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Self-adhesive flexible patches of oxide heterojunctions with tailored band alignments for electrocatalytic H₂O₂ generation⁺

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The new class of oxide heterojunctions with mixed dimensionalities holds great promise for energy and environmental applications. However, the existing fabrication strategies typically involve low-yield and multistep processes leading to the formation of powders that necessitate binding agents when used for electrochemical applications; thereby, the durability and performance of the resultant electrode may be adversely impacted. To address these challenges, the present work first reports a high-temperature counter-current gas flow technique for rapid fabrication (5-10 min) of centimetre-size, self-adhesive, free-standing 3D patches made of ZnO-based woven nanowires. Furthermore, the high applicability of the method was shown by layer-by-layer assembly of the ZnO and layers of 0D heteroatoms including Bi₂O₃, CdO, SnO₂, and carbon forming stratified oxide heterojunction (SOH) nanostructures with midgap states within their electronic bandgap region. This work is innovative in that the ZnO and the fabricated SOHs are synthesised through a sustainable and large-scale method based on microrecycling of waste materials. The engineering of the electronic band positions can modify the functionality of the SOH patches by optimising the potentials required for catalytic reactions. As a representative, the SOH nanostructures were tested for anodic electrocatalytic water oxidation to H₂O₂. The results showed that the ZnO-CdO patch has the lowest overpotential of 150 mV and outstanding stability at 2.33 V vs. RHE. Furthermore, the results of first-principles density functional theory (DFT) calculations (i) confirmed realignments of the band position due to the formation of midgap states, and (ii) revealed that significant improvements in the electrocatalytic H_2O_2 performance can be achieved with overpotentials as low as 0.19 and 0.31 V for ZnO-CdO and ZnO-Bi₂O₃, respectively. This work offers an ultrafast fabrication strategy to synthesise binder-free SOH nanostructures with an engineered electronic structure that can be an alternative to state-of-the-art noble metal electrocatalysts such as Pt.

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Introduction

Mixed oxide heterojunction (MOH) nanostructures are promising alternatives to conventional oxide materials in surface-

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sensitive applications including energy and environmental remediation.^{1,2} The superiority of such materials originates from their engineered electronic structure, through alignment of the electronic band positions and high concentration of active atomic sites.3 These sites are formed at the interfaces between the oxide phases, where intervalence charge transfer (IVCT) between the multiple oxidation states may reduce the activation energy required for certain redox reactions.^{4,5} The MOH materials have recently been used in wearable electronics, transparent and flexible ultrathin supercapacitors, optoelectronics, and catalysts.^{6,7} Nonetheless, shortcomings such as a complex fabrication process, thermal stability, low charge carrier mobility, and a lack of chemical stability in vigorous acidic or basic aqueous media have limited their widespread applications. Furthermore, existing fabrication strategies for MOHs rely on a multistep process that is mainly focused on deposition of zero-dimensional (0D) metal oxides on nanosheets (2D) or bulk scaffolds (3D).8-11

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To date, several techniques have been reported for the synthesis of hybrid heterostructures such as hydrothermal,^{12,13} electrospinning,13-15 multistep evaporation,16-19 flame synthesis,20,21 and surface-charge assisted electrostatic deposition.5 These methods often require templates or substrates such as Au,^{13,16} Cu, Al₂O₃,¹² and Ga/SiO₂/Si,¹⁷ which typically have an adverse impact on the electrical conductivity, stability, and mass permeability of the final device. Recently though, several studies have been reported with the focus on the template-free synthesis of heterostructures such as 1D/0D MXene/CoNibimetal MOFs using bottom-up techniques,²² 3D/0D Fe₂O₃/ Li₂O²³ and Ag using the hydrothermal process, 2D/0D ZnO/Bi₂S₃ using the sonochemical process,²⁴ and 3D/0D CeO₂/RuO₂ and CeO₂/CuO both by self-assembly from disassembled metalbased coordination polymers.25,26

The concerns associated with mixed 0D/3D heterostructures involve their limited access to the inside or bulk of the 3D structures. In addition, the 0D nanoparticles may form microclusters, which are normally buried into inaccessible sites within the bulk or passivated by organic molecules.⁹ As for mixed 0D/2D materials, although the contact surface area can be improved considerably, nonetheless, the irreversible stacking of the 2D nanosheets limits ionic access to the interlayer spaces, thereby reducing the functionality of such materials.²⁷

Despite progress in the fabrication of interconnected porous 3D structures and creation of extremely thin holey 2D polycrystalline nanosheets,5,28 there persist technical impediments in producing an actual device out of these materials, the most critical of which are as follows: (1) a mixed heterostructure is generally synthesised in the form of nano/micro powders; therefore, to make a device, post-treatments including deposition of the powder on special flexible substrates, which are generally carbon-based materials, and addition of a conductive binder are essential;²⁹ and (2) limited chemical and thermal stability as well as low functionality, which is mainly determined by the physical properties of the employed flexible templates. Therefore, there has always been a need for a novel approach by which a stretchable, flexible, and template-free MOH can be achieved. Single-step fabrication of flexible semiconductors, which is yet to be reported to the best of our knowledge, would be of great interest for a range of applications, where repetitive elastic deformation occurs. This includes wearable sensors, washable and wearable batteries that could be woven into cloth, and self-powered wearable biosensors. This allows synthesis to be conducted with fewer challenges than conventional synthesis. For example, homogeneous deposition, binding agents, and surface treatment can be eliminated. Furthermore, the template-free and flexible heterostructure provides higher mechanical stability without delamination or pulverisation, which are common restrictions in templatebased semiconductors.

