2D MnO$_x$ composite catalysts inspired by natural OEC for efficient catalytic water oxidation

Lizhou Fan,† Biaobiao Zhang,†* Fan Zhang, Brian J.J. Timmer, Oleksandr Kravchenko, Licheng Sun*†

1 Department of Chemistry, KTH Royal Institute of Technology, 10044 Stockholm, Sweden

2 Division of Surface and Corrosion Science, KTH Royal Institute of Technology, Drottning Kristinas väg 51, SE-100 44 Stockholm, Sweden

3 State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), 116024 Dalian, China

4 Center of Artificial Photosynthesis for Solar Fuels, School of Science, Westlake University, 310024 Hangzhou, China

*Corresponding author Email: biaobiao@kth.se, lichengs@kth.se

†These authors contributed equally to this communication.
Abstract

Birnessite MnOₓ is a close inorganic model of natural oxygen-evolving complex (OEC) that has been widely investigated for catalytic water oxidation, yet its activity is limited by the poor active site exposure and sluggish charge transfer. Herein, starting from typical birnessite MnOₓ, we fabricated a hybrid of 2D manganese oxide nanosheets and pyridyl modified graphene (MnOₓ-NS/py-G) for electrocatalytic water oxidation. Benefiting from the synergy of structural exfoliation, graphene substrate and molecular pyridyl modification, the MnOₓ-NS/py-G exhibits abundant catalytically active sites exposure, fast electron transport, and promoted proton transfer at catalyst surface, which imitates the key features of natural OEC. Consequently, the MnOₓ-NS/py-G reached over 600 times higher activity compared to the typical birnessite MnOₓ. Inspired by nature, this work provides a well-designed and effective strategy to develop highly active manganese oxide-based water oxidation catalysts.
INTRODUCTION

Water oxidation reaction plays an essential role as ideal electron and proton source in artificial photosynthetic strategies, such as hydrogen production, CO$_2$ reduction, and N$_2$ reduction. Limited by the multiple proton/electron transfer and high energy barrier, water oxidation suffers from sluggish reaction kinetics and is the bottleneck for most renewable energy systems. Noble metal-based catalysts have been reported as efficient water oxidation catalysts with tolerable activity, yet their scarcity and high cost restrict the large-scale industrialization. One of the biggest challenges in this field is the exploration of cost-effective highly efficient catalysts based on cheap metals.$^{1-3}$

Natural photosynthesis provides a textbook for renewable energy harvesting, in which water oxidation is catalyzed by the oxygen-evolving complex (OEC), a Mn$_4$CaO$_5$ cluster, assisted by many functional cofactors for electron and proton transfer (Scheme 1a)$^{4-6}$ In addition, manganese possesses a series of advantages, i.e. high natural abundance, low-cost, non-toxicity, and rich redox chemistry for bearing charge accumulation, inspiring the investigation of manganese oxides-based water oxidation catalysts.$^{7-11}$ One of the most studied manganese-oxide catalysts is the layered birnessite-type manganese oxide (birnessite MnO$_x$), which possesses similar structure properties to Mn$_4$CaO$_5$ cluster in PSII, e.g., the cubane-like local construction, the mixing of Mn$^{3+}$ and Mn$^{4+}$ oxidation states (Scheme 1b). However, crystalline birnessite MnO$_x$ generally shows moderate water oxidation activity, which is much lower compared with other transition metal-based catalysts. Early studies suggested that the activity of birnessite MnO$_x$ can be influenced by its interlayer ions, interlayer spacing, surface modification and crystallinity.$^{12-14}$ Recently, our group fabricated a “c-disordered” birnessite (MnO$_x$-300) as an efficient water oxidation catalyst.$^{15-16}$ Detailed investigation revealed that the partially opened layered structure can facilitate the active site exposure and electron transfer process, which promotes the formation of high-valent Mn$^{VII}$-oxo active species, improving the activity.$^{17}$ These enlightenments suggested that generally applicable strategies to effectively access abundant active sites and fast charge transport need to be explored for the improvement of OER activities of birnessite-type catalysts.
To acquire sufficient exposure of Mn cubic units, as the Mn$_4$CaO$_5$ cluster in PSII, we turned to the structural exfoliation approach (Scheme 1). Two-dimensional (2D) materials have attracted intense attention in recent years owing to several unique properties. On one hand, the high aspect ratio in their dimensions can dramatically promote the exposure of coordinatively unsaturated “edge and corner sites” and defects, which have been identified as the highly reactive sites in the δ-MnO$_2$ catalyst. On the other hand, the high surface energy and unique electronic structure make it feasible to achieve rational modification at the 2D material surface, which can specifically modulate the catalytic kinetics and influence the activity. Inspired by the OEC’s well-organized electron and proton transfer channels (Scheme 1a), a combination of exfoliated 2D manganese oxide nanosheets with graphene is further designed to establish a fast electron transportation pathway, and the graphene was in advance modified with a pyridyl molecule to provide a good proton transfer relay for water oxidation by manganese oxides (Scheme 1c), synergistically improving the water oxidation activity.

