrications has occurred as a result of critical milestone aspects of well-suited pH sensing platforms for mass production and commercial sophisticated applications in the biomedical field. Particularly, in ex vivo applications of nanostructured pH sensing platform are including urine test, saliva test, and tooth decay analysis. In case of

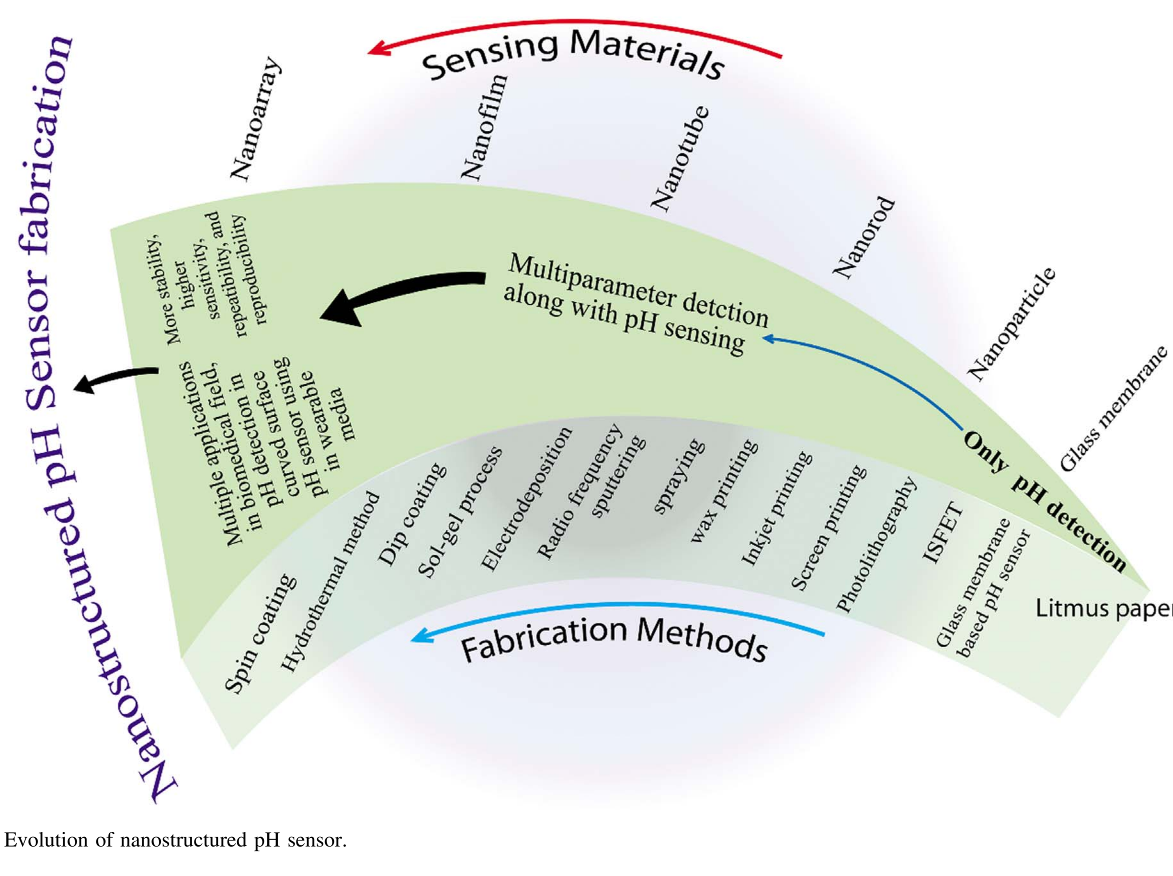

Figure 6. Evolution of nanostructured pH sensor.