The present work reports a high-yield and effective strategy to synthesise a centimetre squared-size, flexible, adherent, and free-standing ZnO porous scaffold with controllable thickness. This 3D porous scaffold, which is composed of one-dimensional nanowires (NWs) with a lateral size of up to 5 cm and a thickness ranging between 40 and 500 μ m, was fabricated by microrecycling of Zn-rich waste materials. The broad applicability of our fabrication technique was demonstrated by the formation of several representative mixed 0D/3D heterojunction nanostructures of CdO, Bi2O3, SnO2, and carbon nanoparticles (0D) deposited on the surface of the ZnO NWs without applying any binder (that typically diminishes the performance). The synthesis of metal oxide (MO) heterostructures is based on delivering high-temperature (1550 °C) metal vapour towards the ZnO 3D scaffold, followed by oxidation, and then trapping the as-formed 0D MO nanoparticles within the porous structure of the 3D ZnO scaffold. The concentration-controlled nature of the nanoparticle penetration into the scaffold enabled the establishment of a new pathway towards the fabrication of fabric-like multilayer heterostructures consisting of rich- and deficient-0D only-oxide regions. Introduction of MO heteroatoms was shown to be a promising approach towards engineering the electronic structure of the ZnO-based NWs, through band position alignments, for energy and catalytic purposes.

Through engineering the band position, a broad range of applications, such as sensors, energy storage, catalysts, and photocatalysts, can be conducted by this type of patch. As a representative application, the applicability of the selfadherent and stable patches was confirmed by observing the excellent electrocatalytic behaviour of the ZnO-CdO heterostructure for the anodic electrochemical generation of hydrogen peroxide (H_2O_2) via two-electron water oxidation. The product of water oxidation at the anode can be O_2 (via a four-electron pathway), H_2O_2 (via a two-electron pathway), or/and OH' (via a one-electron pathway), among which H₂O₂ offers a 20-fold economic value³⁰ compared to O2. The details of existing methods for H₂O₂ generation are given in Section 4 in the ESI.[†] Finally, a theoretical Sabatier volcano plot, which is constructed from density functional theory (DFT) calculations, for the H_2O_2 catalytic activity of CdO/ZnO showed minimum performancedeviation (η) values of 0.19 V which introduces a highly promising alternative to the state-of-the-art noble metal electrocatalyst Pt ($\eta = 0.22$ V) for this reaction.

Results and discussion

Fabrication and characterisation of the highly flexible, 3D, free-standing ZnO patch

The fabrication strategy is based on a rapid multistep process, as schematically shown in Fig. 1a, including (a) preferential generation of metal vapours by heat treatment (at 1550 °C) of oxide-rich waste materials with carbon in an Ar atmosphere (in the hot zone), (b) delivery of the vapours into a pre-designed cold zone by flowing the Ar gas, (c) instantaneous formation of MO nanowires (NWs) through oxidation/growth of the metal vapour within macroscopic turbulence at the intersection of the hot and cold zones. The intersection forms due to the injection of air, from the cold zone, with a flow in the opposite direction relative to that of the Ar, and finally (d) deposition of the MO NWs on the surface of a collector disk resulting in the formation of a 3D patch-like MO network. The 3D patch is extremely flexible, porous, and adherable, as evident in Movie S1.[†]



Fig. 1 Synthesis strategy and characterisation of the ZnO patch. (a) Schematic of the designed chamber for fabrication of the MO patch, (b) SEM and optical images of ZnO patches showing variations of thickness as a function of Ar gas flow rate.

To successfully achieve the 3D ZnO network, the following two key factors were found to be of great significance: (1) metal vapour generation rate, which is subject to the mass of the metal source, and (2) the flow accumulation of the carrying and oxidative purging gases (injected from the opposite ends of the tube furnace) that determines the horizontal direction of the gas stream.

At a flow accumulation of zero, diffusion is the primary mechanism, and hence there would be no preferred flow direction. In the case of non-zero flow accumulation, the transfer of metal vapours is based on convection.³¹ At a very low Ar flow rate (1.6 $\text{cm}^3 \text{ s}^{-1}$), diffusion of the vapours resulted in deposition of the MO adjacent to the Ar/air intersection region in the tube (near the cold zone). In contrast, a 10-fold increase in the flow rate $(16 \text{ cm}^3 \text{ s}^{-1})$ resulted in the transfer of the vapours towards the cold zone, predominantly through convection. Consequently, MO NWs can be deposited on the surface of the collector disk (which can be made from any material withstanding up to 200 °C) to form a thin, porous ZnO patch with thickness in the range of 40-500 µm. At the highest flow rate (80 $\text{cm}^3 \text{ s}^{-1}$), where convection is the predominant mechanism, increasing the concentration of MO in the downstream region led to the formation of a sponge-like MO patch with a larger thickness of up to 1000 µm. This is attributed to the enhanced flow front velocity as a result of raising the flow rate.31 Fig. 1b shows MO patches with varying thickness due to the changes in flow rate of the carrier gas. It is significant to note that, according to the continuity equation, the gas with low/medium flow rate coils inside the tube while increasing the flow rate led to transforming the turbulent into the laminar flow pattern.32

The final stage of the synthesis process involves nucleation and preferential growth of the MO nuclei,³³ which occurs in the near cold zone. The temperatures of the cold and hot zones, as well as the profile of the temperature, play key roles in the

nucleation stage.34-36 The scaffold template formation was not achieved as long as the hot zone temperature was below 1550 °C. Lower temperatures led to the formation of powdery deposits that cannot be detached from the substrate as a solid flexible patch. In the near cold zone, at temperatures in the range between 419 °C (the melting point of Zn) and 907 °C (the boiling point of Zn), Zn vapour condenses into nano-sized droplets, which then get oxidised as a result of exposure to O₂. Unlike the vapour-liquid-solid (VLS) growth mechanism, in which metal droplets first deposit on the surface of a substrate, the present work represents in situ nucleation, where the surface of the nano-droplet, which is condensed during the gasliquid (GL) phase transition, acts as the nucleation site.³⁷ Meanwhile, injection of O₂, shown in Fig. 1a, with a countercurrent flow direction against the carrier gas, *i.e.*, Ar, results in oxidation and continuous growth of ZnO NWs. The as-synthesised ZnO ultrathin NWs with clean tips indicate that the initial liquid Zn droplets acted as a catalyst by a self-catalysis mechanism.

Furthermore, the relative velocity as well as accumulation flow rate determines the final microstructure of the oxide and its growth direction through alteration of the dominant flow patterns, including turbulent, coil-like, and laminar.³² Since we employed a fixed-length reactor in this research, it was found that placing less than 0.5 g (*e.g.*, 0.2 g) of the metal source causes a very thin layer of patches that are pretty impossible to detach *via* manual handling, while more than 0.5 g (*e.g.*, 1 g) of metal source led to a very thick, dense, and brittle layer of heterostructure. Thus, 0.5 g loading of the source under our experimental conditions was chosen as the optimum mass.

