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nanocomposites: benign electrocatalysts toward

Bifunctional gold-manganese oxide

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Gold-manganese oxide nanocomposites were synthesised by seedmediated epitaxial growth at the water/*n*-heptane interface under mild reflux conditions. These nanocomposites exhibit efficient electrocatalytic activity toward the water oxidation reaction (WOR) and the simultaneous oxygen reduction reaction (ORR) at a low overpotential ($\eta \approx 370$ mV) and under neutral pH conditions.

1. Introduction

Industrial scale production of clean energy could replace finite fossil fuels with abundant, renewable, environmentally benign energy sources and would lead to the survival of the planet in a sustainable manner that poses a significant challenge to humanity in the 21st century.^{1,2} There is a growing need for electrocatalytic water oxidation to produce dioxygen for the conversion of electrical energy to stored chemical energy in the form of fuels.^{3,4} Plants utilize complex catalytic systems for the breakdown of water into its elements. In nature and in many protocols designed for artificial photosynthesis, water oxidation, $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$, is a key step and hence our better understanding of these systems could pioneer new designs of effective catalysts.5,6 The activity of electrocatalysts for water oxidation is of fundamental importance for the development of promising energy conversion technologies, including integrated solar water-splitting devices, water electrolyzers, and lithium-air batteries.⁷ Therefore, to meet future challenges, water oxidation has become an important area of research, which is inspired by energy challenges and bioinspired by the emerging understanding of photosystem II.8,9 The salient features of the technical impediments to such a reaction is the requirement of efficient and inexpensive electrocatalysts

capable of oxidizing water to drive this energetically highly unfavorable reaction ($\Delta H^{\circ} = 572 \text{ kJ mol}^{-1}$).¹⁰ Several protocols have been adopted in the literature to design efficient, inexpensive and robust electrocatalysts for the water oxidation reaction based on metallic platinum,¹¹ various oxides and complexes of iridium,¹² ruthenium,¹³ nickel,¹⁴ cobalt,¹⁵ iron¹⁶ and copper complexes,¹⁷ and to evaluate the oxygen evolution activity in acidic and/or alkaline conditions Amongst the materials considered so far for water oxidation catalysts, first row transition metal oxides can are abundant and have reasonable stability compared with their noble metal analogues.¹⁸

In particular, manganese oxides are materials of considerable importance due to their interesting structural, magnetic and transport properties that arise from their excellent structural flexibility combined with novel chemical and physical properties.¹⁹ Among the series of manganese oxides available in various oxidation states of manganese (II, III, IV), Mn₃O₄ (hausmannite) has been found to be an effective and inexpensive catalyst in a number of oxidation and reduction reactions.²⁰ On the other hand, gold nanoparticles have also attracted increasing attention due to their unique properties, such as high biocompatibility, tunable electronic and optical behavior, good conductivity and high catalytic activity, which make them fundamental building blocks for the development of innovative functional materials.²¹ The assembly of different nanomaterials with specific optical, magnetic, or electronic properties to multicomponent composites can change and even enhance the properties of the individual constituents.22 Bifunctional composite nanostructures containing gold have found tremendous importance in the field of nanocatalysis due to the rich surface chemistry of gold.23 The fabrication of nanocomposites containing two or more different functionalities has also started attracting attention due to their enhanced catalytic properties.24

Several reports have been published in the literature using manganese oxides and complexes as electrocatalysts for water oxidation. Dismukes *et al.*²⁵ described the thermodynamic and

