

## ON-LINE SUPPORTING INFORMATION

### **Electro-enzymatic viologen-mediated substrate reduction using pentaerythritol tetranitrate reductase and a parallel segmented fluid flow system**

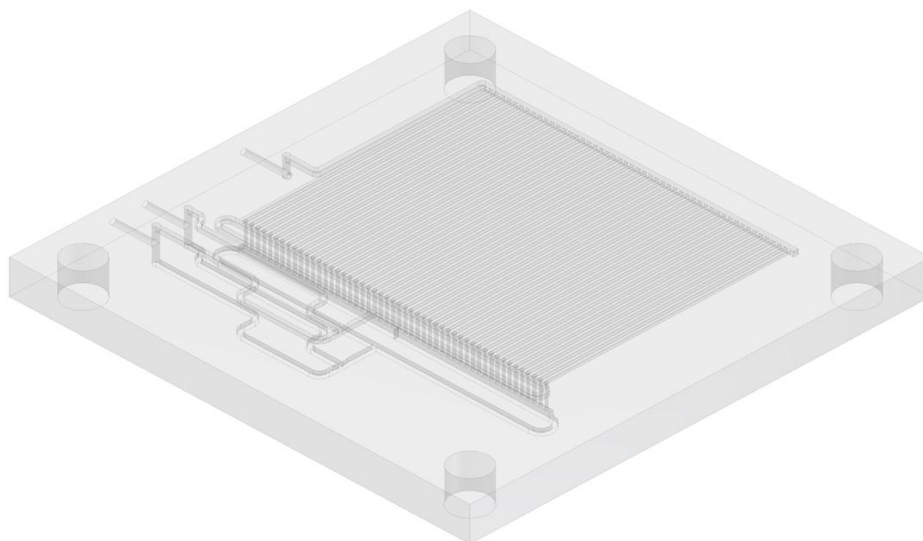
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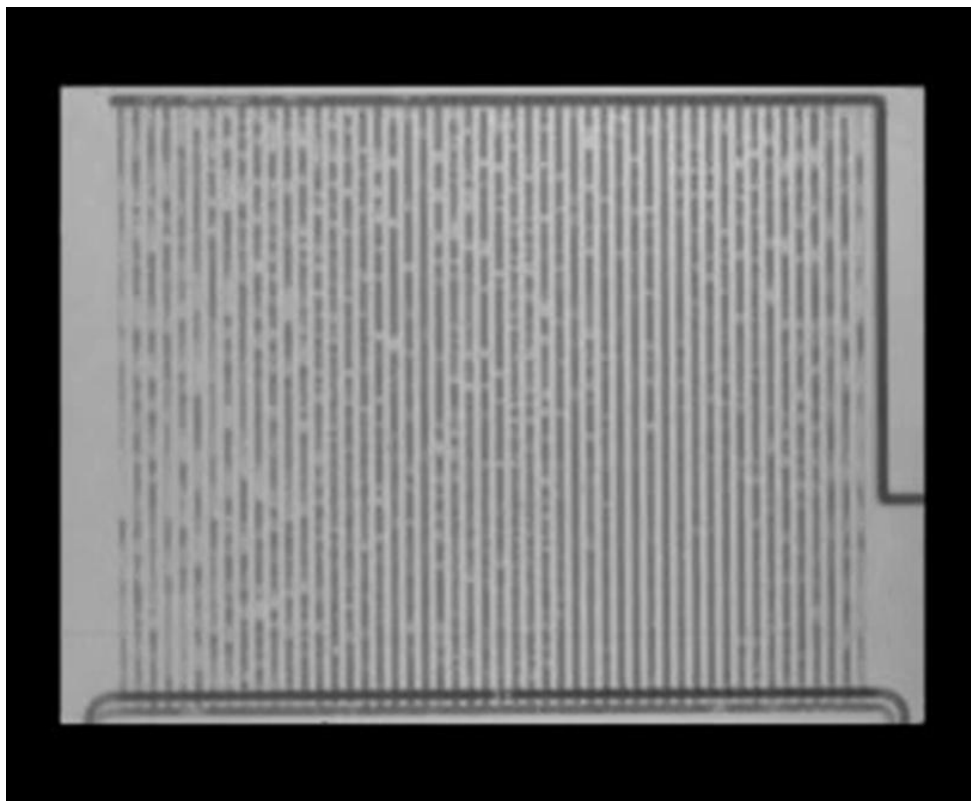
- 1. CAD Design of fluidic device
- 2. Video of 50 channel chip in operation
- 3. Enzyme and mediator dependence
- 4. Bioelectrocatalysis using TOYE

## 1. CAD design of fluidics device



**Supporting Information Figure S1:** CAD design of the fluidic chip used in this study. For increased efficiency, both sides of the device have been machined to perform the initial droplet breakup (see main text for details) and re-joined into the main channel matrix via through holes.