In summary, the feeding rate, nucleation/growth rate, and the presence of either turbulent or coil-like flow streams are responsible for intertwining the individual NWs and consequently the formation of a free-standing 3D ZnO network. It is significant to note that this strategy yielded an outstanding amount of ~5 g min⁻¹ of the 3D ZnO patch which makes such a method suitable for rapid, cost-effective, and large-scale fabrication processes. However, one of the main limitations of this method is the usage of low boiling temperature metals since the metal sources need to transform into gas phases followed by controlled oxidation and deposition.

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Fig. 2a shows a representative ZnO patch with a cut lateral size as large as 1.2 cm. The high flexibility and stretchability of the patch are demonstrated in Movie S2.† Furthermore, morphological analysis of the ZnO patch was carried out using SEM imaging. Fig. 2b shows a low magnification SEM image of the ZnO 3D patch, which is constructed through an assembly of entangled NWs, with an average length of several tens of micrometres. Fig. 2c and d depict high magnification SEM images of the NWs, where the average diameter is measured to be ~ 40 nm. The interspaces between the NWs were also measured to be $\sim 0.5-4$ µm indicating the highly microporous nature of the ZnO patch. The presence of micropores in three dimensions is expected to provide a quick and high penetration capability for the ZnO patch in contact with aqueous and nonaqueous solutions. Fig. 2e-g reveal the results of scanning transmission electron microscopy (STEM) analysis of the NWs. The homogeneous distribution of Zn and O elements confirms the pristine nature of the ZnO NWs.

The structure of the NWs was further characterised using transmission electron microscopy (TEM) imaging (Fig. 2h) which highlights the single-crystalline nature of the ZnO with

a hexagonal structure and preferred growth orientation along [0001]. Fig. 2i shows a high-resolution TEM (HRTEM) image of a single ZnO NW, in which a cluster of atomic defects create a nanohole with an area of 16 nm². This can be ascribed to the incomplete growth of the ZnO NWs or preferential etching during post heat treatment.^{38,39} These mesopores have been shown to significantly improve the catalytic and electrocatalytic performance through shortening charge-carrier diffusion pathways and enhancing the accessible surface area. The distribution of nanoholes was confirmed *via* BET analysis, as shown in Fig. S3,† where the concentration of the pore width peaks between 2.2 and 4 nm.

To measure the diameter of a single ZnO NW, atomic force microscopy (AFM) imaging was carried out by drop-casting the NWs on a silicon oxide substrate. The AFM image and the corresponding height profile are shown in Fig. 2j, unveiling a diameter of ~75 nm, which is one of the thinnest flexible NWs reported to date. The diameter is in agreement with that obtained by SEM (Fig. 2d).

Heterojunction nanostructures of the ZnO-based patch

The applicability of the 3D ZnO network was broadened by the synthesis of several heterojunction nanostructures using oxide/ non-metal heteroatoms. Fig. 3a shows a schematic illustrating the fabrication of mixed 0D/3D heterojunction nanostructures, which is based on the penetration of MO (0D) dots through the 3D microscopic spaces of the porous ZnO patch, following their



Fig. 2 Physical and chemical characterisation of the ZnO patch. (a) Optical microscopic image of a centimetre-size ZnO patch, (b–d) SEM images of the ZnO patch, (e–g) EDS elemental mapping of the ZnO patch, (h and i) TEM and high-resolution TEM images of a single ZnO NW, (j) AFM and corresponding height profile of a ZnO NW.



Fig. 3 Fabrication of heterojunction nanostructures. (a) Schematic of heteroatoms decorated on the ZnO patch, (b) polarised optical image of triple layer ZnO/CdO/C heterostructures, (c, d) SEM and TEM images of Zn–Cd, (e, f) SEM and TEM images of Zn–Sn, (g, h) SEM and TEM images of Zn–Bi, (i, j) SEM images of the Zn–C heterostructure, (k) Raman microspectra for pristine ZnO and the heterojunction nanostructures, (l) XPS spectra for the Zn 2p orbital of pristine ZnO and heterojunction nanostructures, (m) 3d orbital of Cd in Zn–Cd, (n) 3d orbital of Sn in Zn–Sn, (o) 4f orbital of Bi in Zn–Bi, (p) 1s orbital of C in Zn–C.

nucleation and growth on the NWs' surface. The penetration depth of the MO dots is determined by the extent and direction of the accumulated flow, precursor source, and porosity of the ZnO network.

Furthermore, taking advantage of the high flexibility of the fabrication method, synthesis of multilayer heterojunctions through a layer-by-layer assembly of oxides or non-metal-based materials was carried out, for the first time, to the best of our knowledge. The representative triple layer of the Zn–Cd–C heterojunction nanostructure was synthesised, the optical microscopy (OM) image of which is shown in Fig. 3b. As shown, the interfacial regions between the layers are distinguishable while showing large penetration depths to each layer. Such engineered layer cross-fading justifies the high stability of the heterojunction nanostructure, particularly at interfaces. Further confirmation of the applicability of our synthesis approach is provided in Fig. S4,† where an optical image of a multilayer Zn– Cd–Zn–Cd–C is shown. Such a controllable fabrication strategy would open up a new pathway towards a new generation of advanced ceramic functional heterostructures that can be readily tailored for a specific purpose for a wide range of energy and environmental applications, where no binder can interfere with the performance of the functional patch.