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mechanistic aspects that Nature appears to use for catalyzing in vitro water oxidation by photosynthesis using bioinspired and photoactive Mn₄O₄-cubane clusters. Drawing inspiration from the cubane-like CaMn(4)O(x), the biological catalyst found in the oxygen evolving centre in the photosystem II, Gorlin and Jaramillo²⁶ investigated the electrocatalytic activity of nanostructured manganese oxide surfaces that exhibited similar oxygen electrode activity to the best known precious metal nanoparticle catalysts, viz., platinum, ruthenium and iridium. In a recent communication, Jaramillo and colleagues²⁷ demonstrated the addition of Au to MnO_r to produce an order of magnitude higher turnover frequency than that of the best pure MnO_x catalysts and a local, rather than bulk, interaction between Au and MnO_x, which led to the observed enhancement in the activity of the reaction. Zaharieva and co-authors²⁸ showed that the binuclear manganese molecular complex $[(OH_2)(terpy)Mn(\mu-O)_2Mn(terpy)(OH_2)]^{3+}$, which is the most prominent structural and functional model of the wateroxidizing manganese complexes operating in plants and cyanobacteria, could be supported on montmorillonite clay and, using Ce(IV) as a chemical oxidant, the complex could act as one of the best manganese-based molecular catalyst toward water oxidation. Wiechen et al.29 reported the syntheses of layered manganese oxides, where the interlayer cations, viz., K-, Ca-, Srand Mg-containing birnessites, were varied and also observed that the oxygen-evolving complex required the presence of calcium in their structures to achieve maximum catalytic activity. Spiccia and co-workers³⁰ showed that for the nanoparticulates of manganese oxides, formed in Nafion polymer, the catalytic activity toward the water oxidation was dependent on the dispersivity of the nanoparticles. They also reported synthetic methodologies for the preparation of highly active mixed valent MnO_x catalysts by the partial oxidation of crystalline Mn^{II}O nanoparticles and analysed the catalytic activity in water splitting devices.³¹ In a review, the group elucidated the perspectives of a cluster that contains four manganese and one calcium ions bridged by five oxygen atoms in a distorted chairlike arrangement in the current structural and mechanistic understanding of the oxygen evolving complex in photosystem II.32 Being inspired by the structural diversity of manganese oxides that occur naturally as minerals in at least 30 different crystal structures, Dismukes and colleagues33 chose to systematically compare eight synthetic oxide structures containing Mn(III) and Mn(IV) with cubic phases, and concluded that electronically degenerate Mn(III) imparts lattice distortions, due to the Jahn-Teller effect, that are hypothesized to contribute to the structural flexibility, which is important for catalytic turnover in water oxidation at the surface. Suib and group³⁴ compared the catalytic activity of mixed valent porous amorphous manganese oxides, cryptomelane-type tunnel manganese oxides, and layered birnessite as water oxidation catalysts, and observed that amorphous manganese oxides exhibit significantly higher turnovers compared to tunnel and layered structures. In spite of all these investigations with molecular and solid-state electrocatalysts capable of mediating water oxidation, many fundamental questions and practical challenges remain, and clear improvements are needed in cost, durability, and overpotential.

In this communication, we have explored the controllable integration into gold–manganese oxide nanocomposites by seed-mediated epitaxial growth at the water/*n*-heptane interface, and also investigated the electrocatalytic activity of the combinatorial catalysts toward water oxidation and oxygen reduction at low overpotential (370 mV) and, most importantly, under neutral pH conditions.

2. Experimental section

2.1. Reagents and instruments

All the reagents used were of analytical reagent grade. Gold(m) chloride trihydrate (HAuCl₄·3H₂O, \geq 99.9%), trisodium citrate (\geq 99%), manganese acetate tetrahydrate (Mn(ac)₂·4H₂O), 4-aminothiophenol (4-ATP), and phosphoric acid were obtained from Sigma Aldrich and were used as received. Sodium perchlorate, sodium hydroxide, methanol, *n*-heptane, and ammonia were purchased from Sisco Research Laboratories, India, and were used without further purification. An aliquot of 0.1 M phosphate buffer saline (PBS) was prepared by mixing an equimolar solution of phosphoric acid and sodium perchlorate, followed by the dropwise addition of sodium hydroxide. Double-distilled water was used throughout the course of the investigations. The temperature was 298 \pm 1 K for all experiments.

Absorption spectra were recorded in a Shimadzu UV-1601 digital spectrophotometer (Shimadzu, Japan), taking the sample in a 1 cm well-stoppered quartz cuvette. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2100 microscope with a magnification of 200 kV. Samples were prepared by placing a drop of solution onto a carbon coated copper grid and drying overnight under vacuum. Dark field scanning tunneling electron micrograph (DF-STEM) and selected area electron diffraction (SAED) patterns were obtained using the same instrument. Energy dispersive X-ray (EDX) analysis was performed on an INCA Energy TEM 200 using an Xray detector. Fourier transform infrared (FTIR) spectra were recorded in the form of pressed KBr pallets in the range (400-4000 cm⁻¹) on a Shimadzu-FTIR Prestige-21 spectrophotometer. X-ray diffraction (XRD) pattern was obtained using a D8 ADVANCE BROKERaxs X-ray diffractometer with CuKa radiation ($\lambda = 1.5418$ Å); data were collected at a scan rate of 0.5° min⁻¹ in the range of 10–80°. Electrochemical measurements were performed by a CHI-660C electrochemical workstation. A Ag/AgCl electrode (in 3.0 M KCl) and a Pt wire were used as the reference and auxiliary electrodes, respectively. Catalytic reactions were performed by the immobilized nanoparticles or nanocomposites over a 4-aminothiophenol monolayer modified gold working electrode, with 0.1 M phosphate buffer saline (pH \sim 7.5) used as the electrolyte and at a scan rate of 100 mV s^{-1} .

