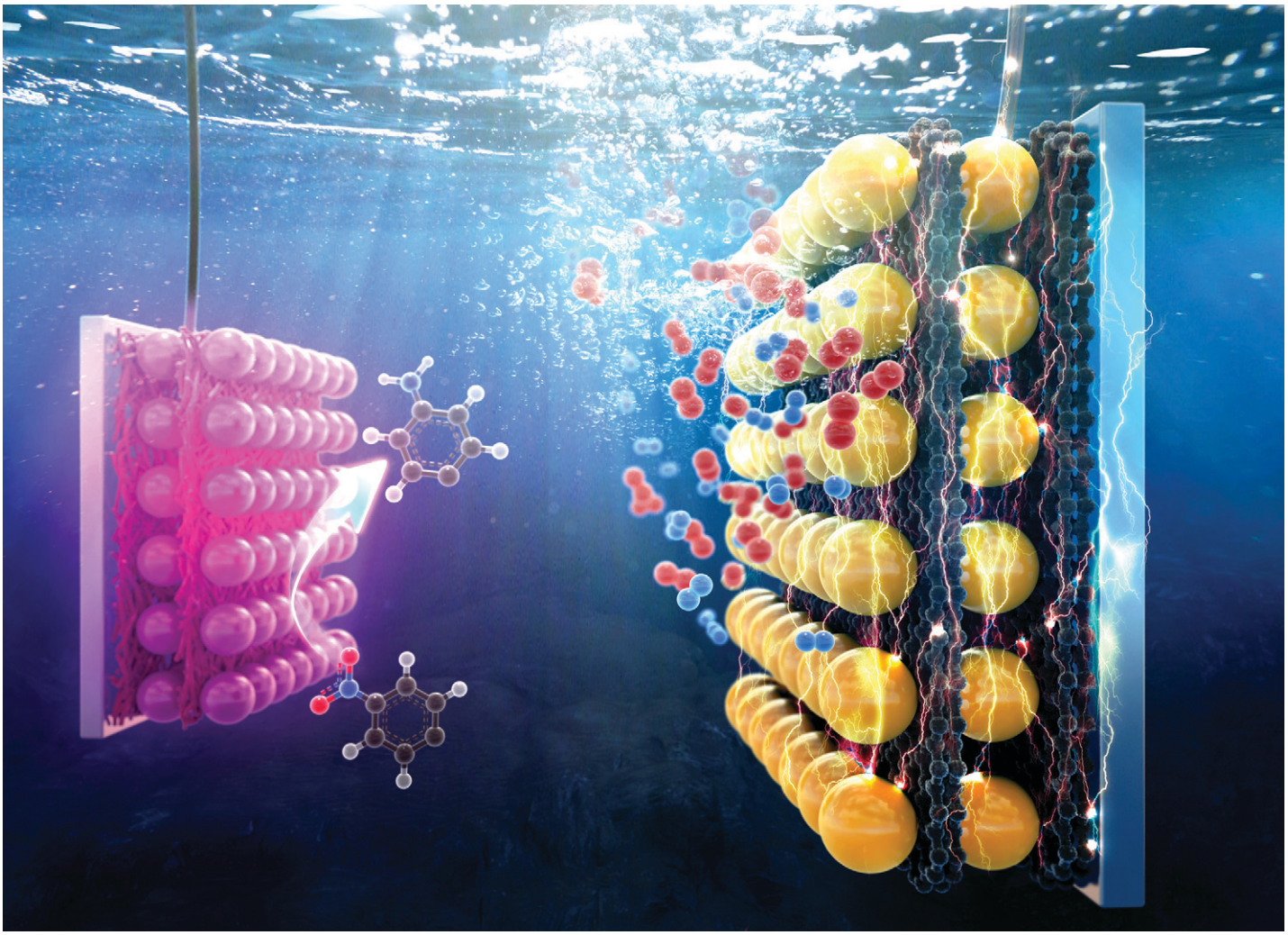

Showcasing research from Prof. Byeong-Su Kim's group in the Department of Chemistry at Yonsei University.

Layer-by-layer assembly for photoelectrochemical nanoarchitectonics

In this minireview, we introduce the recent progress of photoelectrochemical nanocomposite electrodes tailored by layer-by-layer assembly toward various energy devices.

As featured in:

See Byeong-Su Kim *et al.*, *Mol. Syst. Des. Eng.*, 2019, **4**, 65.

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Layer-by-layer assembly for photoelectrochemical nanoarchitectonics

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A recent increase in the demand for energy and the environmental issues related to the existing energy production processes have necessitated the production of clean and renewable energies using alternative sources, such as solar energy and the development of high-performance photoactive nanomaterials. To this end, another notable challenge in nanotechnology and molecular engineering for the development of photoactive devices is finding suitable ways to assemble various photoactive nanomaterials into a single platform, while maintaining an efficient photocatalytic activity. In this regard, layer-by-layer (LbL) assembly is one of the most versatile nanoscale blending methods to assemble diverse materials on various surfaces through the sequential adsorption of materials with complementary interactions. The photoactive properties of LbL-assembled hybrid electrodes are highly tunable through coupling with diverse groups of photoactive nanomaterials. Although LbL assembly has often been chosen for designing hybrid nanostructures that combine the advantageous features of each constituent, recent studies on photoactive LbL thin films for use in emerging novel nanomaterials are still limited. Therefore, in this mini-review, we introduce the recent progress made in the field of advanced device applications, with a particular focus on photo-electrochemical devices of LbL-assembled thin film electrodes. We anticipate that this review will offer new insights into the synthesis and assembly of various photoactive nanocomponents toward the development of novel photoelectroactive devices and fundamental analysis of the photo-electrochemical properties of thin film electrodes.

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Design, System, Application

Under visible-light irradiation, photoexcited exciton transfer within photoactive materials with suitable band structures is highly important in photo-electrochemical (PEC) cells. Therefore, hybridization of materials and architectural control are important in enhancing the performance and efficiency of devices. This study focuses on the nanoscale architectural control of PEC cells using layer-by-layer (LbL) assembly, which is one of the versatile methods for fabricating multifunctional structures with nanoscale control of the composition and structure. This review explores the hybridization of photoactive materials in multi-layered films and high-performance PEC systems with respect to their various applications. Furthermore, recent research trends in LbL assembly for PEC cells, ranging from previous application fields to emerging and potential application fields, are summarized.