For the bilayer heterojunction nanostructures, a representative mixed heterojunction of 3D ZnO and 0D CdO (Zn-Cd) was synthesised through simultaneous nucleation and growth of the ZnO 3D network and deposition of the CdO nanodots. The outstanding mechanical flexibility of the fabric-like Zn-Cd is shown in Movie S3.[†] The SEM image of the Zn-Cd heterostructure is shown in Fig. 3c. Also, the energy dispersive spectroscopy (EDS) elemental mapping of the Zn-Cd sample is shown in Fig. S5.[†] Fig. 3d shows the TEM image of an interfacial region between the CdO and ZnO, where there is a strong chemical bond (developed at low temperatures in the cold zone) between the crystallites supported by apparent intergrowths at the grain boundaries. This is further confirmed using HRTEM imaging as shown in Fig. S6,† where the intergrowth facets of the crystals is an indication of such chemical bonds, as previously reported.5

Furthermore, the excellent flexibility of our fabrication method enabled us to synthesise mixed 0D/3D heterojunction nanostructures in a two-step process. Therefore, additional heterojunction nanostructures were fabricated using Bi2O3 and SnO₂ heteroatoms. The corresponding SEM and HRTEM images are shown in Fig. 3e, f and g, h, respectively, revealing the presence of SnO₂ nanoparticles and Bi₂O₃ nanospheres in contact with the ZnO NWs. The details of the morphological and structural analysis of these heterojunctions are shown in Fig. S7 and S8.† The wide use of the ZnO 3D template to synthesise heterojunction nanostructures is not limited to MOs and can also be applied to non-metal materials such as carbonbased nanostructures. Therefore, we successfully synthesised a heterojunction of graphite nanoparticles and ZnO by purging a carbon-rich gas into the microporous structure of ZnO. The SEM images of the Zn-C heterojunction are shown in Fig. 3i, while the corresponding EDS elemental mapping image is shown in Fig. S9.†

Additionally, partial diffusion of graphite into the ZnO network, as a scaffold, resulted in the formation of a double layer heterojunction. This forms a layer of carbon on one side of the ZnO patch, while the other side remains intact. The camera and SEM images of the ZnO patch and several multilayer heterostructures are shown in Fig. S10 and S11.[†] Further investigation on the architecture of the heterostructure was carried out using HRTEM images of Zn–Bi and Zn–Sn at their interfacial regions, as shown in Fig. S12 and S13,[†] respectively.

The chemical analysis of the samples was carried out using Raman microspectroscopy. Fig. 3k shows the Raman spectra of the heterojunctions in comparison with pristine ZnO NWs. There are two predominant peaks at 430 and 580 cm⁻¹ attributed to E_{1T} and E_{1L} vibrational modes of ZnO.⁵ E_{1T} is assigned to

the oxygen vibrations within the ZnO lattice. The pronounced asymmetry of the peak is owing to the lattice disorder, as well as to the anharmonic phonon-phonon interactions. Additionally, the E1L is ascribed to the second-order Raman scattering that is highly sensitive to impurities/defects due to the impact of the phonons outside of the Brillouin zone. More importantly, the band at 275 cm⁻¹ can be due to the presence of vacancies (Zn vacancies) in the ZnO NWs,40 as such can be confirmed by the TEM image shown in Fig. 2h. The addition of CdO resulted in (1) asymmetrical broadening of the ZnO peaks, which can be ascribed to the formation of defects and (2) the appearance of two additional bands at \sim 350 and \sim 941 cm⁻¹. These bands can be attributed to the second-order Raman scattering of 2LA and 2LO vibrational modes.41 It is worth mentioning that the presence of CdO led to an asymmetrical broadening and redshift of the ZnO-related band at 561 cm⁻¹. This can be associated with either decrease in crystallinity of the ZnO structure as a result of the addition of amorphous CdO and/or the formation of defects at the interfacial sites between CdO and ZnO, which leads to strong chemical bonds.42 The former was observed from the HRTEM images (Fig. S6[†]), while the latter can be confirmed by the formation of trapping states in XPS valence band results (Fig. S14[†]), as has been previously reported.^{5,43}

For the ZnO–SnO₂ (Zn–Sn) sample, the deposition of SnO₂ resulted in the appearance of new peaks at Raman shifts of ~472 and ~638 cm⁻¹. The former is attributed to the E_g doubly degenerate vibrational mode of SnO₂, while the latter is ascribed to the A_{1g} mode associated with the stretching vibration of Sn–O bonds in SnO₂.⁴⁴ Additionally, the asymmetrical broadening of the ZnO-related peaks is owing to the electron interaction between the MO nanodots and the ZnO NWs at their interfacial region. Similarly, the Raman spectra for Bi₂O₃ and graphite nanoparticles deposited on the 3D ZnO scaffold are shown in Fig. 3k. As for Zn–Bi₂O₃ (Zn–Bi), there is a predominant peak appearing at a Raman shift of ~300 cm⁻¹ which is ascribed to the displacements of O atoms in α -Bi₂O₃.⁴⁵ An incomplete formation of graphite may also be concluded by measuring the intensity ratio of $I_D/I_G \approx 0.8$.⁴⁶

The surface analysis of the ZnO-based heterostructures was carried out using X-ray photoelectron spectroscopy (XPS) for the Zn 2p_{3/2} orbital (Fig. 31). The full spectrum XPS results for Zn 2p_{1/2 and 3/2} of the samples are shown in Fig. S15.[†] Besides, the XPS spectra for Zn-Cd revealed that the chemical attachment of CdO in the ZnO structure resulted in a positive shift of the Zn 2p_{3/2} orbital toward higher binding energies, while the presence of Bi yielded a peak shift to lower binding energies. The shifts of XPS peaks can be associated with changes in electronic charge distributions at the interface of the oxides. This is owing to the strong electronic interactions between Zn and Cd, Bi, C or Sn heteroatoms.⁴⁷ Such interaction affects the electron density around the active sites and thus manipulates ΔG_{H^*} on the surface which is the key to improving the catalytic performance.47,48 Therefore, the changes in O-Zn binding, as a result of the attachment of Cd, i.e., Cd-O-Zn, and Bi, i.e., Bi-O-Zn, imply chemical bonding formed between the heteroatoms and parent ZnO, which is consistent with the CdO and ZnO intergrowth along the grain boundaries as shown in Fig. S6.† The

addition of Sn and C heteroatoms in the ZnO system showed insignificant changes in the $2p_{3/2}$ orbital of Zn and hence minimal alteration in the electronic structure of the pristine ZnO. Furthermore, the presence of Cd, Sn, Bi, and C heteroatoms in the heterostructure was investigated. Fig. 3m and n show the 3d orbitals of Cd and Sn elements in Zn–Cd and Zn–Sn, respectively. It is significant to note that only the XPS spectrum related to Sn $3d_{5/2}$ is shown since the other pair ($3d_{3/2}$) overlaps with a strong Auger peak of Zn at ~493 eV. Furthermore, the XPS spectra shown in Fig. 3o and p are attributed to the 4f and 1s orbitals of Bi and C in the respective Zn–Bi and Zn–C samples.