in vivo applications, glioblastoma identification, intracellular and extracellular pH identification, oral hygiene management, ischemia analysis, and sweat analysis are noteworthy.[15] Regarding urine test, pH sensing of the excreted fluid provide information of patient health conditions. Because pH of this discarded body fluid can act as a biochemical maker. During saliva and tooth decay analysis, nanostructured pH sensing platform offer advantages like easy implantation and accurate pH quantification.[132] To identify, monitor, and treatment of glioblastoma, nanostructured platform is mandatory. Because solid tumors are known to be acidic and till now, measurement of pH is mostly relied on optical imaging system, magnetic resonance spectroscopy, and magnetic resonance imaging. However, gaps are still remained to provide scope for the in vivo pH measurement of cancerous cells with the facilities of nanostructured sensing platforms. Additionally, before mentioned methods are need to be reconsidered to overcome their drawbacks.[133,134] Similarly, nanostructured pH sensor is also noteworthy in oral hygiene management. In consequence, research is carried out to fabricate flexible and insertable nano pH sensor for accurate monitoring facilities of oral health. In generally, saliva is collected and analyzed externally. But if it's possible to insert the nano structured pH sensor, data accuracy will be increased along with the reduction of process complexities and required time. So research gap exists in this specific area. In sweat analysis, the use of nanostructured pH sensing platform should be mandatory because sweat consists of different cations including potassium, sodium, and magnesium. In this case, the selectivity and sensitivity of pH sensor should be maintained only for the H^+ to avoid the falsely counting of other cations during pH measurement.[135] Apart from medical applications, nanostructured pH sensor is also promising to use in sea water monitoring. However, the traditional glass electrode pH sensors are widely used in this purpose due to its faster response, reliability, and affordability. But lots of drawbacks are limiting its sensing performance including instability of signal, and requirement of constant re-calibration. As a result, significant errors are noticing and calling into question its sensing quality as well as user significance.[136] In addition, reference electrode is another source of error as variable potential develops across the junction according to the external consequences of pressure. However, glass electrode is bulky, brittle, and demands storage solution. As a result, research is improved towards nanostructured pH sensors (polymers, carbon nanomaterial, metal, and metal oxide based) with excellent performance and minimum cost. For example, in 2017, Salovo et al.[137] developed a graphenic materials (reduced graphene oxide) based pH sensor with sensitivity of 40 ± 4 mV pH^{-1} in effective pH range between 4 and 10. Again in 2019, Park et al.[57] introduced polyaniline nanofiber array-based pH sensor with 62.4 mV pH^{-1} sensitivity, 12.8 s response time, and repeatability of 97.9% retention. The author recommend its multidimensional applications for water monitoring, health analysis, and investigation of chemical reactions. Thus, gradual emergence of nano-engineered pH sensing materials with improved sensitivity, flexibility, quick response time, easy fabrication are noteworthy. However, metal oxide based nanostructured pH sensors are more competitive regarding sensing performance along with higher stability in the field applications of seawater monitoring. Because, carbon-based nanomaterial are not possess with stable response and difficult to handle and reproduce. While polymeric nanomaterial are poor in terms of signal stability and precision.[138] But these limitations can be overcome by combining polymeric and inorganic nanomaterial with optimum ratio. This ratio is the integral factor to fabricate robust and long lasting pH senor for seawater management purpose. Till now, very few dedicated sensors are introduced in seawater monitoring. But it's imperative to ensure design adjustment and rapid field testing to construct sustainable pH sensor for seawater monitoring. It's also emergent to ensure complete replacement of glass electrode pH sensor and spectrophotometry for realistic applications. Thus nanostructured electrochemical pH sensor in near future will be the praiseworthy alternative for specific applications.

Relative challenges and recommendations.—Relative challenges regarding sensing reliabilities (repeatability, reproducibility, and stability), field applications and mass production of nanostructured pH sensor are still remained. Furthermore, the relationship between theoretical concepts and modeling aspects of pH sensing mechanisms, in particular, compatibility between predictive concepts and experimental results of pH sensors, remains a challenge in terms of long-term implementation.

Stability.—Substantial progress has been noticed for the augmentation of pH sensing performance while stability is still remained as a challenging factor. More exactly, electrode is encountered with potential drifting which make difficulties to have consistent pH values. Here, several influencing factors can be noted as fabrication manner, materials for reference electrode as well as sensing electrode, and experimental setup.