1. Introduction

1.1 Photoelectrochemistry and semiconductors

Artificial photosynthesis is considered as one of the most promising solutions to the growing energy and environmental concerns, and as an alternative technology for the solar production of clean and renewable energies.[1,2] In this regard, photoelectrochemical (PEC) cells such as liquid junction photovoltaics, photoelectron synthesis, and photocatalysis have received significant attention as potential candidates for use in high-performance PECs.[3] Efficient photosensitizers and photocatalysts are essential components that absorb photons in PEC cells.[4] In principle, the photon absorption by photocatalysts generates an exciton, resulting in the generation of a hole in the highest occupied molecular orbital.[5–9] This exciton of an electron–hole pair leads to photophysical and chemical reactions, such as representative water-splitting reaction, including hydrogen evolution reaction (HER) at the photocathode and oxygen evolution reaction (OER) at the photoanode.[10–12] To efficiently achieve this PEC catalysis, it is necessary to tune the suitable energy level for efficient carrier transport. Thus, there has been significant progress in the development of various photoactive materials with

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suitable band gaps and band-edge positions for the desired photochemical reactions.[13–16]

To date, semiconducting materials or organic molecules have been used for solar energy conversion as photoactivators.[17–20] Significant advances have recently been made in developing efficient and cost-effective materials, for example, integration with additional catalytic components such as metal nanoparticles, graphene, and co-catalysts. Electrocatalysts are designed not only to facilitate electron–hole transport within semiconducting materials, but also to catalyse electrochemical redox reactions (Fig. 1a).[21–23] These strategies can effectively inhibit electron–hole pair recombination and improve electron collection from photogenerated semiconductors, which facilitates the design of nanostructures and the assembly of various photoactive materials within an electrode for high conversion efficiency.[24–26]

1.2 Layer-by-layer (LbL) assembly

The word nanoarchitectonics was first coined by the Aono group in 2000 to describe the fabrication of functional hybrid nanomaterials, considering atomic/molecular-level manipulation, chemical reactions, self-assembly and self-organization.[27,28] From the perspective of nanoarchitectonics, the utilization of electrode fabrication techniques that allow nanoscale blending of active components is necessary for investigating the effect of nanoscopic hybridization of photoactive materials.[29–31] Typically, various photoactive materials fabricated into thin films are applied in energy conversion devices by a simple casting process or other deposition methods such as electrodeposition, chemical vapour deposition, and atomic layer deposition.[32] However, these traditional electrode fabrication methods remain challenging to understand the interactions between individual active materials for the overall performance of the electrode.

To address these concerns, layer-by-layer (LbL) assembly has been proposed with its advantages such as simplicity, low cost, scalability, and environmentally benign features.[33–35] LbL assembly is one of the most versatile tools used for assembling multifunctional nanomaterials with nanoscale control over their composition and structure. LbL-assembled thin films are simply prepared through sequential adsorption of different macromolecular components that exhibit attractive forces such as electrostatic interactions, hydrogen bonding, and van der Waals forces. In that context, we presented a well-established protocol for the assembly of LbL nanocomposites in our previous contribution.[36] Specifically, we formulated a detailed protocol to share reliable procedures with other researchers in the field. Furthermore, we described the LbL assembly procedure from preparation methods for the necessary substrates and suspensions of components to fabricate LbL assemblies for potential applications. Readers interested in the detailed protocol for the preparation of a high quality LbL-assembled film are highly encouraged to resort to this protocol.

In addition to their structural advantages, the optical and photoelectrochemical properties of the photoactive materials could be improved through the interactions within the assembled layer. The hybridization of the assembled photoactive materials results in the efficient transfer of photoinduced excitons within the multilayer film with band adjustment for a suitable structure, leading to high performance of PEC devices.[37,38] Due to these unique opportunities, there are active research studies on LbL-assembled thin films for various energy storage and conversion applications, including lithium-ion battery, supercapacitor, fuel cell, and electrocatalyst.[39–45]

1.3 LbL assembly for PEC applications

The most essential factors in PEC cells are the generation of electron–hole pairs and their migration within semiconductors.[46,47] Hybridization of semiconductors could improve electron migration to the surface of catalytic materials and engineer the band gap and structure of the redox potentials suitable for specific applications such as water splitting, biodegradation or CO_2 reduction.[48–51] Though several research

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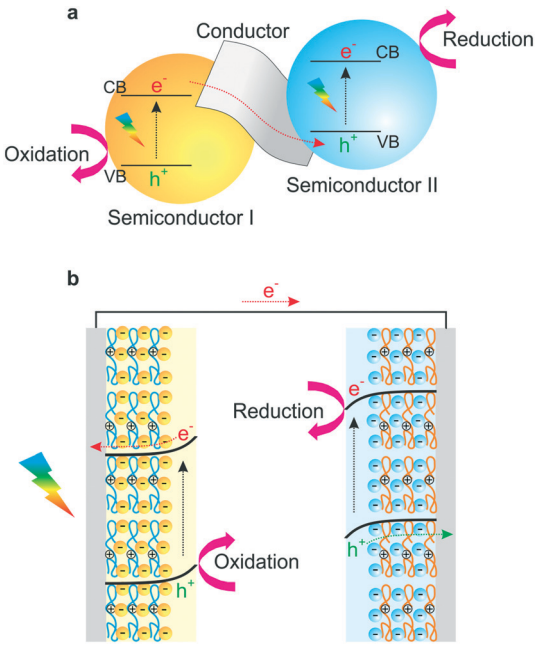

Fig. 1 (a) A Z-scheme diagram of hybrid nanocomposites for high conversion efficiency and (b) a schematic representation of an LbL-assembled PEC system.

studies have been conducted focusing on electron transfer in PEC cells based on suitable band structures, efficient photoelectron transfer has posed a considerable challenge in the field. In that regard, a LbL-assembled multilayer system presents an elegant solution because it could offer advantages in photoelectrochemical or photocatalytic properties through the hybridization of semiconductors in thin films (Fig. 1b).[37,52] First, alternative deposition of individual building blocks can attain precisely controllable architectures and enhance structural stability.[33] Second, the combination of band structures for each semiconductor can adjust the Z-scheme in heterojunction films for efficient electron transfer and applicable energy level for specific redox reactions.[10,53–55] Third, photogenerated carriers can efficiently be transferred inside multilayered films, which would possibly suppress photoexcited electron–hole pair recombinations.[38,56–58] These notable advantages of LbL-assembled PEC systems (LbL-PEC hereafter) have spurred vigorous research studies related to LbL-PEC systems, with a gradually increasing number of published papers from 1990 (Fig. 2).

As a pioneering work in LbL-based photoelectrochemical applications, Kotov *et al.* reported ultrathin LbL nanostructured films using the Langmuir–Blodgett technique with semiconducting nanoparticles.[59] Lead sulfide (PbS), titanium dioxide (TiO_2), and highly fluorescent cadmium sulfide (CdS) were used as semiconductors with polyelectrolytes to investigate the behaviour of photo-generated charge carriers in a multi-layered LbL film. It was found that not only was maximum photocurrent in the LbL photoactive film attainable with respect to the number of bilayers, but it was also possible to transport photogenerated charge carriers based on the position of the active layer within LbL films and the magnitude of the photocurrent. Following this seminar contribution, numerous studies have been reported to apply LbL assembly towards developing highly active photoelectrochemical systems.