Engineering the electronic structure of 0D/3D heterostructure patches

The electronic structure of the ZnO NWs was analysed using Kelvin probe atomic force microscopy (KPAFM), X-ray photoelectron spectroscopy (XPS), and UV-vis spectroscopy to obtain the work function (ϕ), gap between the valence band and Fermi level (E_{vb}), and bandgap (E_g) between the conduction and valence band, respectively. Fig. 4a illustrates the Tauc plot derived from the UV-vis spectrum, where the E_g value was determined to be ~3.11 eV. The ϕ value was measured to be 4.2 eV using the potential profile of a single ZnO NW against a Pt-coated SiO₂ tip, as shown in the inset of Fig. 4b. In addition,

Fig. 4c shows the XPS valence band plot, where E_{vb} was determined to be 2.48 eV. The hysteresis area of the XPS valence band plot highlighted in orange is attributed to the trap sites within the bandgap of the ZnO that can be due to structural defects such as vacancies.⁴⁹ The $E_{\rm g}$ value of the ZnO NW is consistent with those reported for pure ZnO, while the valence and conduction bands experienced a negative shift to lower vacuum levels. The band rearrangement occurring for the ZnO NWs is expected to facilitate the hydrogen evolution reaction (HER) in water splitting. According to the chemical reactions required for the HER, oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) applications, the band alignment can be manipulated by the introduction of a heteroatom in the system.5,50 This is shown in Fig. 4d, where the hybrid 0D/3D heterostructures exhibit a quite varied band diagram. The Zn-Cd and Zn-Bi samples show a bandgap shift towards lower vacuum levels, while midgap states, as a result of CdO and Bi₂O₃, are formed close to the conduction band. More importantly, the valence bands have shifted close to the H2O2/H2O standard potential at $E_{\rm NHE} = 1.76$. In contrast, the addition of SnO₂ and carbon into the 3D ZnO patch led to the shift of the bandgap into high vacuum levels, while it appears there are no midgap states formed.



Fig. 4 Electronic band structure characterisation of the 3D ZnO network and the mixed 0D/3D heterojunction nanostructures. (a) Tauc plot from UV-vis spectrophotometry data for the 3D ZnO network (Tauc plot model $(\alpha h\nu) = A(h\nu - E_g)^2$ applied, where A and α are absorption and absorption coefficient, respectively; $h\nu$ is the photon energy; and E_g is the indirect optical bandgap), (b) Kelvin atomic force microscopy (KPAFM) imaging and corresponding voltage profile of a single ZnO nanowire, (c) X-ray photoelectron microscopy (XPS) valence band plot for the 3D ZnO network, (d) electronic energy level diagram for pristine ZnO and mixed 0D/3D heterojunction nanostructure.

By engineering the electronic band structure of the patches, a broad range of applications such as sensors, energy storage, catalysts, and photocatalysts can be considered. The present work investigated the performance of the patches for H_2O_2 generation, only as a representative application.

The H_2O_2 catalyst preparation typically involves the mixing of binding agents with catalyst powders for the purpose of making an adhesive ink. Although the ink can be readily used for the catalysis application, the insulating nature of the binders may cause adverse impacts on the performance.⁵¹ However, the mechanical and solvent-free methods have shown improvement in the catalytic performance in terms of overpotential and stability compared to the inked catalysts.⁵² In this research, the synthesised patches were attached to the substrate without solvent or binder for oxidative H_2O_2 generation. This is attributed to the electrostatic attraction at the interfacial region between the substrate and the patches.

The electrocatalytic performance of the binder-free ZnObased heterojunction patch was investigated for the anodic H_2O_2 formation reaction. In this regard, the onset potential, overpotential, effective current density, stability, generation rate, accumulation rate, and faradaic efficiency (FE) of H_2O_2 generation, which are critical factors in evaluating a promising catalyst, were studied. In addition, the dominant reactions occurring during H_2O_2 generation were comprehensively analysed, the results of which are provided in Section 4 in the ESI,† including a complete literature review on anodic $\rm H_2O_2$ generation.

For this particular application, the selectivity of products is a key concern. The two-electron anodic oxidation of H_2O to generate H_2O_2 is preferred (instead of the four-electron reaction to generate O_2 , and the one-electron reaction to produce OH' radicals) where the high activity of the catalyst is benchmarked by a low overpotential for the reaction.⁵³ It should be considered that there is an inverse correlation between the selectivity for H_2O_2 evolution and the current density implying that at low overpotentials, the H_2O_2 efficiency is quite high;⁵⁴ however, obtaining high selectivity at high current densities is still challenging with regard to competition among the three one-, two-, and four-electron reactions (represented in eqn (1)–(3)).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E^\circ$$

(four-electron WOR) = +1.23 V vs. RHE (1)

$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-, E^\circ$$
(two-electron WOR) = +1.76 V vs. RHE (2)

$$2H_2O \rightarrow OH^{\bullet} + H^+ + e^-, E^{\circ}$$

(one-electron WOR) = +2.38 V vs. RHE (3)

The onset potential and catalytic current densities of the samples, in comparison with bare FTO (which is one of the most promising candidates for anodic H_2O_2 generation) were measured using linear sweep voltammetry (LSV), as shown in



Fig. 5 Electrocatalytic performance of the ZnO-based patches. (a) Linear voltammogram for FTO, ZnO NWs, Zn–Sn, and Zn–Cd heterojunction patches; (b) a comparative plot summarising the overpotential of H_2O_2 generation, onset potential for H_2O_2 generation, and the maximum current densities for the FTO and ZnO-based heterojunction structures at 50 mV s⁻¹ in a one-compartment cell, 2 M KHCO₃, and Pt as the counter electrode; (c) linear plot of electrochemical surface area (ECSA) evaluation (*i.e.*, current density against scan rate in the range of 1.23–1.33 V vs. RHE) showing double layer charging during anodic and cathodic reactions for FTO and Zn–Cd to determine C_{dl} . H_2O_2 performance of (d) FTO, and (e) Zn–Cd patch using a two-compartment cell with 2 M KHCO₃ at room temperature under a constant passed charge of 5C.