## 2. Video of 50 channel chip in operation

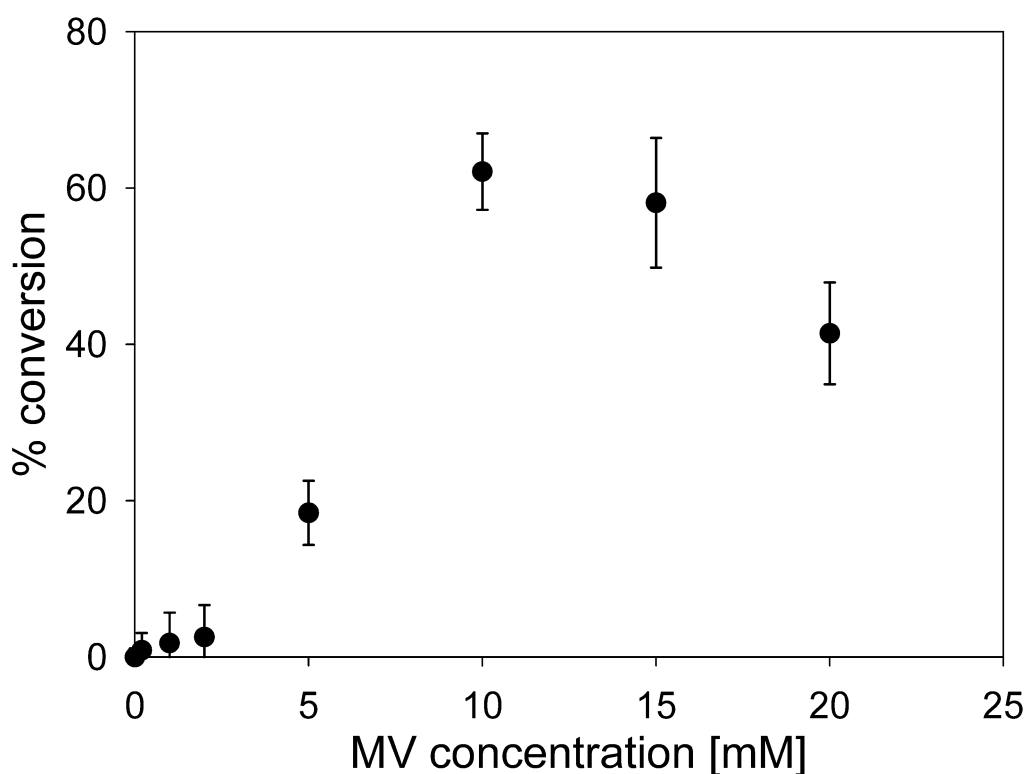


**Supporting Information Figure S2:**

Figure.S2 : Parallelised slug flow pattern in 50 channels. (Video)

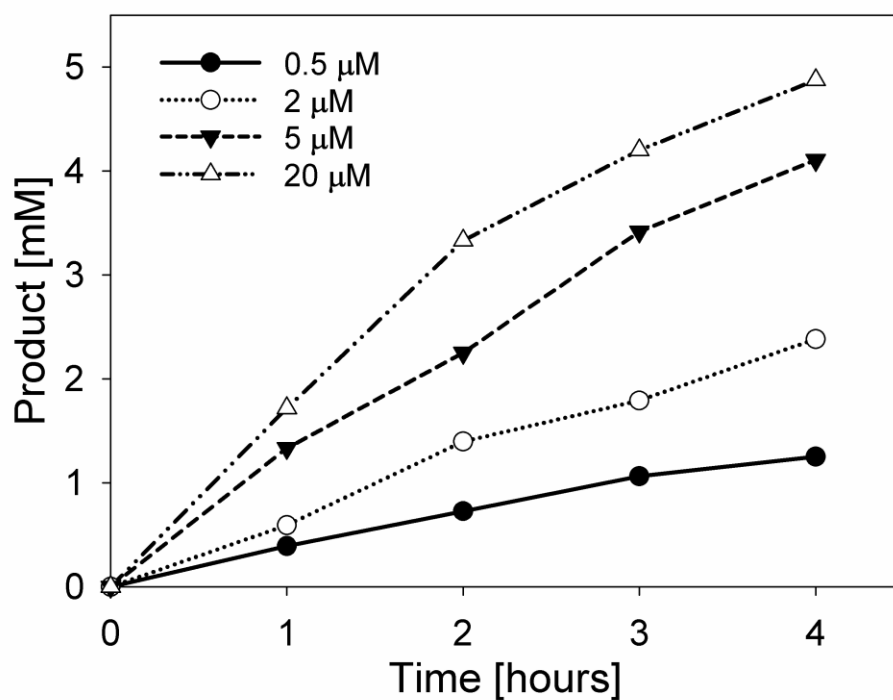
**Supporting Information video 1.** (parallel biphasic flow.avi):