Photovoltaic devices, particularly dye-sensitized solar cells (DSSCs), were one of the most popular research topics in LbL-PEC systems, which advanced the progress of development of various photoactive materials.[60–63] For example, Li and coworkers combined graphene with CdS quantum dots (QDs) on indium tin oxide (ITO) to construct an efficient electron transfer system.[64] Due to the light-harvesting properties of CdS QDs, photoexcited charge carriers could be generated and transported through graphene, which acted as a good charge mediator. Through the analysis of energy level diagrams and photocurrent generation, the mechanism of electron transfer in high-performance LbL-based PEC devices was demonstrated for next-generation solar cells. In another noteworthy endeavour, Kim and coworkers assembled two different QDs on TiO_2 to enhance the favourable optoelectronic properties of QDs in multilayered films for efficient solar cells (Fig. 3a).[65] The QD bilayer film showed significantly improved photoelectrochemical performance (power conversion efficiency (PCE) of 0.05%) compared to single QD layer films, originating from the efficient transfer of electrons between the QDs. As another promising materials for efficient DSSCs, Hammond and co-workers engineered M13 bacteriophage nanowires into a polymeric network on porous TiO_2 photoanodes (Fig. 3b).[66] A percolative network created from the inclusion of phage and TiO_2 nanowires contributed to the preservation of the electron diffusion length and the improvement of electron transport properties in LbL-assembled DSSC photoanodes, demonstrating large improvement on PCE to 6.21%.

Meanwhile, the development of LED devices based on LbL assembly has been demonstrated with QDs, taking advantage of their superior photoluminescent properties.[67–72] In an early example, Lee and coworkers employed various QDs and successfully demonstrated multi-coloured QD-based LED films with high brightness by appropriately arranging various QDs in the LbL-assembled film (Fig. 3c).[73] Furthermore, the sensing profile within the QD multilayer films was investigated through electroluminescence emission, and it was discovered that approximately 90% of the total electroluminescence was due to the top QD layer while the remainder originated from the second QD monolayer. In addition, a significantly improved device performance was achieved in terms of its brightness (450 cd m^{-2} at 50 mA cm^{-2}) and device efficiency (0.3% at 50 mA cm^{-2}) at 2.5 QD bilayers. To improve sensing behaviour with tunable light-emitting QD-containing LbL multilayers, the Duan group assembled negatively charged CdTe QDs with positively charged MgAl-layered double hydroxide (LDH) nanosheets (Fig. 3d).[74] By adjusting the size of the QDs, deposition sequence and number of layers, the luminescence colour of the multilayered thin films could easily be controlled over a wide range from red to green, with a strong luminescence intensity and high photostability.

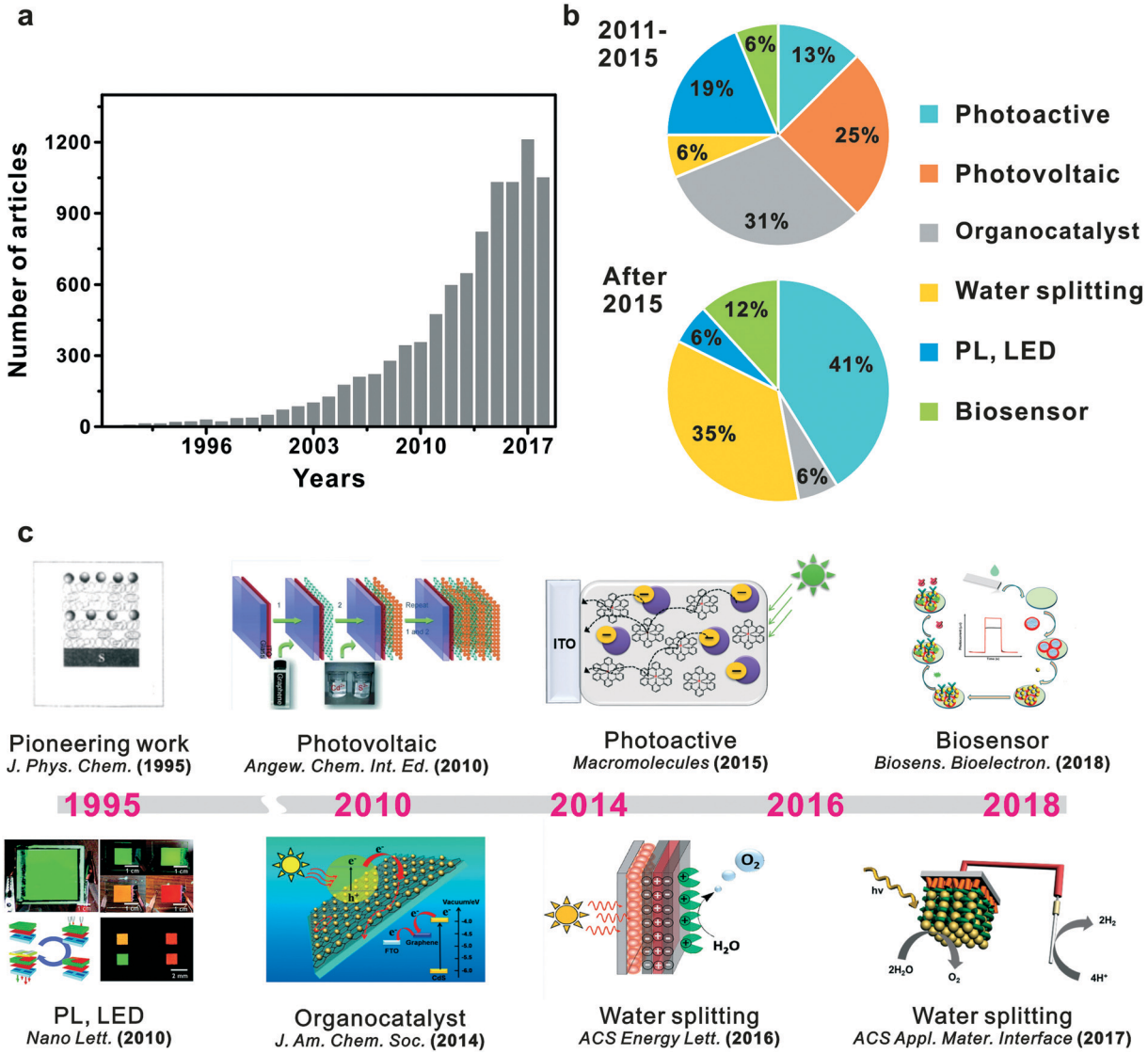

Fig. 2 Trend of research in LbL assembly for PEC systems: (a) growth of publications since 1990, (b) types of applications and (c) chronicles with some significant studies in the field since 1995. Reprinted with permission from ref. 59, copyright 1995 American Chemical Society. Reprinted with permission from ref. 64, copyright 2010 John Wiley and Sons. Reprinted with permission from ref. 73, copyright 2010 American Chemical Society. Reprinted with permission from ref. 83, copyright 2014 American Chemical Society. Reprinted with permission from ref. 96, copyright 2015 American Chemical Society. Reprinted with permission from ref. 102, copyright 2016 American Chemical Society. Reprinted with permission from ref. 108, copyright 2017 American Chemical Society. Reprinted with permission from ref. 122, copyright 2018 Elsevier.