We therefore in this work developed composite water-oxidation catalysts of ultrathin 2D
manganese oxide nanosheets and pyridyl modified graphene (denoted as MnO$_x$-NS/py-G). By the synergy between structural exfoliation and molecular modification, the MnO$_x$-NS/py-G achieved 600-fold enhanced catalytic activity compared to bulk birnessite MnO$_x$. Further in-depth studies indicate that the activity improvement results from the sufficient exposure of catalytically active sites, fast electron transport and efficient proton transfer relay, which arise from adopting the material design inspired by the natural OEC.

RESULTS & DISCUSSIONS

Preparation and Characterization

General synthetic procedures of 2D MnO$_x$-nanosheet (MnO$_x$-NS) and MnO$_x$-NS/py-G are demonstrated in Scheme 1c. A colloidal solution of 2D MnO$_x$-NS was first obtained from the exfoliation of bulk birnessite MnO$_x$ by an ion-exchange approach, which is shown in the inset of Fig. 1a. Typical Tyndall effect is presented on the brown and transparent solution under laser beam illumination, demonstrating its well dispersion and colloidal property. Fig. 1a shows the powder X-ray diffraction (XRD) spectrum of birnessite MnO$_x$ and MnO$_x$-NS. In contrast to the XRD pattern of birnessite MnO$_x$ with typical sharp peaks, the XRD spectrum of MnO$_x$-NS presents no distinct diffraction peak. The disappearance of XRD peaks, e.g., the peak at 2θ =12.4° that is related to the layered structure with interlayer spacing of 0.7 nm, illustrates the delamination of long-range ordered layered structure to individual irregularly oriented nanosheets after exfoliation.
Transmission electron microscopy (TEM), ultraviolet-visible (UV-Vis) spectroscopy, and atomic force microscopy (AFM) were then conducted to characterize the obtained MnO$_x$-NS. The TEM image of MnO$_x$-NS displays a clear single layer nanosheet morphology (Fig. 1b). The selected area electron diffraction (SAED) pattern of MnO$_x$-NS exhibits hexagonally arranged diffraction spots (inset of Fig. 1b). All these results are in sharp contrast to birnessite MnO$_x$, which exhibits a multilayered morphology and polycrystal-like SAED image with diffraction rings, showing the
exfoliation of multi-layered structure to monolayer nanosheets (Fig. S3).\textsuperscript{26} Notably, both the SAED results of birnessite MnO\textsubscript{x} and MnO\textsubscript{x}-NS present hexagonal reciprocal lattices, indicating that the MnO\textsubscript{x}-NS retains similar crystalline structure as the birnessite MnO\textsubscript{x} crystal. The HRTEM image of MnO\textsubscript{x}-NS presents lattice fringe with interlayer spacing of 0.24 nm, which can be assigned to the \{100\} plane of $\delta$-MnO\textsubscript{x}.\textsuperscript{27-28} The UV-Vis spectrum of MnO\textsubscript{x}-NS shows a broad absorption peak around 400 nm, which can be attributed to the d-d transition of Mn ions in MnO\textsubscript{6} octahedra (Fig. 1c).\textsuperscript{24,26} At last, the successful exfoliation of birnessite MnO\textsubscript{x} to 2D MnO\textsubscript{x} monolayer nanosheets was evidently confirmed by AFM imaging of MnO\textsubscript{x}-NS (Fig. 1d and e). A thickness of 0.7 nm was determined for the MnO\textsubscript{x}-NS, which is close to the thickness of the MnO\textsubscript{x} monolayer.\textsuperscript{24,26} An apparent change in the MnO\textsubscript{x}-NS compared to the birnessite MnO\textsubscript{x} is the increased ratio of Mn\textsuperscript{3+}/Mn\textsuperscript{4+} oxidation states, which was determined by X-ray photoelectron spectroscopy (XPS). Birnessite MnO\textsubscript{x} shows Mn peaks at 643.0, 642.1 eV and 640.7 eV, which can be assigned to Mn\textsuperscript{4+}, Mn\textsuperscript{3+}, and a minimal amount of Mn\textsuperscript{2+} respectively (Fig. S4a).