Both ISFET and glass electrode-based pH sensor have limited stability in long run while EGFET have sufficient sensing stability. This is happened due to separate framing of EGFET structure at which the fluctuation of environmental parameters (temperature as well as light) cannot infuriate the channel directly. In consequence, sensitive membrane surface potential can be influence by these fluctuations.[139] Different experimental setup with same sensing electrode material exhibits different behaviors. For example, IrO_2 imparts excellent sensing stability in both aqueous and non-aqueous media as well as corrosive and nonconductive media. But in case of miniaturized multiparameter monitoring chip, this pH sensing material demonstrated higher potential drifting about 0.3 mV h^{-1} for more than 86 h, and 0.6 mV h^{-1} for first 30 h. So, this challenge must be addressed in terms of nanostructured pH sensing materials for sophisticated applications.[140] Same drifting phenomena is also noticed for hydrothermal aluminum doped ZnO nanorod based pH sensor and still remained as a challenging factor.[141]

In case of nanofilm fabrication, several encounters have to be addressed. For example, thermal oxidation is mostly used for this nanofilm construction but this method is responsible for the film drying and causes higher aging effects of pH sensors.[126] So prospective solution should be finding out to minimize the sensor aging and to suppress drifting during analysis. However, hydration during nanostructured electrode fabrication can be a significant solution against potential drifting. Specifically, hydrothermal hydration of sensing electrode at 220 °C for 24 h and then soaking with dimineralized water. Electrode construction with this manner shows significant stability for more than 40 d of working periods and can be extended through the optimization of sensor hydration.[126] Moreover, carbonate melt oxidation could be a potential option for drifting mitigation. Such as iridium oxide based nanofilm coating through carbonate melt oxidation on iridium metal wire provides lower drifting and still needs to consider for further investigation.[142] In addition, short-circuiting of ion-selective electrode with metallic wire to traditional RE (Ag/AgCl) has also be considered to reduce the demand for regular calibration and thus increased electrode stability.[143]

Repeatability.—Repeatability of pH sensor is also remained as difficult challenge likewise sensor stability. Here, repeatability is considered as the output of the pH sensor should be same in every time of detection for similar solution. Till now, the repeatability is quite impossible to ensure but its obvious to minimize to have accuracy in pH detection. This addressing phenomenon is most crucial for biomedical sensors where precise data is the prime concern. So, in order to ensure precision of data, several factors need to be optimized that influenced sensor repeatability including fabrication, materials for sensing and reference electrode, and sensor setup. In generally, sensor repeatability is determined via several pH measurement in one buffer solution and calculating the standard deviation of each trial. Moreover, determination of hysteresis can also be utilized for repeatability evaluation. For pH sensing repeatability, applied materials are playing a vital role including graphene oxide nanofilm, ZnO/Si nanowires, PANI nanopillar, Si nanowires, iridium oxide film.[144] Among them, iridium oxide nanofilm shows lower repeatability because of subtle fluctuation in nanoscale pore size embedded in sensing film.[122] On the other hand, silicon nanowire-based pH sensor has higher repeatability due to its stable single crystalline structure.[145] To have more repeatability, composite materials like ZnO and Si nanowire is fabricated where more specific surface area and higher binding sites for connecting additional H^+ ions was prime consideration.[146] So, surface area should be the actual consideration for maximum repeatability. In sum, its worthy to mention that compatible material is the main criteria for significant repeatability of pH sensor while other parameters like more sensitivity, fast response, and minimum potential drifting are also responsible for sufficient repeatability.

Reproducibility.—This is the most important parameters for biomedical applications while device is needed to be replaced for degradation of its structure and for hygiene reasons. Reproducibility is defined as the same response as well as same stimuli of pH sensing platforms from different device to device.[147] For the ultimate reproducibility of sensor, stability, response time, drifting behavior, and sensitivity are also the responsible parameters and still it's quite challenging the optimization of all these parameters simultaneously in a nanostructured sensing platform. Different experiments are carried out to check the pH sensing reproducibility measurement like as ZnO nanotube as well as nanorod based sensing electrodes are trailed and found the excellent reproducibility with minimum standard deviation (5%).[67] On contrary, Bartic et al. and Fulati et al. both experimented interdigitated electrodes with organic semiconductors and diamond-like carbon thin films with Tantalum pentoxide-ISFET respectively and found significant reproducibility in terms of pH sensing.[148] In addition, Li et al. confirmed good reproducibility with standard deviation below 5% through the engagement of different SWNTs sensors.[149] Finally, it's clear to consider that one dimensional (1D) nanotube structured materials with maximum surface area and additional binding site are more competitive for higher stability, repeatability and reproducibility in case of pH sensing platforms.