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Fig. 5a. In addition, details of the overpotential values for H_2O_2 generation, onset potential, and the maximum current densities of the samples are illustrated in Fig. 5b. The results reveal the superior performance for the mixed Zn–Cd heterojunction scaffold with the lowest onset potential of 1.91 V *vs.* RHE. This value is only 150 mV higher than that of the theoretical value (1.76 V *vs.* RHE). In order to benchmark the H_2O_2 performance of the ZnO-based heterojunctions, their activity was compared with that of state-of-the-art catalysts reported in the literature (Table S1[†]).

Furthermore, the results of electrochemical impedance spectroscopy (EIS) of FTO and Zn–Cd patches at four different potentials (Fig. S18†) show that despite the higher initial resistance (at open circuit potential (OCV)) for Zn–Cd compared to FTO, the electrochemical resistance (*i.e.*, Re(Z)) of the Zn–Cd decreases significantly quicker after applying the potential, which means higher electrocatalytic activity of Zn–Cd at the optimum working potential.

For the electrochemical tests, the geometrical surface area for both Zn–Cd and FTO was similar (\sim 1.5–2 cm²); however, the electrochemically active surface area (ECSA) is a more reliable indicator to compare the intrinsic activity of electrocatalytically active materials55 within a solution. The ECSA analysis is based on the measurement of the electrochemical double-layer capacitance $(C_{\rm dl})$.⁵⁶ The ECSA plots in Fig. S19[†] show the CVs at different scan rates for FTO and Zn-Cd patch attached on FTO. Fig. 5c illustrates a comparison between the slopes of the linear fittings which demonstrates that the ECSA determined from the anodic reaction/s is 5% higher for FTO, while this value for the cathodic reaction/s is 25%. Since in this research, the H_2O_2 generation occurs during the anodic reaction/s, the anodic ECSA is applicable. This ECSA for FTO is 5% more than that for Zn-Cd heterostructures, indicating less active sites in the Zn-Cd patch; however, the higher efficiency and selectivity of the Zn-Cd patch reveals that although the number of active sites is fewer, the intrinsic activity of each individual site is higher compared to that of FTO.

Furthermore, the FE and accumulation of H_2O_2 are also significant challenges and are associated with the material/ catalyst and electrolyte in use. Previous experiments on many other materials in the literature have shown that the combined FE of H_2O_2 and O_2 generation is near 100%,^{57,58} signifying a lack of production of OH[•] radicals. To evaluate the efficiency and selectivity of H_2O_2 generation, the FTO substrate and the Zn–Cd heterostructure were examined under a constant anodic charge of 5C within the potential range of 2.13 to 3.73 V *vs.* RHE. The corresponding results are shown in Fig. 5d, where the FE value for FTO is almost constant between 2.53 and 3.53 V *vs.* RHE, which is consistent with the literature.⁵⁹ An optimum potential window and maximum FE is found for each metal oxide sample owing to the nature of the competition between the two-electron and four-electron oxidation reactions.⁵³

In contrast, the potential window for the Zn–Cd scaffold was determined to be in the range of 2.33–3.33 V vs. RHE. Fig. 5e reveals that the FE value for the Zn–Cd scaffold increases from 2.13 to 3.33 V vs. RHE with a peak reaching 15% and generation rate of 2.5 μ mol min⁻¹ cm⁻². It is worth mentioning that the

fluctuations in the FE, within the range of 2.33–3.33 V vs. RHE, are less than 10% which is in agreement with that reported by Miyase *et al.*⁵⁹

The outstanding performance obtained for Zn–Cd, compared to the other ZnO-based materials and FTO, is attributed to the dual characteristic of CdO, which is readily transformed into CdCO₃ in an HCO_3^- aqueous solution, which then gets oxidised to CdO when exposed to air at temperatures greater than 200 °C. It is assumed that the CdCO₃ phase plays a critical role in the suppression of O₂ evolution owing to its excellent insulating properties, which can be similar to the functionality of PTEF particles on the surface of glassy carbon as reported recently;⁶⁰ however, CdCO₃ is a significantly cheaper alternative and might not be as efficient as PTFE. This carbonate transformation was confirmed by XRD patterns, shown in Fig. S20.†

Comparing the results obtained for FTO (Fig. 5d) with that achieved for Zn–Cd (Fig. 5e), there is an overall 50% improvement in FE and generation rate for the Zn–Cd scaffold. The decrease in *e* efficiency after 3.53 V can be ascribed to the decomposition of H_2O_2 at high potentials, eqn (4) and (5), and a decrease in the conductivity of the current collector in a severely oxidative environment.⁵⁶

$$2H_2O_2 + catalyst \rightarrow O_2 + H_2O \tag{4}$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-, E^\circ = +0.68 \text{ V vs. RHE}$$
 (5)

The transformation of CdO into CdCO₃ makes the surface more of an insulator; however, it should be noted that the CdCO₃ nanodots are distributed uniformly on ZnO NWs. This homogeneous distribution would deactivate some potential sites where H₂O₂ could be decomposed, leading to higher FE. This theory is in agreement with the hindrance effect of an Al₂O₃ layer on BiVO₄.⁵⁸ Park *et al.*⁶¹ also used the insulating characteristic of CaSnO₃ to demonstrate this effect on FTO. Since CaSnO₃ with a bandgap of \approx 4.4 eV is not electrically conductive, the thickness of the coated film was a compromise between conductivity and coverage over FTO.