2.2. Synthesis of the nanomaterials

2.2.1 Synthesis of gold nanoparticles (NPs). Gold nanoparticles were synthesized by the Frens citrate reduction procedure,³⁵ where the standard procedure for the preparation

of 10 nm gold nanoparticles is as follows. An aliquot of 50 mL aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.25 mM) is heated to boiling and 0.5 mL of trisodium citrate (1%) is added. In about 25 s, the boiling solution turns faintly blue (nucleation). After approximately 70 s, the blue color suddenly changes into a brilliant red, indicating the formation of gold particles. The boiling was continued for half an hour and then cooled to room temperature.

2.2.2 Synthesis of gold-manganese oxide nanocomposites (NCs). Gold-manganese oxide nanoparticles were synthesised at the environmentally benign water/n-heptane interface under mild reflux conditions. In 25 mL binary solvent mixture of water and *n*-heptane (3: 1 v/v), 2.5 mM Mn(ac)₂·4H₂O was added and brought to reflux (ca. 65-70 °C) under stirring. After about 30 min, 150 µL of ammonia was added, and immediately after, 1.0 mL of preformed gold nanoparticles (0.25 mM) was added dropwise for 10 min to the solution under reflux. The refluxing was continued overall for 1.5 h. After the addition of the gold colloid, the color of the sol slowly began to change, and finally, a brownish red coloration was seen at the end of the reaction. Then, the heating was stopped and the mixture was stirred for 12 h at room temperature. The particles obtained were retrieved from the solvent mixture by centrifugation at 10 000 rpm for 15 min and subsequently, redispersed into water. The dispersion was found to be stable for a month when stored in a vacuum desiccator. Manganese oxide nanoparticles were synthesised following the same procedure, but without the addition of any gold nanoparticles.

3. Results and discussion

In the present experiment, the water/*n*-heptane binary solvent mixture plays an important role in the evolution of gold–manganese oxide nanocomposites by epitaxial growth without any external stabilizing agents.³⁶ The controllable integration of gold and manganese oxide into single nanostructures was characterised by absorption, Fourier transform infrared (FTIR) spectroscopy and by X-ray diffraction (XRD) techniques, which revealed the epitaxial growth of manganese oxide on the surface of gold nanoparticles, as described in ESI 2.[†]

The morphology, composition and crystallinity of the particles are depicted in Fig. 1. Transmission electron micrographs (panels a, b and c) of gold, manganese oxide and gold-manganese oxide show that the particles are 10 \pm 2 nm, 15 \pm 3 nm and 20 ± 5 nm, respectively. In the image of the nanocomposites, the Au particles appear black, while Mn₃O₄ are light colored, because Au has a higher electron density and allows fewer electrons to transmit.¹⁹ Dark field scanning tunneling electron micrographs (DF-STEM) (panel d) highlight the epitaxial growth of manganese oxide on gold nanoparticles. The energy dispersive X-ray spectrum (panel e) of Au-Mn₃O₄ particles reveals that the particles are composed of Mn, C, O, Cu and Au elements. Among these elements, the signals of Mn, O and Au result from the Mn₃O₄ and Au particles, which form the product and the signals of C, while the O and Cu elements come from the precursor and the supporting TEM grid. From the SAED pattern of the composites, it is clear that a bright reflection appears



Fig. 1 (a–c) Transmission electron micrographs of Au, Mn_3O_4 and $Au-Mn_3O_4$ nanoparticles, respectively; (d) dark field scanning tunneling electron micrographs, (e) energy dispersive X-ray and (f) selected area electron diffraction pattern of Au.