\textsuperscript{29-32} Based on the peak integration, its Mn\textsuperscript{3+}/Mn\textsuperscript{4+} content ratio was calculated to be 0.44. Similar Mn 2p XPS peaks were presented for MnO\textsubscript{x}-NS. However, the ratio of Mn\textsuperscript{3+}/Mn\textsuperscript{4+} oxidation states increased to 0.67, which is much larger than the 0.44 observed for birnessite MnO\textsubscript{x}. Moreover, the ratio of Mn-OH (531.0 eV)/Mn-O-Mn (529.7 eV) is calculated to be 0.46 for MnO\textsubscript{x}-NS, much higher than 0.34 of birnessite MnO\textsubscript{x} (Fig. S4b).\textsuperscript{29-31} These XPS results demonstrate that abundant Mn\textsuperscript{3+} species and coordinatively unsaturated sites are exposed on MnO\textsubscript{x}-NS upon 3D $\rightarrow$ 2D structural exfoliation. Then, the single layer MnO\textsubscript{x}-NS were assembled with graphene and pyridyl modified graphene (py-G), to give the MnO\textsubscript{x}-NS/G and MnO\textsubscript{x}-NS/py-G samples (Scheme. 1c, see supporting information for details). The Raman spectrum of MnO\textsubscript{x}-NS/G and MnO\textsubscript{x}-NS/py-G are presented in Fig. 1f. Both the samples show additional scattering bands at 1360 and 1598 cm\textsuperscript{-1} compared with MnO\textsubscript{x}-NS, which are the typical Raman signals of graphene.\textsuperscript{33-34} The TEM image (Fig. 1g) and energy dispersive spectroscopy (EDS) mapping (Fig. 1h) of MnO\textsubscript{x}-NS/py-G display randomly distributed MnO\textsubscript{x}-NS on the surface of graphene, without apparent aggregation.
Nitrogen fluorescence signal was evidently presented in the EDS mapping of MnO$_x$-NS/py-G, confirming the homogeneous modification by the pyridyl molecule. The presence of the pyridyl molecule in MnO$_x$-NS/py-G can be further depicted by the electrochemical cyclic voltammetry (CV) performance. A broad reduction wave was distinctly presented between -1.0 and -1.35 V (vs Ag/AgCl) for MnO$_x$-NS/py-G, which is the typical redox peak of pyridine moiety (Fig. S6). Overall, these above characterizations thoroughly demonstrate the successful assembly of the MnO$_x$-NS/py-G composite.

**Electrocatalytic water oxidation**

Electrocatalytic oxygen evolution reaction (OER) performances of birnessite MnO$_x$, MnO$_x$-NS, MnO$_x$-NS/G and MnO$_x$-NS/py-G were evaluated by loading on glass carbon (GC) electrodes under alkaline conditions (1 M KOH). Birnessite MnO$_x$ sample shows negligible activity within a wide potential range, which is consistent with the generally low OER activity characteristics of birnessite (Fig. 2a). The MnO$_x$-NS displays significantly enhanced OER activity, which provides approximately 30 times higher current densities compared with that of birnessite MnO$_x$ (Fig. 2a). Notably, after assembling with graphene, the catalytic current density of the MnO$_x$-NS/G increases a further ten-fold compared to MnO$_x$-NS (Fig. 2b). Then, with the effect of the pyridyl molecule modification, two times improvement in OER performance was further achieved for the final MnO$_x$-NS/py-G catalyst compared with MnO$_x$-NS/G. Added up, in contrast to the initial birnessite MnO$_x$, the MnO$_x$-NS/py-G eventually displays 600 times higher OER activity due to structural exfoliation and molecular modification, being ranked as a highly active manganese-based water oxidation catalyst (Fig. S7).
Figure 2 a) Polarization curves of birnessite MnO$_x$ and MnO$_x$-NS. b) Polarization curves of MnO$_x$-NS, MnO$_x$-NS/G and MnO$_x$-NS/py-G. c) Nyquist diagrams of birnessite MnO$_x$, MnO$_x$-NS, MnO$_x$-NS/G and MnO$_x$-NS/py-G. d) Tafel slope of MnO$_x$-NS, MnO$_x$-NS/G and MnO$_x$-NS/py-G. e) Chronoamperometry curve of MnO$_x$-NS/G and MnO$_x$-NS/py-G under 450 mV overpotential. f) The experimental and theoretical O$_2$ evolution amount by electrolysis of MnO$_x$-NS/py-G for OER under 400 mV overpotential. Evaluated by loading the catalysts on glass carbon (GC) electrodes under alkaline conditions (1 M KOH).