In another application field, photocatalytic degradation of organic pollutants under light irradiation has become an active research area in the LbL-PEC field.[20,75,76] The incorporation of various photocatalytic materials into multilayered films can provide significant benefits for efficient photocatalytic performance.[77–82] For instance, Liu and coworkers constructed graphene–semiconductor nanocomposites *via* LbL assembly using polymer-modified graphene nanosheets and negatively charged CdS QDs as efficient photocatalysts for the reduction of nitro-aromatic compounds (Fig. 3e).[83] A significant performance enhancement was achieved due to improvement in charge separation and transport within the multilayered film. As another example of the photocatalytic reduction for nitro-aromatic compounds, Zhang and coworkers employed carbon dots with CdS to fabricate heterojunction nanohybrid films (Fig. 3f).[84] The combination of carbon dots with CdS resulted in efficient transfer of photoinduced electrons while suppressing charge recombination. These various examples of LbL assembled PEC application are summarized with type of applications and photoactive materials (Table 1).

2. Emerging applications in photoactive LbL electrodes

2.1 Photoactivity of LbL films

Since the importance of renewable energy cannot be overstated with the exhaustion of fossil fuels, various studies

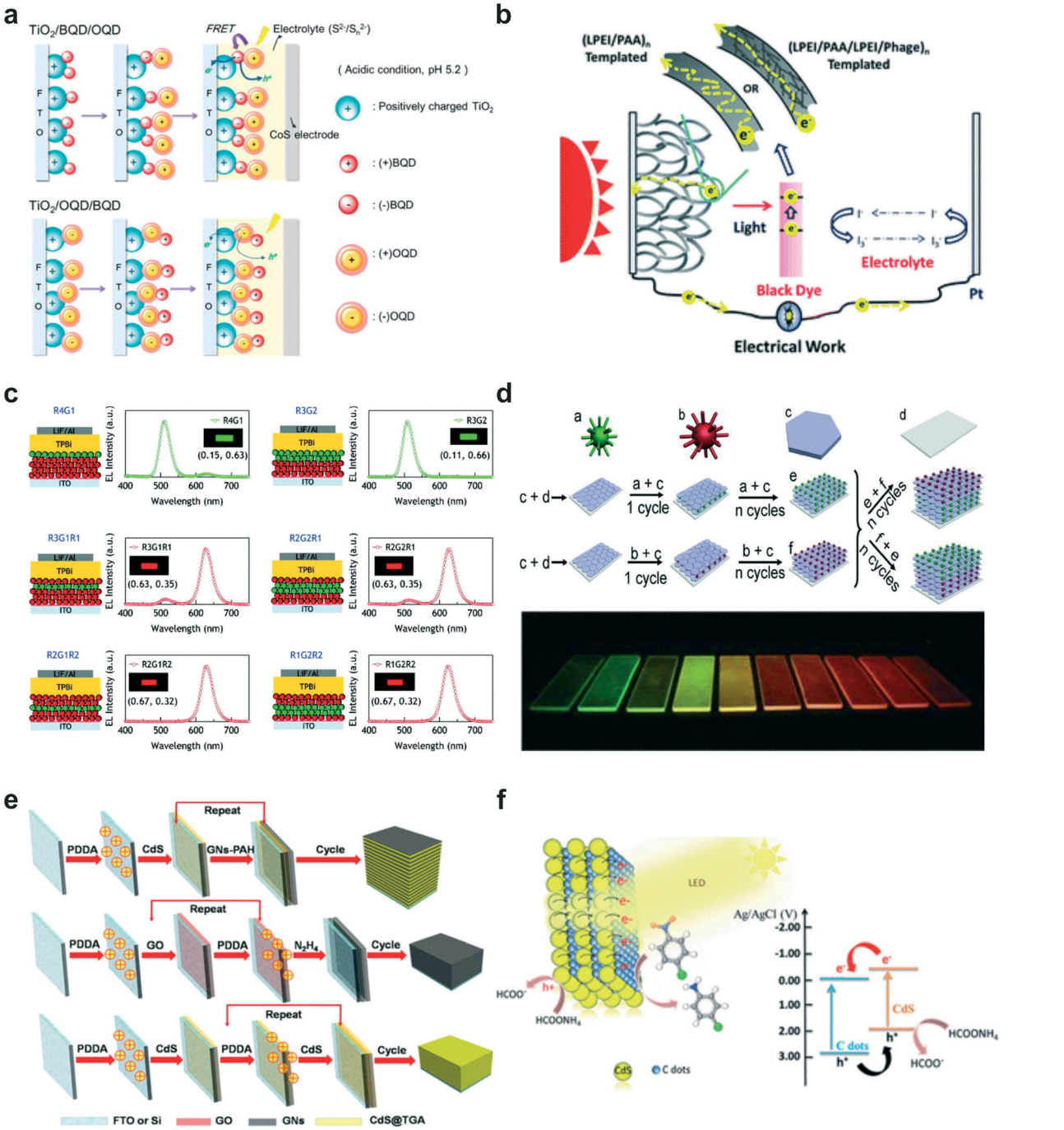

Fig. 3 Representative early examples of LbL assemblies for various PEC applications: (a) LbL quantum dot (QD) multilayer assemblies with two different QDs for efficient electron transfer from QD to TiO_2. Reprinted with permission from ref. 65, copyright 2012 American Chemical Society. (b) Percolation system of TiO_2 nanowires templated by a bacteriophage for dye-sensitized solar cells (DSSCs). Reprinted with permission from ref. 66, copyright 2013 Royal Society of Chemistry. (c) Systematic engineering of an exciton-recombination zone within QD LbL films for highly bright QD-based LEDs. Reprinted with permission from ref. 73, copyright 2010 American Chemical Society. (d) LbL-assembled multicolour luminescent films tunable over the whole red-green region using CdTe QDs and MgAl-layered double hydroxide. Reprinted with permission from ref. 74, copyright 2012 John Wiley and Sons. (e) A hybrid multi-layered film with graphene nanosheets and CdS QDs for photoelectrochemical and photocatalytic activities. Reprinted with permission from ref. 83, copyright 2014 American Chemical Society. (f) Carbon dot (C-dot)/CdS QD heterojunction films for efficient photoelectrochemical and photocatalytic reduction of nitro-aromatic compounds. Reprinted with permission from ref. 84, copyright 2015 Royal Society of Chemistry.

on energy conversion, storage, and catalysts for alternative energy production have been reported recently.[85–87] Solar energy conversion, especially solar to hydrogen conversion and water splitting, constitutes a large proportion of renewable energy research.[12,88,89] Accordingly, various recent research studies in LbL-PEC films have been geared towards the

Table 1 Summary of representative early applications of LbL-PEC systems based on photoactive materials