from the (111) plane of the fcc-structured gold and the strong ring pattern corresponds to the (101), (103) and (211) planes of the tetragonal hausmannite structure. In addition, a combined multireflection results, due to the Au- Mn_3O_4 composite formation, confirming the crystallinity of the resultant materials.¹⁹

Nowadays, Au, Mn_3O_4 and Au- Mn_3O_4 nanoparticles are employed to investigate the electrocatalytic activity toward the water oxidation reaction. A detailed procedure of the modification of the electrodes is described in ESI 3.[†]

Fig. 2 displays the cyclic voltammogram of 4-ATP/gold (red), Au NPs/4-ATP/gold (green), Mn_3O_4 NPs/4-ATP/gold (blue) and Au-Mn_3O_4 NCs/4-ATP/gold (black) electrodes in PBS at pH ~ 7.5. A specific amount (20 µg) of the catalysts was dissolved in 10 mL of water in each case. These dispersions were then employed for the loading of catalysts by dipping the electrodes and allowing them to equilibrate overnight under vacuum. It was observed that the Au-Mn_3O_4 nanocomposites (black) caused a shift of the oxidation potential in the less



Fig. 2 Cyclic voltammograms of water oxidation in the presence of 4-ATP/gold (red), Au NPs/4-ATP/gold (green), Mn_3O_4 NPs/4-ATP/gold (blue) and Au-Mn_3O_4 NCs/4-ATP/gold (black) electrodes in PBS at pH ~ 7.5.

positive potential and a large increase in the current height compared to that of the only Au (green) or Mn₃O₄ nanoparticles (blue). In spite of the ideal electrocatalytic process at its thermodynamic potential (for example, at 0.62 V vs. Ag/AgCl, pH \sim 7.0 and 1 atm O₂), the actual electrode reaction occurs at a more positive potential (i.e. overpotential) whose magnitude reflects the electrode kinetics of the solution. It is seen that Au NPs/4-ATP/gold, Mn₃O₄ NPs/4-ATP/gold, and Au-Mn₃O₄ NCs/4-ATP/gold electrodes display an anodic response at +1.13 $V (\eta \approx 0.51 \text{ V}, \text{pH} \sim 7.5), \pm 1.12 \text{ V} (\eta \approx 0.50 \text{ V}, \text{pH} \sim 7.5), \text{ and}$ +0.998 V ($\eta \approx 0.37$ V, pH \sim 7.5) vs. Ag/AgCl, respectively, in the potential window of 0.3-1.3 V, signifying water oxidation in 0.1 M PBS (pH \sim 7.5) and a corresponding cathodic peak at \sim + 0.5 V for $O_2 + 4H^+ + 4e \rightarrow 2H_2O$ at pH \sim 7.5, which is indicative of the reversibility of the process,³ whereas no such signal appears for 4-ATP/gold electrode. It was noted that the particles synthesized in the present experiment are stable for a couple of weeks without any significant agglomeration or precipitation of the particles. After the deposition of the particles at the electrodes, the catalytic activity of the particles was measured and the electrodes were rinsed in distilled water after the experiments. It was noted that the electrodes retained their catalytic activity even after 48 h of the loading of the catalysts. Therefore, it could be conceived that the particles do not suffer from dissolution or corrosion during the measurement of their electrocatalytic activity. However, assuming that the particles are nearly spherical and that the densities of Mn₃O₄ and Au-Mn₃O₄ are 4.86 and 12.09 g cm⁻³ (taking an average of the density of Au and Mn₃O₄) respectively, the number of Mn₃O₄ and Au-Mn₃O₄ particles is *ca.* 2.3×10^{12} and 3.8×10^{11} , respectively, and the corresponding surface areas are ca. 1625 \times 10^{12} and 477 \times 10^{12} nm², respectively.³⁷ Therefore, it is evident that Au-Mn₃O₄ composites are better electrocatalysts than Mn₃O₄ particles.

