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BIOFUEL CELLS

Powered by blood

> The nano-engineered red blood cells maintain the original properties of natural red blood cells … but show greatly enhanced electrocatalytic oxygen reduction

Biofuel cells use enzymes as catalysts to convert the chemical energy of natural compounds, such as sugars, into electrical energy. Enzyme biofuel cells can serve as wireless self-powered energy supplies for implantable devices, for example, glucose sensors or cardiac pacemakers. However, the use of enzymes as catalysts in these settings is challenging owing to low catalytic performance, enzyme inactivity and instability in the body. Now, reporting in *Angewandte Chemie International Edition*, Jun Lu, Lin Yang, Zhengyu Bai and colleagues engineered a non-enzymatic cathode catalyst by embedding haemoglobin-binding hydroxylapatite nanodots in red blood cells.

Like traditional fuel cells, biofuel cells use catalysts at oppositely charged electrodes to generate power through an electrochemical reaction. For example, at the anode, oxidation of glucose to gluconolactone, catalysed by glucose oxidase, leads to the release of electrons, which enables the catalytic reduction of oxygen at the cathode. In red blood cells, oxygen reduction reactions are catalysed by the Fe-containing protein haemoglobin, which binds oxygen to transport it from the lungs to the different tissues. Although less kinetically favourable, oxygen binding to haemoglobin can also cause the oxidation of Fe^{2+} to Fe^{3+} in the active centre of the protein, which in turn leads to the reduction of oxygen.

To leverage the electrocatalytic oxygen reduction capability of red blood cells and to increase the reaction rate, the researchers created hydroxylapatite nanodots inside the cells by applying a simple two-step ion permeation process. Incubating the cells first with Ca^{2+} and then with PO_4^{3-} leads to the formation of haemoglobin-bound $Ca_{10}(PO_4)_6(OH)_2$ nanodots with diameters of ~3 nm. "The nano-engineered red blood cells maintain the original properties of natural red blood cells in terms of morphology and permeability, but show greatly enhanced electrocatalytic oxygen reduction through the interaction of the OH group in the hydroxylapatite nanodots with haemoglobin," explains Lu. The strong interaction of Fe and oxygen with the adsorbed OH weakens the O–O bond and thus benefits oxygen reduction.

Lu and colleagues employed the nano-engineered red blood cells as a cathode for a biofuel cell, in combination with a glucose anode. By measuring the maximum current density in a physiologically relevant glucose solution, the performance of the biofuel cell equipped with the nano-engineered red blood cells was shown to be ~1.5 times better than that of a device with native red blood cells.

However, the increase in electrocatalytic activity and thus in electron transport can have adverse effects on the red blood cell membrane. "As a next step, we want to implement suitable ions or electron transport mediators that mediate electron transport to the cathode," comments Lu. "The nano-engineered cells could also be attached to the electrode surface and oriented to improve electron transport efficiency."

The researchers envision the biocompatible nano-engineered red blood cells to be used not only for biosensors and biological monitoring, but also as carriers for drug delivery and for the adsorption of heavy metals in vivo.

Christine-Maria Horejs

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