Application	LbL assembly (+) component	LbL assembly (−) component	Substrate	Ref.
Solar cells	PVP	PbSe NC	ITO	60
	CdSe QDs	CdSe QDs	FTO//TiO_2	61
	TiO_2 NPs	Nb_2O_5 NPs	FTO	62
	TiO_2 NPs	TiO_2 NPs	FTO	63
	Graphene[a]	CdS[b] QDs	ITO	64
	TiO_2, CdSe/CdS/ZnS QDs	CdSe QDs	FTO	65
	PEI	PAA, M13-bacteriophage	FTO	66
Light-emitting diodes	PDDA	CdSe QDs	Glass	68
	CdSe@CdS QDs	PMMA-SH	Glass	69
	PDDA	CdSe QDs	Glass	70
	PAH-CdTe QDs	MMT	Quartz glass	71
	QAICS, PDDA, PAH	ZnSe, CdTe QDs	Glass	72
	CdSe@ZnS QDs	CdS@ZnS QDs	ITO	73
	LDH	CdTe QDs	Quartz	74
Organocatalyst	POSS	TiO_2 NPs	PSEI	20
	PVP[c]	Na_2PdCl_4	Quartz//$O_3SiC_6H_4CH_2$	75
	TiO_2 NPs	PW_{12}	ITO	76
	PAH	PAA, metal (Au, Ag, Pt) colloidal NPs	TiO_2 nanotube	77
	SePEI	Alginate	Quartz	78
	b-PEI, PAH	PSS, SnS_2 NS/TiO_2 NF	Textile	79
	Graphene	Au NPs	PET	80
	PAA-rGO	TALH	Quartz	81
	PDDA	Titanate	Quartz	82
	PAH-GNs	CdS QDs	FTO	83
	C-dot,[a] graphene oxide	CdS[b] QDs	ITO	84

[a] Electrodeposition. [b] Successive ionic layer adsorption and reaction (SILAR). [c] Covalent binding. * NC: nanocrystal/QD: quantum dot/NP: nanoparticle/NS: nanosheet/NF: nanofiber/ITO: indium tin oxide/FTO: fluorine-doped tin oxide. ** PVP: poly(4-vinylpyridine)/PEI: poly(ethyleneimine)/PAA: poly(acrylic acid)/PDDA: poly(diallyldimethylammonium chloride)/PMMA-SH: poly(methyl methacrylate) containing thiol groups/PSS: poly(sodium 4-styrene sulfonate)/PAH-CdTe QDs: poly(allylamine hydrochloride)-CdTe QDs/MMT: montmorillonite/QAICS: quaternary ammonium ion cationic starch/LDH: layered double hydroxide/POSS: polysilsesquioxane/PSEI: poly(dimethylsiloxane-*block*-etherimide)/PW_{12}: tungsto(molybdo)phosphate/SePEI: organoselenium-modified PEI/b-PEI: branched PEI/PAA-rGO: PAA-modified reduced graphene oxide/TALH titanium(IV) bis(ammoniumlactato)dihydroxide/PAH-GNs: PAH-modified graphene nanosheet.

development of solar energy conversion systems.[90] As shown in Fig. 2b, the researches associated with solar energy conversion, such as photocurrent generation and photo-water splitting, have increased considerably since 2015, unlike traditional research trends.

In general, high photocurrent and photon-to-current efficiencies from specific redox potentials are the main parameters required to achieve efficient solar energy conversion in photoelectrochemical systems. In that regard, John and coworkers showed practical benefits that the LbL technique offers to PEC systems using reduced graphene oxide (rGO) and ZnO (Fig. 4a).[91] In the case of rGO–ZnO hybrids, the presence of graphene enhanced the dark conductivity, however, the passivation of oxygen vacancies due to the diffusion of oxygen from rGO to ZnO during the reduction process resulted in depletion of the visible-light photoconductivity. Meanwhile, an improvement in photoinduced charge separation and efficient electron transfer in multilayer systems was demonstrated through the LbL assembly technique, leading to the generation of highly enhanced photocurrent (33.80 μA cm^{-2} at −0.5 V bias voltage).

In addition, various photoactive materials have been used to design efficient photoelectrochemical multilayered films by exploiting the prominent advantages offered by LbL-PEC systems.[92] For instance, Li and coworkers utilized photosystem II (PSII) as the photosensitizer and rGO to design an efficient solar energy conversion system. A biomimetic hybrid photoanode displayed a reliable electron pathway by which the photoinduced electron from P680* was transferred to the ITO substrate passing through plastoquinone (Q_A) and pheophytin (Q_B), leading to the generation of significant photocurrent (Fig. 4b).[93] Moreover, a two-fold enhancement of photocurrent and stability improvement was further demonstrated *via* an optimal LbL assembly process with graphene materials and photoactive proteins. As another promising photoactive material, a metal–ligand complex was utilized in an LbL-PEC system because of its strong visible-light harvesting characteristics and outstanding photochemical properties.[94,95] Consequently, Song and coworkers introduced the Ru–terpyridine ($Ru(tpy)_2$) complex with various metal–terpyridine ($M(tpy)_2$) coordination complexes (M = Fe, Co, Ni, Cu, and Zn) to enable the self-assembly of polymeric thin films. The transfer rates for photoexcited electrons from $Ru(tpy)_2$ inside the multilayered film were compared with different $M(tpy)_2$ linkers to reveal the diffusion rate constant of the generated photoelectrons (Fig. 4c).[96] It was observed that the photoinduced electrons were transported to the electrode *via* $M(tpy)_2$ linkers through an electron hopping