The turnover frequency (TOF) of the catalysts could be calculated using the equations: 38

$$I_{\rm cat} = nFAk_{\rm cat}\Gamma_{\rm cat} \tag{1}$$

$$\Gamma_{\rm cat} = Q/nFA \tag{2}$$

where, I_{cat} is the catalytic current density, n is the moles of electron transfer, F is the Faraday constant, A is the geometric surface area of the underlying anodic surface, k_{cat} is the rate constant of the electron transfer, Γ is the surface coverage in moles per square centimeter, and Q is the charge obtained by integrating the cathodic peak (= $\int i_f dt$, where i_f is the Faradaic current). However, the concept of turnover frequency is based on the number of active sites of the catalysts. In the above equations, the active sites have been replaced by surface area, which is an apparent value; therefore, the calculated TOFs provide only apparent values rather than the real TOFs of the catalysts. In addition, for the catalyst of Au-Mn₃O₄, the active sites for Au are different from those for Mn₃O₄ and, as a result, the calculated TOF is a hybrid or average of that of the constituent particles. From eqn (1) and (2), we can estimate the electroactive site turnover rate during O₂ evolution as:

$$k_{\rm cat} = I_{\rm cat}/Q \tag{3}$$

The catalytic current densities for Au, Mn_3O_4 , and Au- Mn_3O_4 are 3.8, 5.8 and 17.4 μ A, respectively, and the charges obtained by integrating the cathodic peak for Au, Mn_3O_4 , and Au- Mn_3O_4 is 2.4, 2.6, and 3.8 μ C, respectively. Therefore, the turnover frequencies corresponding to Au, Mn_3O_4 , and Au- Mn_3O_4 are *ca.* 1.6, 2.2, and 4.6 s⁻¹, respectively. The catalytic activity for water oxidation by Au- Mn_3O_4 nanocomposites is considered as not only combining the properties of both noble metal and metal oxides, but also the unique collective and synergistic effects of its component parts, compared to single component materials.^{27,39}

Variation of the gold particle size in the nanocomposites shows that the catalytic activity increases with a decrease in the particle size of the nanocomposites (ESI 4[†]); this study elicits the reproducible electrocatalytic activity of the nanocomposites. Therefore, it could be conceived that Au-Mn₃O₄ composites are more efficient catalysts for the water oxidation reaction than the individual Au or Mn₃O₄ nanoparticles. The enhanced catalytic activity of the Au-Mn₃O₄ catalysts could be attributed to the beneficial presence of higher amounts of oxidizable gold species and surface oxygen vacancies, resulting from the strong interaction between Au and the reactive surface of Mn₃O₄ nanoparticles.40 An increase in the 5d vacancy of Au increases the interaction of O_2 and Au, thereby, enhancing the catalytic activity of Au in the composites.41 However, interestingly, it was noted while the electrode was cycled to the cathodic potential after several scans through the catalytic anodic wave, an irreversible peak was observed at ca. -0.001 V to -0.2 V for different modified electrode systems, as presented in Fig. 3. This peak could be attributed to the O₂/O₂⁻ couple⁴² and indicates that O2 evolved from water oxidation on the electrode surface. A digital camera photograph showing the evolution of oxygen gas during water oxidation and the corresponding cyclic voltammogram of the Au-Mn₃O₄ NCs/4-ATP/gold electrodes in normal and N₂-saturated PBS at pH \sim 7.5 is shown in ESI 5.†



Fig. 3 Cyclic voltammograms for oxygen reduction in the presence of 4-ATP/gold (blue), Au NPs/4-ATP/gold (green), Mn₃O₄ NPs/4-ATP/gold (red) and Au–Mn₃O₄ NCs/ATP/gold (black) electrodes in PBS at pH ~ 7.5.

Under ambient conditions, the current height due to oxygen reduction is higher than in the N2-sparged solution, which authenticates that the origin of this peak originated from O₂ reduction. In a likewise manner to water oxidation, the higher cathodic peak current and lower reduction potential with the Au-Mn₃O₄ NCs (black) electrode rather than with the Mn₃O₄ NP (red) and Au NPs (green)- modified gold electrodes authenticate that Au-Mn₃O₄ composites are better ORR catalysts than the individual Au or Mn₃O₄ particles.³⁷ The Au-Mn₃O₄ particles upon exposure to oxygen form radical species on the surface of the catalysts. The ability to form such radical species in the presence of oxygen leads to enhanced performance of the Au-Mn₃O₄ composites in the oxygen reduction reaction.⁴³ It is also likely that oxygen can dissociate on the Au surface and spill over from Au to the oxygen vacancies in the oxide, which synergistically promotes the adsorption and dissociation of O2.44 Therefore, the different surface structural features clearly determine the strength of the metal-support interaction and, thus, the catalytic activity. The overpotentials for Au, Mn₃O₄, and Au-Mn₃O₄ are 514, 505, and 370 mV, respectively. When Au interacts with transition metal oxides to form a reduced oxide and an oxidized metal at the interface of the two materials,45,46 it dissolves at an oxidizing potential relevant to the water oxidation reaction.47 Therefore, the presence of Au during the water oxidation reaction could lead to an enhancement in the electrocatalytic activity of Mn₃O₄ particles.