The improved water oxidation catalysis can be further reflected by the electrochemical impedance spectroscopy (EIS) measurements. The MnO$_x$-NS/py-G exhibits charge transfer resistance ($R_{ct}$) of 41.09 Ω, which is 20 times lower compared with 584.8 Ω of the initial birnessite MnO$_x$ (Fig. 2c). A low Tafel slope of 86 mV/dec was determined for the MnO$_x$-NS/py-G catalyst (Fig. 2d). Chronoamperometric curve was performed on the MnO$_x$-NS/py-G catalyst to assess the catalytic stability. A stable current density of 21 mA/cm$^2$ was maintained during 10 h electrolysis under 450 mV overpotential, indicating the excellent electrocatalytic durability of MnO$_x$-NS/py-G (Fig. 2e). In a separate experiment, the OER Faradaic efficiency was determined to be 98% for MnO$_x$ NS/py-G under 400 mV overpotential.
electrolysis, verifying that a vast majority of charges was contributed to water oxidation (Fig. 2f).

Overall, following our design strategy in Scheme 1c, the OER activities of the birnessite MnO$_x$, MnO$_x$-NS, MnO$_x$-NS/G and MnO$_x$-NS/py-G catalysts have been successively advanced owing to the directed improvement in each sample, achieving the remarkable OER performance for the final MnO$_x$-NS/py-G. To get insightful understanding on the activity enhancement from the starting inactive birnessite MnO$_x$ to the final active MnO$_x$-NS/py-G, we then thoroughly examined the specific effects of structural exfoliation, graphene substrate assembly, and pyridyl molecule modification on electrocatalytic water oxidation.

**Effects of the structural exfoliation**

From birnessite MnO$_x$ to MnO$_x$-NS, the activity has been increased by 30 times, indicating the significant effects of the structural exfoliation. This dramatic improvement may be induced by two possible ways: i) enlarged electrochemically active surface area (ECSA) caused by morphology change; ii) increased numbers of catalytic sites due to 3D → 2D structural changes.

To identify effects of the structural exfoliation, we first estimated the ECSA of birnessite MnO$_x$ and MnO$_x$-NS from their electrochemical double layer capacitance (C$_{dl}$, Fig. 3a and Fig. S8). The linear slope of MnO$_x$-NS was calculated to be 0.045 mF/cm$^2$, which is only 18% higher compared with 0.038 mF/cm$^2$ of birnessite MnO$_x$. The similar ECSA of birnessite MnO$_x$ and MnO$_x$-NS indicates that the layered structure of birnessite MnO$_x$ is already widely accessible for electrochemical charging, which has also been reported on layer double hydroxide materials.$^{37}$ Obviously, this slight increase in ECSA cannot account for the 30 times increase in activity upon exfoliation of birnessite MnO$_x$ to MnO$_x$-NS.

Mn$^{3+}$ species have been commonly recognized as an indicator of active sites for Mn-based water oxidation catalysts.$^{38-39}$ To investigate the influence of exfoliation on active sites, pyrophosphate (PP) was introduced to the solution of birnessite MnO$_x$ and MnO$_x$-NS as a Mn$^{3+}$ trapping agent (Fig. 3b)$^{16,39-40}$ Depicted by the UV-Vis absorption, the MnO$_x$-NS presents much more Mn$^{3+}$ than birnessite MnO$_x$, which is consistent with the XPS results, demonstrating the
abundant Mn³⁺ species exposure upon exfoliation. These Mn³⁺ species can positively involve in water oxidation as highly reactive sites, improving the catalytic activity.