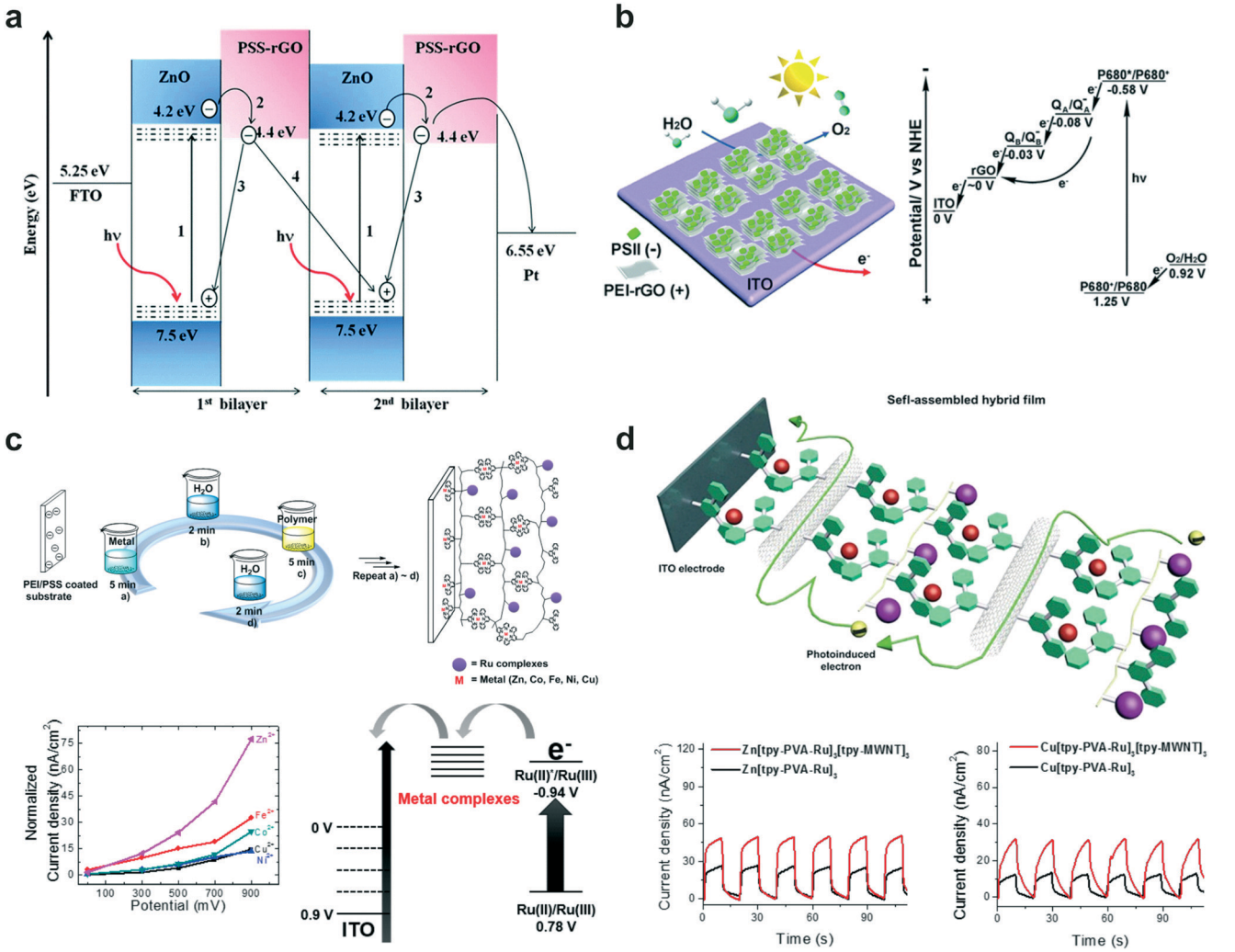

Fig. 4 Recent representative examples of LbL assembly for PEC systems in energy conversion applications based on photocurrent generation: (a) photoinduced electron transfer between reduced graphene oxide (rGO) and ZnO in multilayered films. Reprinted with permission from ref. 91, copyright 2015 Royal Society of Chemistry. (b) Multilayered film utilizing photosystem II (PS II) and rGO for efficient transfer of photoexcited electrons in a PEC system. Reprinted with permission from ref. 93, copyright 2015 Royal Society of Chemistry. (c) LbL assembly using various metal–terpyridine coordination complexes for efficient photocurrent generation. Reprinted with permission from ref. 96, copyright 2015 American Chemical Society. (d) LbL assembly employing multi-walled carbon nanotubes (MWNTs) to enhance photoinduced electron hopping rate in multilayered films. Reprinted with permission from ref. 97, copyright 2015 Elsevier.

process. In addition, $Zn(tpy)_2$ displayed the highest electron diffusion rate among several $M(tpy)_2$ linkers tested. In a subsequent work, the authors additionally employed multi-walled carbon nanotubes (MWNTs) to provide an efficient electron transfer pathway (Fig. 4d).[97] The fabricated photoactive polymer–MWNT hybrid thin films achieved 35% enhancement in photocurrent, attributed to the improved electron-hopping rate constants due to inclusion of the MWNTs. These $Ru(tpy)_2$-incorporated photoactive polymer–MWNT hybrid thin films hold huge promise for artificial photosynthesis or solar energy conversion.

2.2 Photo-water splitting of LbL films

Hydrogen gas is a green energy carrier that is considered a key element in the field of future sustainable energy.[98,99] In this regard, photocatalytic water splitting offers a promising and competitive technique for producing hydrogen gas to address future environmental and energy concerns.[1,100,101] Although most research studies thus far have focused on the development of new materials for photo-water splitting reactions, their integration into photoelectrodes is another critical factor to enhance their photocatalytic performance and stability through the ensemble effect on hybrid photoactive materials. Therefore, LbL assembly can offer a unique and ideal platform for assembling various functional components within the electrode in a highly controllable manner.

As a representative example, Schanze and coworkers reported the application of LbL for the construction of chromophore–catalyst assemblies consisting of a cationic polystyrene-based Ru polychromophore and a $[Ru(tpy)(2\text{-pyridyl-}N\text{-methylbenzimidazole})(OH_2)]^{2+}$ water oxidation

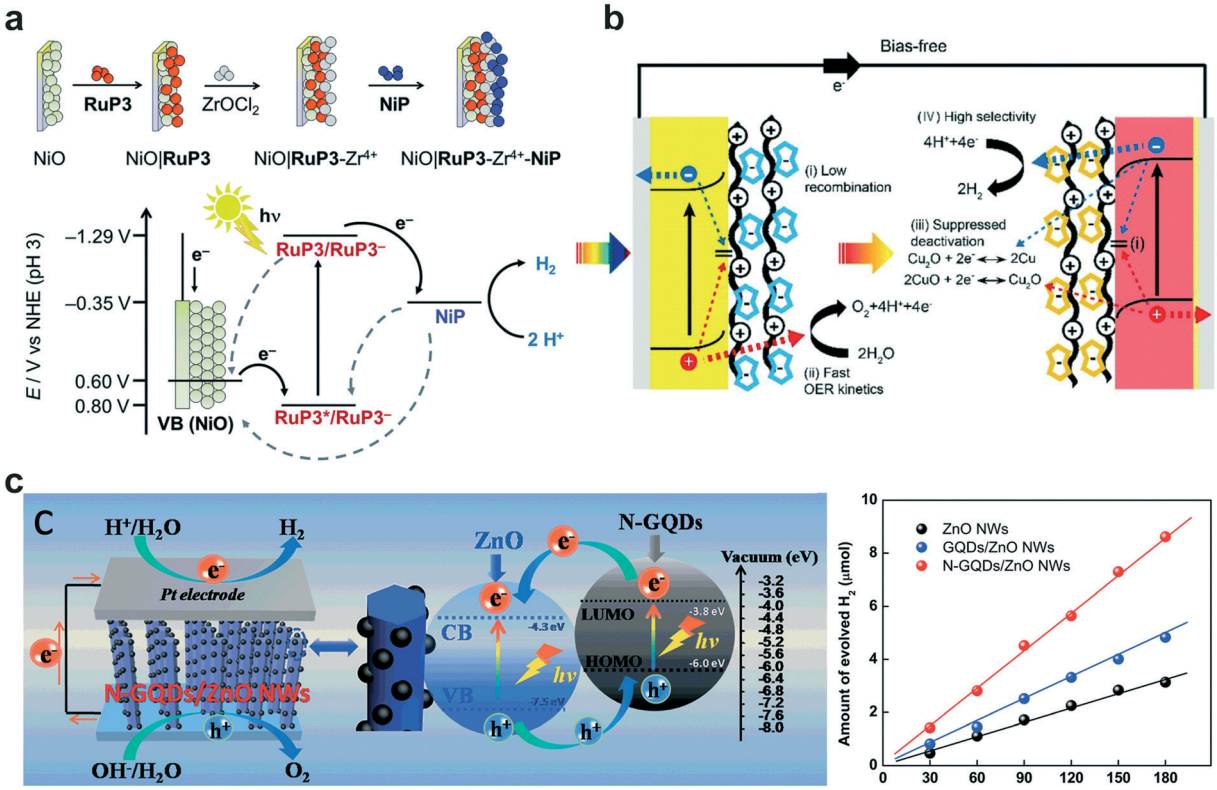

Fig. 5 Schematic illustration of LbL multilayers for water splitting reactions: (a) energy diagram of dye–catalyst deposition on p-type NiO and current responses under light irradiation. Reprinted with permission from ref. 103, copyright 2016 Royal Society of Chemistry. (b) PEC cell with LbL-modified electrodes and LSC curves with a functionalized photocathode and photoanode. Reprinted with permission from ref. 52, copyright 2018 Royal Society of Chemistry. (c) Mechanism of N-GQDs/ZnO NW under light irradiation and hydrogen evolution performance. Reprinted with permission from ref. 109, copyright 2016 Royal Society of Chemistry.