In another study by Kelly *et al.*,⁶² it was found that the (1010) surface of ZnO has high selectivity and FE, and a lower onset potential for anodic H_2O_2 evolution compared to the (0001) surface. The lower FE in this research compared to the previous literature is due to the high current passed during the experiment (5C) that resulted in the degradation of H_2O_2 . Miyase *et al.*⁵⁹ claimed that at a passed charge of 0.05C, the FE(H_2O_2) was 47% for FTO at 5 °C, which decreased to 13% when the charge passed was 1.8C, which is consistent with the result in this study. This drop was even more noticable for mixed metal oxides, which decreased from 98% (0.05C) to less than 30% (1.8C) for CuSb₂O_x.⁵⁹ Moreover, when higher concentrations of H_2O_2 are produced, oxidative H_2O_2 degradation takes place faster due to the accumulated amount of H_2O_2 .⁶³

The stability of electrocatalysts at high potentials⁶¹ while generating H₂O₂ plays a critical role in their practical application. The stability appears to be limited by the pH of the electrolyte, oxidation potential, and nature of the materials to maintain the performance during a long period of electrolysis.⁶² It is generally believed that mixed oxides such as $Al_2O_3/BiVO_4$,⁵⁸ $WO_3/BiVO_4$,⁶⁴ and Sb-containing oxides.⁵⁹ are more efficient and stable than single oxides.⁶¹ However, there is no mixed heterojunction nanostructure reported for H_2O_2 applications to date. The details of all the H_2O_2 catalysis reported since 2016 are provided in Table S1.[†]

Fig. S21[†] shows the results of the stability of the Zn-Cd patch at 2.33 V vs. RHE for 18 h of electrolysis under mild agitation in a two-compartment cell, which is among the highest stabilities reported to date. It is noteworthy that rigorous agitation can lead to elevated rate of H2O2 degradation,64 so the mild agitation seems to be optimal. The trend of stability can be divided into three stages: (1) establishment of the electrical double layers and polarisation of the electrodes; (2) accumulation of H_2O_2 and thus increasing concentration; (3) H_2O_2 decomposition on the surface of the anode at a higher rate than H_2O_2 generation. Furthermore, the intense fluctuations appearing in the total stability test can be attributed to the evolution/explosion of some O₂ bubbles. The reconstructed surface of the Zn-Cd patch after a long-term stability test with relevant SEM, EDS, and proposed reconstructing mechanism is discussed in Section 3 in the ESI and shown in Fig. S22.[†]

To assure that the Cd was not dissolved in the solution, ICP elemental analysis was conducted which showed that the concentration of Cd in the solution after the stability test was below 0.34 ppm (Fig. S23a†), far less than the limit in H_2O_2 (which is 1 ppm).⁶⁵ The Pourbaix diagram of Cd (Fig. S23b†) also indicated the precipitation and separation of Cd²⁺ as Cd(OH)₂ in our working pH.

Accumulative H_2O_2 is another critical factor in benchmarking the efficiency of the catalyst.⁵⁸ It has been reported that H_2O_2 with a concentration as low as 0.9 mM is necessary for disinfectant application.⁶³ Fig. S24† demonstrates H_2O_2 accumulation data for a period of 10 h, where accumulated H_2O_2 reached 2 mM at 2.33 V vs. RHE. The generated H_2O_2 with such a high concentration can be directly applied in pollutant degradation, bleaching, and antibacterial applications.⁶⁵

Mechanistic impacts of CdO and Bi_2O_3 heteroatoms on the H_2O_2 generation efficiency of ZnO

By using first-principles methods based on density functional theory (DFT), we estimated an energy bandgap (E_{gap}) of 3.12 eV for bulk ZnO (zinc-blende polymorph), which is in excellent agreement with our experimentally measured value of 3.11 eV. As for the Zn–Cd and Zn–Bi heterostructure systems, our DFT calculations give E_{gap} values that are very similar to the one

 Table 1
 Electronic properties for ZnO and its Zn-Cd, and Zn-Bi

 heterojunctions achieved by DFT methods

System	$E_{\rm gap}$ (eV)	CB (eV)	VB (eV)	$CB-E_{mid}$ (eV)
ZnO Zn–Cd	3.12 3.12	-4.04 -3.76	-7.16 -6.87	 ∼0.2−0.8
Zn-Bi	3.12	-3.87	-6.99	$\sim 0.0 - 0.5$

estimated for bulk ZnO. The conduction (CB) and valence band (VB) alignments were estimated for the heterostructure systems, which revealed considerable changes compared with those of bare ZnO, similar to the trend observed in the experiments. To be more precise, the CB and VB energy levels experienced upshifts by 0.3 and 0.2 eV for Zn–Cd and Zn–Bi, respectively (Table 1).

The electric potential changes estimated for the heterostructure systems originated from a moderate electronic transfer (\sim 0.1 eV) from the adsorbed Cd and Bi-metal ions into neighbouring Zn atoms on the ZnO surface. Although it is hard to ascertain the exact position of the midgap states for the heterostructures using DFT calculations, due to the sparse nature of the electronic density, it was revealed that such states tend to form close to the CB level (Fig. 6a–c). The details of the electronic properties for the samples are given in Table 1.

To theoretically characterise the catalytic activity and selectivity of bare ZnO and the heterojunction systems, Zn–Cd and Zn–Bi for the electro-reduction of O_2 into H_2O_2 was studied, where we employed the DFT free energy of the sole adsorbed intermediate HOO*, $\Delta G_{\text{HOO}*}$, as the key descriptor.^{53,66–68} Our analysis is based on the accepted hypothesis that the transformation of O_2 into H_2O_2 involves two coupled electron and proton transfers:

$$O_2 + * + (H^+ + e^-) \to HOO^*$$
 (6)

$$HOO^* + (H^+ + e^-) \to H_2O_2 + *$$
 (7)

where * represents an unoccupied active site on the surface of the electrocatalyst and HOO* represents the sole absorbed intermediate for the reaction. Through the calculation of $\Delta G_{\text{HOO}*}$ (see the Experimental section in the ESI[†]) it is possible to construct a Sabatier volcano plot, in which the highest electro-reduction activities correspond to the points on the surface that render the most suitable interactions between the HOO* molecules and the substrate. In particular, for an ideal electrocatalyst, the $\Delta G_{\text{HOO}*}$ value should be ~4.23 eV, which is the tip of the Sabatier volcano.67,68 The points on the right-hand side of the Sabatier volcano (i.e., weaker binding to HOO*) correspond to electrocatalytic reactions that are limited by the hydrogenation of O_2 (eqn (6)), whereas the points on the lefthand side of the volcano (i.e., stronger binding to HOO*) correspond to the electrocatalytic reactions limited by the overpotential leading to the dominant reduction of HOO* into H_2O_2 (eqn (7)). Deviations from the ideal electrocatalyst behaviour are quantified by the performance parameter $\eta = U_{\rm L}$ $- U_0$ for the O₂/H₂O₂ reaction, where U_L represents the lowest potential, for which the two reactions above are downhill in free energy, and $U_0 O_2/H_2 O_2$ represents the equilibrium potential for H₂O₂ electrosynthesis (*i.e.*, 0.69 V vs. RHE). For an ideal electrocatalyst, such a performance parameter is close to zero, while for known state-of-the-art electrocatalysts, η is typically of the order of 0.1 V (ref. 67 and 68) (*i.e.*, the smaller the value of η , the better the electrocatalytic performance of the material that will be achieved).