Figure 3 a) The ECSA measurement: ΔJ (Jₐ − Jₐ) from the CV curves of birnessite MnOₓ and MnOₓ-NS plotted against scan rates. b) UV–Vis absorption spectra of a 20 mM sodium pyrophosphate solution after dipping of birnessite MnOₓ and MnOₓ-NS. c) Comparison of the required overpotential for 0.5 mA/cm² current density on MnOₓ-NS with particle size of 45, 90, and 125 nm. d) CV curves of MnOₓ-NS and MnOₓ-NS/G in 0.1 M KCl electrolyte containing 10 mM Fe(CN)₆³⁻/⁴⁻ ions. e) LSV curves of birnessite MnOₓ, birnessite MnOₓ/G and birnessite MnOₓ/py-G. f) Comparison of I(MnOₓ-NS/py-G)/I(MnOₓ-NS/G) under pH 14, pH 6 and pH 4 conditions.

Two aspects can result in the effective increase of catalytically active sites by exfoliation. On one hand, the full structural exfoliation can spontaneously promote the active site exposure at the surface of the monolayer nanosheets. To verify this, Na⁺ was introduced to MnOₓ-NS colloidal suspension to promote the self-reassembly of MnOₓ-NS, regenerating layered birnessite MnOₓ.²⁶ The XRD pattern of the re-assembled sample presents typical diffraction peak of layered
structure with interlayer space of 0.73 nm, indicating the reformation of the layered bulk birnessite MnO\textsubscript{x} (Fig. S9a). The electrocatalytic performance of this reformed birnessite MnO\textsubscript{x} dramatically decreased compared with MnO\textsubscript{x}-NS (Fig. S9b). The remarkable activity difference between MnO\textsubscript{x}-NS and birnessite MnO\textsubscript{x} as well as our previous active “c-disordered” δ-MnO\textsubscript{x} demonstrate the importance of surface active site exposure for efficient electrocatalytic water oxidation on δ-MnO\textsubscript{x} catalyst.

On the other hand, based on the TEM images, the average particle size of MnO\textsubscript{x}-NS was estimated to be around 90 nm (Fig. S10), which is much smaller compared with the 240 nm of birnessite MnO\textsubscript{x}. Without the well-ordered layered structure, the MnO\textsubscript{x} monolayer collapse and breaks, leading to the decrease in particle size. The formed smaller nanosheets can promote the exposure of coordinatively unsaturated edge- and corner- sites, which are believed to be involved in water oxidation as highly reactive catalytic sites.\textsuperscript{37, 41} To further verify, MnO\textsubscript{x}-NS with different lateral sizes were separated by controlled centrifugation, denoted as MnO\textsubscript{x}-45 and MnO\textsubscript{x}-125 (Fig. S11). A close relationship is presented between the lateral size and OER activity: where the MnO\textsubscript{x}-45 with smaller particle size shows higher activity than MnO\textsubscript{x}-90; whereas the MnO\textsubscript{x}-125 with larger particle size displays lower activity compared with MnO\textsubscript{x}-90 (Fig. 3c). These results clearly demonstrate the OER activity enhancement with particle size decrement. By the exfoliation process, plenty of coordinated unsaturated edge sites were generated on MnO\textsubscript{x}-NS (Fig. S12), which are much easier to be oxidized to essential high valent intermediate states for water oxidation.\textsuperscript{15-16, 40, 42-45}