catalyst.[102] When the polychromophore/catalyst assembly was deposited onto mesoporous substrates consisting of a SnO_2/TiO_2 core/shell structure, it could successfully drive water oxidation with a significant photocurrent (18 μA cm^{-2} at 0.44 V *vs.* NHE) at the photoanode, coupled with O_2 observed at the collector electrode. Dye-sensitized p-type NiO photocathodes for photoreduction were developed with a Ru-based and tetraphosphonated $[Ni(P_2N_2)_2]^{2+}$ proton reduction catalyst (Fig. 5a).[103] The LbL-assembly approach could control the spatial arrangement of individual species while retaining the dye in close proximity to the catalyst and the surface of the semiconductor. It was shown that electron transfer from the excited dye to the catalyst was highly efficient, while the recombination kinetics can be slowed down.

Polyoxometalates (POMs) with a transition metal complex have been considered as both fast and reversible hole scavengers and effective water oxidation catalysts.[104–106] Moreover, due to their highly negative surface charges, POMs can be used as building blocks for the self-assembly of supramolecular hybrid nanomaterials.[107] The Ryu group reported several studies of POM-based photocatalysts for water splitting reactions.[52,108] POMs were employed as model molecular water-oxidation catalysts integrated into various electrode surfaces such as α-Fe_2O_3, TiO_2, $BiVO_4$, and fluorine-doped tin oxide (FTO). They demonstrated that photoelectrochemical properties and stability of photoanodes can effectively be improved by controlling the types of polyelectrolytes and the number of bilayers. Another study involved a model PEC cell constructed using a $BiVO_4$ photoanode and Cu_2O photocathode (Fig. 5b). The prepared electrodes were further functionalized with catalytic multilayers of anionic Co-based POMs and Ni-based POMs, respectively. Due to the unique catalytic multilayer structures of POMs, the PEC performance was significantly enhanced after the modification. Furthermore, the desired PEC cell for overall water splitting could be conducted under the bias-free conditions with a photocurrent of 0.2 mA cm^{-2} and 1.46% incident photon-to-electron conversion efficiency (IPCE).

Apart from metal-based substrates, the hybridization of carbon nanomaterials and the nanoscale construction of multilayer LbL films have opened even wider research opportunities. In addition, a facile chemical modification towards the different functionalities of carbon-based materials offers a new platform for hosting and growing functional nanomaterials on the surface of carbon-based materials. Yang Tan and co-workers introduced highly ordered nitrogen-doped graphene quantum dots (N-GQDs) decorated with 1-dimensional ZnO nanowire heterostructures through LbL assembly (Fig. 5c).[109] It was revealed that the well-defined LbL-assembled N-GQDs/ZnO nanowire photoanode resulted

Table 2 Summary of representative emerging and potential applications of LbL-PEC systems based on photoactive materials

Application	LbL assembly (+) component	LbL assembly (−) component	Substrate	Ref.
Energy conversion	PAM-ZnO	PSS-rGO	FTO	91
	P3TOPA	CCG-P3TOPS	Al	92
	PEI-rGO	PS II	ITO	93
	Metal (Ru) ion[a]	tpy-MWCNTs	ITO	94
	$RuL(ClO_4)_2$	GO	ITO	95
	Metal ion[a] (Zn, Cu, Co, Fe, Ni)	tpy-PVA-Ru	ITO	96
	Metal ion[a] (Zn, Cu)	tpy-PVA-Ru, tpy-MWNT	ITO	97
Water splitting	PEI	NiPOM, CoPOM	FTO//Cu_2O, FTO//$BiVO_4$	52
	PS-Ru, RuC	PAA	FTO//SnO_2/TiO_2	102
	Metal ion (Zr)	NiP	ITO//NiO/RuP3	103
	b-PEI	CoPOM	FTO//Fe_2O_3, FTO//$BiVO_4$, ITO//TiO_2	108
	PEI	N-GQDs	FTO//ZnO	109
	GQD-NH_2	Metal NCs (Au, Ag, Pt)	FTO	110
Bioapplication	CdS NPs	Glucose oxidase	Pt//Nafion	120
	PDDA	MAA-CdSe QDs	ITO	121
	Poly(L-lysine)-GO	GO	Liposome	123

[a] Metal–ligand coordination binding. * NC: nanocrystal/QD: quantum dot/NP: nanoparticle/ITO: indium tin oxide/FTO: fluorine-doped tin oxide. ** PAM-ZnO: poly(acrylamide)-ZnO/PSS: poly(sodium 4-styrene sulfonate)/PDDA: poly(diallyldimethylammonium chloride)/rGO: reduced graphene oxide/P3TOPA: poly-2-(3-thienyloxy)propyltrimethylammonium/CCG: chemically converted graphene/P3TOPS: poly-2-(3-thienyloxy)propanesulfonate/PEI: poly(ethyleneimine)/PS II: photosystem II/tpy: terpyridine/MWNT(MWCNTs): multi-walled carbon nanotubes/GO: graphene oxide/$RuL(ClO_4)_2$ {L = 2-(2,6-di(pyridin-2-yl)pyridine-4-yl)-1*H*-imidazo[4,5-*f*]-1,10-phenanthroline}/PVA: poly(vinyl alcohol)/PEI: polyethylenimine/NiPOM: $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$/CoPOM: $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$/Ps-Ru: polystyrene-based Ru polychromophore/RuC: [Ru(tpy)(2-pyridyl-*N*-methylbenzimidazole) $(OH_2)]^{2+}$/PAA: poly(acrylic acid)/NiP: tetraphosphonated molecular $[Ni(P_2N_2)_2]^{2+}$/RuP3: hexaphosphonated Ru(2,2′-bipyridine)$_3$-based dye/b-PEI: branched PEI/N-GQDs: nitrogen-doped graphene quantum dots/MAA-CdSe QDs: mercaptoacetic acid-capped CdSe QDs.

in significantly enhanced PEC water splitting performances under both simulated solar and visible light irradiations. This result is attributed to the extraordinary photosensitization effect of N-GQDs and the intimate interfacial interactions between N-GQDs and the ZnO nanowire framework afforded by nitrogen doping and LbL assembly. In their subsequent contribution, a series of metal/graphene quantum dot $(M/GQDs)_n$ (M = Au, Ag, Pt) multilayers were fabricated by LbL assembly.[110] The catalytic performance of the $(M/GQDs)_n$ multilayer thin films could effectively be improved and optimized by fine-tuning the number of bilayers and the types of metal nanoparticles. This strategy allows the direct assembly of customized units of positively-charged GQDs and negatively-charged metal nanocrystals, which were integrated in an alternating stacked fashion towards unravelling the architecture-controlled effect of 3D nanoelectrodes, including the prior contribution of our studies towards the development of effective electrocatalysts.[42–44]

2.3 Potential applications of photoactive LbL films

Although LbL-assembled multilayer systems can offer effective solutions for PEC cells, most of the applications have been focused on water splitting reactions. Water splitting is an environmentally friendly process used to produce hydrogen without by-products. However, direct water splitting requires high over-potential of about 1.23 V due to the sluggish kinetics of oxygen evolution reaction (OER).[111,112] In addition, costly gas separation systems are required to prevent the mixing of H_2 and O_2 due to safety concerns.