### 3. Enzyme and mediator dependence



**Supporting Information Figure S3:**

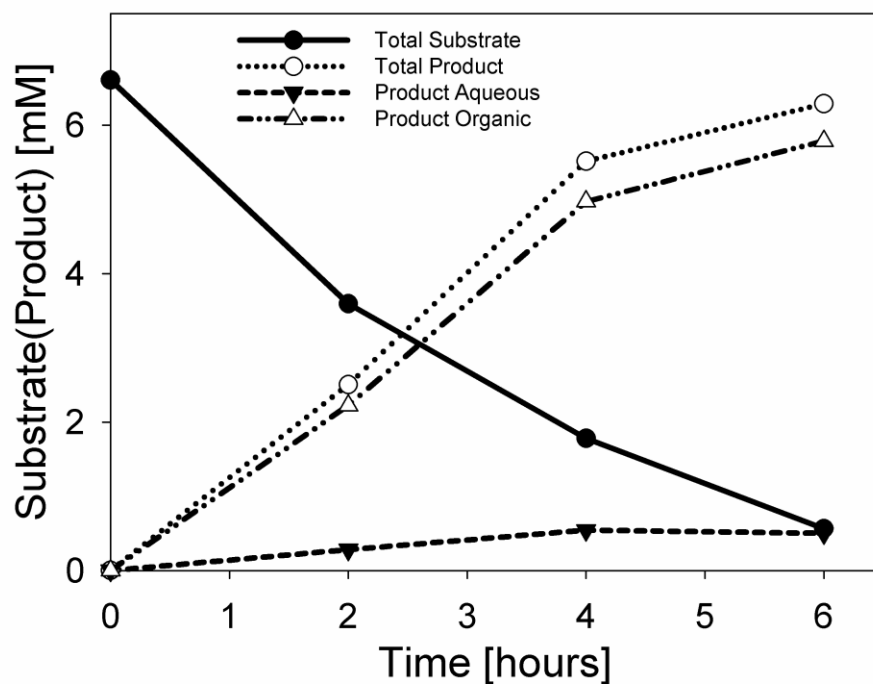
Methyl viologen concentration dependence of the bioelectrocatalytic transformation of 2-cyclohexen-1-one by PETNR. The aqueous phase (10 mL) contained 50 mM  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ , pH 7.0, 50mM potassium bromide, 10 mM methyl viologen, and 2  $\mu\text{M}$  PETNR. The organic phase (5 mL octanol) contained 5 mM 2-cyclohexen-1-one. Samples were taken from each phase after two hours and the % conversion at each concentration is plotted.



**Supporting Information Figure S4:**

PETNR concentration dependence of the bioelectrocatalytic transformation of 2-cyclohexen-1-one. Samples were taken from the organic and aqueous phases every hour and the total product plotted. The 10 mL aqueous phase contained 50 mM  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ , pH 7.0, 50mM potassium bromide, 10 mM methyl viologen, and 2 μM PETNR. The organic phase was 5 mL octanol containing 5 mM 2-cyclohexen-1-one.

#### 4. Bioelectrocatalysis using TOYE



**Supporting Information Figure S5:**

Bioelectrocatalytic transformation of 2-cyclohexen-1-one by TOYE. Substrate consumption and product formation in the aqueous and organic phases are plotted as a function of time. The 10 mL aqueous phase contained 50 mM  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ , pH 7.0, 50mM potassium bromide, 10 mM methyl viologen, and 2  $\mu\text{M}$  TOYE. The organic phase was 5 mL octanol containing 6.5 mM 2-cyclohexen-1-one