**Effects of loading on graphene substrate**

The MnO\textsubscript{x}-NS/G shows 10 times higher activity compared with MnO\textsubscript{x}-NS, indicating the promoting effects of graphene. On one side, the graphene serves as a loading substrate to promote the uniform distribution of MnO\textsubscript{x}-NS with less stacking, which has been displayed in the XRD and TEM images of MnO\textsubscript{x}-NS/G and MnO\textsubscript{x}-NS/py-G (Fig. 1g and S14). More importantly, the graphene substrate with excellent charge transportation capacity can facilitate electron transfer during the OER process.\textsuperscript{46-47} To probe the enhancement in electron transfer by graphene, CV was performed in K\textsubscript{4}Fe(CN)\textsubscript{6} electrolyte (10 mM Fe(CN)\textsubscript{6}\textsuperscript{4-}/Fe(CN)\textsubscript{6}\textsuperscript{3-}) with
MnO₅-NS and MnO₅-NS/G covered GC electrode as working electrode. In contrast to the broad redox peak of Fe²⁺/Fe³⁺ for MnO₅-NS/GC, a sharp Fe²⁺/Fe³⁺ peak was observed in the CV curve measured with MnO₅-NS/G/GC (Fig. 3d). The promoted Fe²⁺/Fe³⁺ redox couple on MnO₅-NS/G/GC illustrates that the combination of MnO₅-NS with graphene effectively solves the slow charge transfer problems. The acceleration of electron transfer can also be demonstrated by the lowered Tafel slopes after graphene introduction (Fig. 2d). The Tafel slopes were calculated to be 89 mV/dec and 86 mV/dec for MnO₅-NS/G and MnO₅-NS/py-G, which are much smaller than the 134 mV/dec of pristine MnO₅-NS, demonstrating the improvement in catalytic kinetics.

Notably, no obvious performance enhancement was observed when the bulk birnessite MnO₅ was assembled with graphene or py-graphene, indicating that the promoting effect of graphene requires optimal assembly between graphene and exfoliated 2D nanosheet structure (Fig. 3e). These results demonstrate that the 10-fold enhanced OER activity of MnO₅-NS/G compared with MnO₅-NS arises from the synergy between graphene loading and 3D → 2D structural exfoliation.

**Effects of molecular pyridyl modification**

It has been reported that the introduction of pyridine into electrolyte can prominently improve the catalytic performance of MnO₅ electrocatalysts and α-Fe₂O₃ photoanodes. In these systems, the pyridine can work as a proton transfer relay, which facilitates the proton-coupled electron transfer in the catalytic process. For the MnO₅-NS/py-G, we directly modified the graphene surface, i.e., the catalytic environment, with a pyridyl molecule to accelerate proton transfer during water oxidation. With this modification, the MnO₅-NS loading on graphene afforded a two-fold increase in activity. A pH-dependence of OER activity was established to evaluate the proton transfer property in the catalytic process. Fig. 3f shows the OER activities of the MnO₅-NS/G and MnO₅ NS/py-G at pH 14, pH 6 and pH 4 electrolyte. In contrast to the significantly enhanced performance under pH 14 and pH 6 conditions, the MnO₅-NS/py-G catalyst showed negligible superiority in OER compared with MnO₅-NS/G catalyst under pH 4 conditions (see the I(py-G)/I(G) ratio in fig. 3f). The loss of activity enhancement of
MnO$_x$-NS/py-G under pH 4 can be attributed to the inhibited proton transfer relay effect of the pyridine group, which possesses a pKa value around 5 and is mostly protonated at lower pH. This pH-dependence evidently illustrates the proton transfer relay effect of the modifying pyridyl molecule.$^{49}$

The above thorough analyses elucidate that the origin of the dramatically enhanced catalytic activity of MnO$_x$-NS/py-G is a combined effect of 3D $\rightarrow$ 2D structural exfoliation, graphene substrate and pyridyl molecule modification. The 2D structure of MnO$_x$-NS achieved by exfoliation significantly increased the number of catalytically active sites in the MnO$_x$-NS/py-G catalyst. A synergy between the 2D MnO$_x$-NS and the graphene substrate provided an efficient electron transfer channel. And the modified proton relay pyridyl molecule promoted proton transfer during water oxidation, accelerating the proton coupled electron transfer (PCET) process.

CONCLUSIONS

In summary, starting from a typical birnessite MnO$_x$, we obtained a composite MnO$_x$-NS/py-G by a series of well-designed modifications, including 3D $\rightarrow$ 2D structural exfoliation, graphene assembling, and molecular modification. Resulting from abundant catalytically active site exposure, facilitated electron transport, and efficient proton transfer, the MnO$_x$-NS/py-G shows remarkably enhanced electrocatalytic water oxidation activity. This work indicates that, to make manganese oxides efficient for electrocatalytic water oxidation, it requires an overall consideration of the full exposure of catalytically active sites and engineered environments for fast electron/proton shuttle, as the team working of OEC in PSII.

CONFLICTS OF INTEREST

The authors declare no competing interest.

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REFERENCE


Graphical Abstract

Natural OEC in PSII

MnO$_x$-NS/py-G

Abundant catalytic sites  Fast electron transport  Mediated proton transfer