The oxidation of water to dioxygen is one of the key reactions that need to be fully understood for water splitting devices. A reasonable mechanism for the water oxidation and oxygen reduction reactions on the nanocomposite surface could be enunciated as follows. From an electrochemical perspective, this reaction can be divided into two half reactions, namely, water oxidation and proton reduction.48 The formation of H2O2 from such species suggests that hydrolysis of an O-O bonded species proceeds more rapidly than the additional oxidation steps needed to form O2. In the presence of the catalysts, an O-O bonded intermediate undergoes rapid electron transfer in the material or to the electrode to enable the selective evolution of O₂. In the present experiment, upon the addition of gold to the metal oxide system, the gold-metal oxide perimeter interface acts as a site for activating the reactants. Therefore, it could be conceived that the very strong metal-support interactions after Au deposition⁴⁹ create a unique interface, which results in enhanced activity for the water oxidation and oxygen reduction reactions.

Cyclic voltammetry data of water oxidation and oxygen reduction in the presence of the nanomaterials are summarized in Table 1. The overpotential of different manganese-based systems as a function of experimental conditions has been discussed elsewhere.²⁷ A comparative account of the pH conditions of the experiments and the overpotential of the Au-Mn₃O₄ composite and some other electrocatalysts is presented in ESI 6.[†]

Fig. 4 illustrates the cyclic voltammograms at varying pHs of the PBS with the Au–Mn₃O₄ NCs/4-ATP/Au electrode. A slight change of current height was observed for the O₂/O₂⁻ couple at -0.18 V, but the anodic peak potential, as well as the peak current, varying with the change in pH of the solution (Fig. 4A). A plot of potential *vs.* pH and the current *vs.* the pH (Fig. 4B) show that the potential is optimum at pH ~ 7.5, and that the electrocatalytic activity for water oxidation increases with the increasing pH (5.5–9.5) of the solution, respectively.

In conclusion, the synthesis of stabiliser-free gold-manganese oxide nanocomposites by seed-mediated epitaxial growth, employing an environmentally benign water/*n*-heptane interface paves a facile strategy through surface attachment for combinatorial catalyst design. We have successfully overcome the key challenge in recent research of electrocatalytic water oxidation, surprisingly, at a nearly neutral pH (pH \sim 7.5) and a low overpotential of 370 mV, which is beyond the typical range of many homogeneous water oxidation catalysts (600–900 mV). As manganese oxides are available in various oxidation states and exhibit extensive biomimetic chemistry with oxygen, this result adds a new feather and illuminates ample opportunities in water oxidation electrocatalysis using a wide variety of inexpensive and earth-abundant materials. This facile and



Fig. 4 (A) Cyclic voltammograms of water oxidation in 0.1 M PBS at pH \sim 5.5 (blue), 6.5 (brown), 7.5 (green), 8.5 (red), and 9.5 (black) with Au–Mn₃O₄ modified electrodes; and (B) Profile showing the variation of current and potential as a function of pH.

Table 1 Cyclic voltammetry data of water oxidation and oxygen reduction in the presence of nanomaterials

Catalysts	Water oxidation potential ($E_{\text{ox, H}_2\text{O}}$), V	I_{pa}^{a} (µA)	1st oxygen reduction potential $(E_{\text{red, O}_2})$, V	$I_{\text{pc}(1)}{}^{a}(\mu A)$	2nd oxygen reduction potential (E_{red, O_2}), V	$I_{\text{pc}(2)}{}^{a}(\mu A)$
Au	1.134	-4.5	0.562	3.3	-0.189	2.9
Mn_3O_4	1.125	-6.8	0.515	6.3	-0.139	3.8
Au-Mn ₃ O ₄	0.998	-17.1	0.546	15.6	-0.001	11.6

^{*a*} Where, $I_{\rm pa}$ and $I_{\rm pc}$ denote the irreversible peak currents at the anode and cathode, respectively.

environmentally benign synthetic strategy for nanocomposites could be upscaled to the industrial level and may offer a promising future for renewable energy technologies.

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