Modeling of sensing mechanism.—Variety of models have been proposed for the understanding of pH sensing mechanisms while the variation of sensing electrode protentional are measured through the change of H^+ ion activity. For glass membrane-based pH sensor, Donnan boundary potential model postulated that H + ion diffusion through the glass membrane causes the potential variation by fluctuating the diffusion rate of ions. But later it was noticed that H + ions have no tendency to diffuse into the membrane.[150] Then at 1967, Durst claimed that H + ion adsorption on glass membrane surface is causing the potential response and provide pH response.[151] Later at 1994, Baku represented that aqueous ion and glass surface group are in dynamic equilibrium and the potential difference between solution and glass surface is caused by dissociation mechanism.[152] At next, in 1999 Cheng represented his hypothesis for potential mechanism where sensing electrode is considered as double layer capacitor on the basis of Poisson−Boltzmann equation.[153] However, the model did not consider the ions adsorption at surface as well as ions diffusion into the membrane. But it considered the interaction behavior between H^+ ions and electrode surface while interaction between interface of metal/electrolyte and other ions are also considered. So, the forming capacitance through these interactions is used to determine potential difference and ultimately the pH calculation. As a result, it's clearly evident that an evolution is happened in terms of modelling for commercially feasible pH sensing mechanism from pristine period. In spite of having different advantages, challenge is still remained to avoid limitations like crowding effect. Specifically, due to this effect lower H^+ ion concentration at the surface is counted and resulting lower capacitance with false pH detection.[154] On the other hand, reverse phenomena can also be happened. In this case, higher sensitivity during pH analysis can be noticed because of the crowding effect of counter ions in buffer solutions, and resulting higher H^+ ions concentrations at surface of pH sensors. Moreover, selectivity of the pH sensor towards H^+ ions is also important to study. During analysis other dissolved ions most probably, sodium can cause the malfunctioning of sensor performance through the impediment of model synchronization. In this condition, mechanism model can be accounted for other ions rather than H^+ and made overestimation for pH value.[85] In addition, defects in terms of substitutional impurity as well as interstitial impurity affects the modelling of pH sensing mechanism which ultimately affects the actual number of ion binding sits and resulting overestimation or underestimation of pH value.[155,156] So, the avoiding of crowding effect, impurities, and confirmation of specific selectivity are still remaining as potential challenge for pH sensing technologies.

Conclusions

From 1889 to the present, successive developments have been identified in the field of pH detection. From chemical laboratories to heavy industrial applications, pH is an important parameter to check the compatibility of any process. During the pristine period, litmus paper was used to detect acid or alkaline media only by color change. Then, the emergence of the glass electrode with an ion selective membrane and reference electrode was achieved. The glass electrode has been successfully used in different applications, but also has encountered drawbacks that imperatively fuel evolution toward more sensitive and stable pH sensing platforms. Therefore, the genesis of nanostructured pH sensing materials is perceived as offering the versatility to fulfil the demands of newly incorporated application fields (in vivo media, curved surfaces, and wearable systems). Additionally, cost minimization is also a prime consideration during commercialization; thus, composite materials were also gradually introduced. Among the experiments with different oxides, IrO_2 and ZnO are mostly studied for pH sensing due to their remarkable sensing potentiality. Regarding the evolution of fabrication, a wide range of fabrication methods have been chronologically introduced focusing on the rationality of sensing materials (RuO_2 is compatible with screen printing, and electrodeposition is rational for IrO_2), lowest manufacturing complexity and favorability in mass production without compromising sensing accuracy in multidimensional applications. In addition, the requirements of sophisticated equipment, extensive pretreatment, and commercialization complexity drive researchers to explore cheaper and more facile methods. Therefore, it is clear that each method is viable for some specific materials, although investigations are carried out with a wide range of materials and with a variety of methods.

There is still a wider scope to conduct research to overcome the challenges regarding nanostructured pH sensing materials, such as modeling a more suitable sensing mechanism for each material with a coherent construction manner for sophisticated applications in the biomedical field. In addition, viable power sources for nanostructured pH sensing platforms and pH sensor construction with higher stability, sensitivity and selectivity for in vivo or ex vivo implementation should be investigated in the future.

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