Alternatively, several reports have recently introduced a new concept of electrochemical reforming, which could replace OER to easily oxidize species such as ethanol, benzyl alcohol, urea, or biomass to improve electrocatalytic performance.[113–116] Among them, replacing OER with biomass oxidation reactions could not only improve the energy conversion efficiency, but also generate value-added chemicals instead of oxygen.[117–119] Recently, our group discovered the potential of LbL films assembled with various metal nanoparticles to improve electrochemical performance of biomass oxidation reactions. Since this is an emerging field in the production of hydrogen, PEC reforming needs to be explored further.

Moreover, LbL films could be utilized as photoelectrochemical biosensors for the quantitative detection of glucose, DNA aptamer and cancer cells.[120–122] While conventional methods for detecting bio-related molecules suffers from time-consuming processes and expensive apparatus, photoelectrochemistry-based analytical methods offer unique opportunities owing to their facile and cost-effective nature, and high sensitivity. LbL multilayers allow the immobilization of photoelectrochemically active sites, which can enhance the sensitivity and selectivity of biosensors. Similarly, this strategy has the potential for use as a drug delivery system through the deposition of photo-responsive therapeutic materials on LbL films.[123] Due to the high versatility of the LbL assembly method, it is easy to alter the surface of substrates by adding different polymers or attaching targeting moieties. Moreover, architectures can be manipulated to create multifunctional carrier systems to meet specific

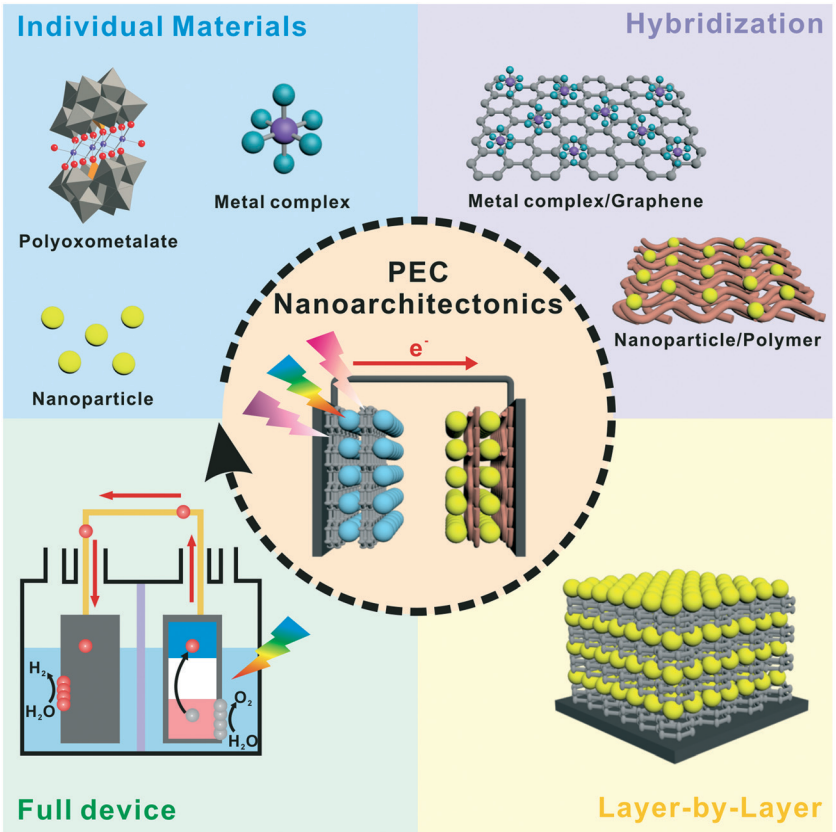

Fig. 6 Summary of PEC-based nanocomposites tailored by LbL assembly.

requirements. We anticipate a variety of drug delivery systems that could be designed with multiple therapeutic agents for effective dual chemo- and photothermal treatments.

3. Summary and outlook

In this review, we presented research progress in the field of LbL assembly towards PEC applications. The LbL assembly has been demonstrated to be an appealing strategy for the hybridization of various semiconducting nanomaterials into functional nanoelectrodes. As a result, LbL-PEC films can play an important role not only in transferring electron–hole carriers, but also in preventing the recombination of electron–hole pairs to induce charge separation. In particular, this review has focused on emerging applications such as water splitting using photoactive LbL multilayer thin films with the remarkable advantages offered by LbL-PEC systems (Table 2). Despite increasing recent examples in the field of LbL-PEC, there remain unexplored fundamental studies and more advanced design strategies for future developments in LbL-PEC systems (Fig. 6).

We anticipate that the following critical issues require further development to advance the field and enrich its wider application for the future and practical implementation in the industry. First, a new design of photoactive components is necessary to overcome the inherent limitations of the existing nanomaterials. It is well known that the PEC properties of semiconducting nanomaterials depend highly on controlling the chemical structure of individual materials such as particle size and dimensions, and light absorption range. In addition, the issue of stability in physical/chemical degradation induced by photoredox reactions during PEC reactions should be improved. Second, individual photoactive nanomaterials can be hybridized with supporting building blocks such as polymer and graphene sheets. This is because the drawbacks of each photoactive nanomaterial can be complementary to enhance the performance and durability through synergy between the coupled photoactive nanomaterials. Third, it should be possible not only to construct hybridized photoactive materials in 3D architectures, but also to maximize the PEC performance with nanoscale control of their composition and architecture.

Furthermore, multicomponent assembly beyond the conventional two-component assembly is expected to assemble multi-functional nanocomposites in the LbL-PEC systems. For example, in a multilayer film, electrocatalysts can be deposited alternately on the photocatalytic layer, or anodic catalysts can serve as bifunctional catalysts by being deposited as layers over cathodic catalysts. Finally, architecture-controlled LbL-PEC electrodes can be employed to construct artificial photosynthetic devices such as optimized high-performance PEC cells. We anticipate that this review will offer researchers new insights into future LbL-PEC systems. Moreover, LbL-PEC systems are not limited to academic research but can

advance gradually to industrial-scale applications due to their scalable, solution-processable nature, and their simple and environmentally friendly design process.

Conflicts of interest

There are no conflicts to declare.

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