Fig. 6 (a–c) Theoretical estimation of the electronic band properties of bare ZnO, Zn–Cd, and Zn–Bi shown in the density of state (DOS) plots. The presence of CdO and Bi_2O_3 heteroatoms results in the appearance of electronic mid-gap states. The solid green arrows in ZnO (a) shows the position of the conduction band, while these arrows in the DOS plots of heterostructures (b and c) show the position of midgap states formed close to the CB. (d) Estimation of the Sabatier volcano and H_2O_2 catalytic performance parameter η for bare ZnO and the heterojunction systems Zn–Cd and Zn–Bi based on first-principles DFT calculations. Different HOO* adsorption sites on the ZnO-based surfaces have been considered in our theoretical analysis as sketched by the ball–stick representations on the left. For comparison purposes, usual Pt and Pd hydrogen peroxide electrocatalyst performances are included in the Sabatier volcano.^{67,68} Zn, O, H and metal (*i.e.*, Cd and Bi) atoms are represented with grey, red, pink, and violet spheres, respectively.

Fig. 6d shows the theoretical Sabatier volcano constructed from DFT calculations for the H2O2 catalytic activity and selectivity of bare ZnO and the heterojunction systems Zn-Cd and Zn-Bi. Several possible HOO* adsorption configurations were considered in the theoretical analysis including hollow (H), which is between the rows of Zn surface atoms, Zn atop (A), which is on top of the surface Zn atom, and metal ion atop (AM), which is on top of the surface TM ion, as represented in Fig. 6d. Pristine ZnO showed inferior H₂O₂ electrocatalytic performance compared to that of usual benchmark noble metal electrocatalysts such as Pt and Pd. For example, the η value for Pd is 0.34 V, while such values were calculated for ZnO (H) and ZnO (A) to be 1.51 and 1.06 V, respectively. Furthermore, the electrocatalytic H₂O₂ performance of the bare ZnO appears to suffer from significant overpotential. Nonetheless, the DFT results show that the introduction of CdO and Bi₂O₃ heteroatoms into the bare ZnO significantly enhances the resulting H_2O_2 electrocatalytic performance, which is quite consistent with the experimental measurements. For the "hollow" configuration, HOO* adsorption sites are close to the metal-ion centres and

the η value was estimated to be 0.80 and 0.31 V for Zn–Cd and Zn–Bi, respectively, while these values for "metal ion atop" HOO* adsorption sites were calculated to be 0.19 and 0.59 V, respectively.

In the case of the "hollow" configuration, the electrocatalytic reactions in the HOO* adsorption sites are likely to suffer from mild overpotential (*i.e.*, appear on the left-hand side of the Sabatier volcano), whereas in the case of the "metal ion atop" configuration, the HOO* adsorption sites suffer from mild O₂ hydrogenation (*i.e.*, appear on the right-hand side of the Sabatier volcano). It is worth noting that there is significant improvement in the electrocatalytic performance of the heterostructures, with minimum η values of 0.19 and 0.31 V, which represent promising alternatives for state-of-the-art noble metal electrocatalysts such as Pt ($\eta = 0.22$ V).

Conclusion

The present work reports a simplified, rapid (5–10 min), and controllable strategy to fabricate a family of 0D/3D mixed

heterostructures, with stratified architecture, through a scalable, high-temperature, counter-current gas flow process. The latter enabled engineering of centimetre-size, adherent, flexible, and porous 3D ZnO-based patches as robust and highly stable templates. The ZnO-based NW was then decorated with MO or carbon heteroatoms, which formed a multi-layered architecture with unlimited numbers of layers of ZnO and MO/carbon. The electronic analysis of the heterostructures revealed that the 0D heteroatoms contributed to the formation of midgap states within the bandgap of the ZnO patch as well as tuning the energy levels of the band positions. Such engineering of electrical properties (e.g., band alignment) makes the heterostructures suitable for a broad range of catalytic purposes. As a representative, the band positions were tailored for the purpose of anodic electrocatalytic evolution of H₂O₂ from H₂O. The results showed a reduced onset potential of 1.91 eV vs. RHE, outstanding stability at 2.33 V vs. RHE, and high H₂O₂ accumulation of 2 mM for the Zn-Cd. Furthermore, the first-principles method was applied to calculate the free energies of the sole adsorbed intermediate HOO* in different configurations. The results suggested that considerable improvement in the electrocatalytic H₂O₂ generation performance can be achieved by forming Zn–Cd and Zn–Bi heterostructures. Excellent η values of 0.19 and 0.31 V were obtained for Zn-Cd and Zn-Bi, respectively, offering promising alternatives to not only the state-of-the-art noble metal electrocatalysts such as Pt ($\eta = 0.22$ V), but also other electrochemical applications, where band alignment and rapid production are critical.

Author contributions

R. K. Nekouei and S. S. Mofarah designed and developed the project. R. K. Nekouei conducted the fabrication of all the ZnObased heterostructures and the corresponding application tests, prepared the first draft of the application test, and worked on all versions of the manuscript. S. S. Mofarah conducted all the characterisation tests, analysed data, prepared the first draft, and worked on all versions of the manuscript. S. Maroufi assisted with the development of the project design, and draft preparation in the fabrication mechanism, revised the manuscripts, and supervised the project. C. Cazorla conducted the DFT calculations, analysed the corresponding data, and revised the final versions of the manuscript. A. P. O'Mullane revised and commented on the final versions of the manuscript. Y. Yao assisted with the KPFM characterisation. S. L. assisted with HRTEM imaging of heterostructures. A. Tricoli revised the final version of the manuscript and commented. V. Sahajwalla assisted with the general concept of the project, revised the final versions of the manuscripts, and supervised the project.

Conflicts of interest

The authors declare no conflict of interest.

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