

## Electronic Supplementary Information

### Instrumentation

TEM analysis was conducted using a Jeol 120EX TEM, TGA measurement was conducted using a SDT Q600 Simultaneous TGA/DSC, TA instruments, with a heating rate of 10 °C/min under Air. Powder XRD was measured using a Bruker D8 diffractometer. Hydrodynamic diameters were determined by DLS measurement using a Malvern Zetasizer Nano-ZS.

### Experimental

*Preparation of Sephadex-Co<sub>3</sub>O<sub>4</sub>:* 3g of Sephadex G-50 (fine) beads were hydrated with 60 mL of water for use as a biopolymer substrate. 2.0 g of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was added with stirring. After standing for 5 min ammonia solution was added until the stirred mixture reached pH11. The mixture was then microwaved until the mixture reached 80°C and then flask cooled in ice water RT to with neutralization to pH7 with dilute HNO<sub>3</sub>. The flask was sonicated for 1min and the contents were then filtered using a 90 micron mesh with thorough washing with DI water and finally rinsed with ethanol. The retained material dried to give free flowing powders of brown coloured Sephadex beads.

*Sephadex-Fe<sub>3</sub>O<sub>4</sub>* was prepared as described above with modifications. 0.27g of FeCl<sub>2</sub>.4H<sub>2</sub>O and 1.42g of FeCl<sub>3</sub>.6H<sub>2</sub>O were added and 30ml of 1M NaOH added with microwaving followed by neutralization to pH 7 with dilute HCl. The retained material consisted purely of dark orange-brown coloured Sephadex beads.

*Sephadex-Mn<sub>3</sub>O<sub>4</sub>* was prepared as with the Sephadex-Co<sub>3</sub>O<sub>4</sub> with modifications. 1.73g of Mn(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O were used followed by ammonia treatment and microwaving followed by neutralization to pH 8.5 with dilute HNO<sub>3</sub>. The retained material consisted purely of light brown coloured Sephadex beads.

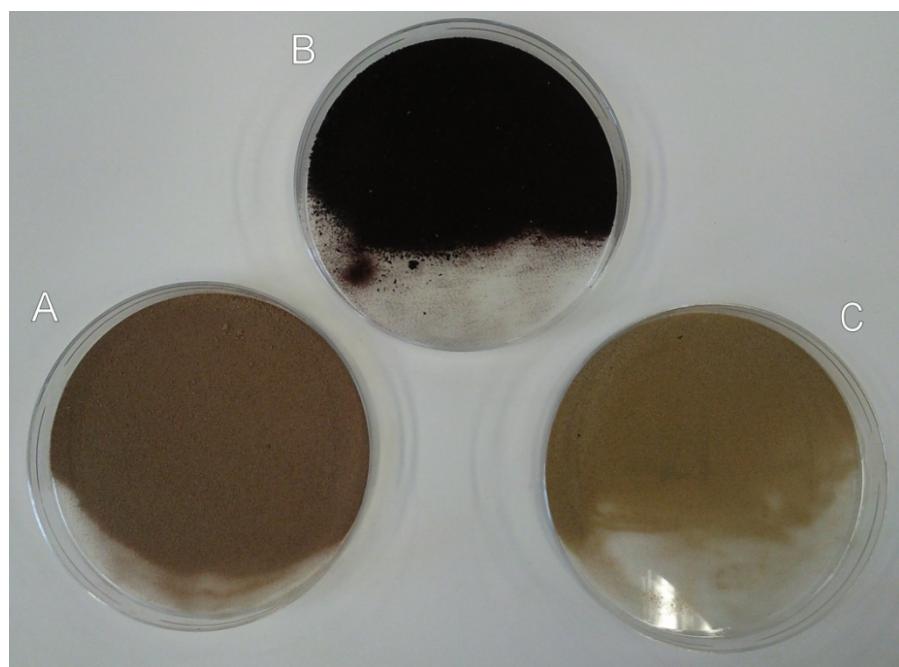
*Dextranase treatment of Sephadex-metal oxides:* 0.5 g of dried Sephadex-metal oxide was suspended in 30ml of deionized water and warmed in a water bath to 34°C, the pH of the solution was adjusted to 5.8 with dilute acetic acid. 250 units of freeze dried

Dextranase *Penicillium* sp. (1,6- $\alpha$ -D-glucan 6-glucanohydrolase, Sigma-Aldrich) was then added and the mixture held at 34°C with gentle stirring for 36 hours. After this time the mixture was centrifuged and the supernatant removed, a brown sedimented pellet was obtained that was washed and centrifuged several times in de-ionized water. The recovered nanoparticle coatings obtained were then used for subsequent TEM and XRD analysis.

*Photocatalytic water oxidations:* Previously reported methodologies were followed with modifications.<sup>4,5,10</sup> Briefly photochemical water oxidation experiments were conducted in a 50 mL conical flask with a fitted rubber septum. A known weight of dry dextran-metal oxide, metal oxide coated dried Sephadex ‘organic’ support or commercial Co<sub>3</sub>O<sub>4</sub> nanopowder was taken such that 9mg of the metal oxide component was present in each case, this was suspended in 40ml of Ar degassed DI water (O<sub>2</sub> probe measurements showed that dissolved O<sub>2</sub> was present at ~1ppm). 390 mg Na<sub>2</sub>SO<sub>4</sub>, 130 mg Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 45 mg [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O and 166mg Na<sub>2</sub>SiF<sub>6</sub>of were added with stirring to the covered reaction flask. NaHCO<sub>3</sub> was added to the stirred reaction mixture to reach a constant pH of 5.8. The reaction mixture was then briefly further degassed with Ar. Following this the flask was uncovered and exposed to a 1W blue LED lamp ( $\lambda_{\text{max}}$  470nm) at a distance of 10cm. Evolved gas was collected from the flask by water displacement from an attached filled vessel and the volume evolved measured for 60min.

*Analysis of gas evolved:* Carbon dioxide content in the gas evolved from the sample systems was determined by direct collection and of the gas into vessels entirely filled with filtered saturated lime water (Ca(OH)<sub>2</sub> content of 1.5mgCa(OH)<sub>2</sub>/ml), the solution was displaced during collection such that air was excluded. The sealed gas and lime water vessels were shaken and left for 24 hours to allow any CO<sub>2</sub> content to fully precipitate as CaCO<sub>3</sub>. Quantitative analysis of the precipitate was conducted to determine the proportion of CO<sub>2</sub> present in the evolved gas.

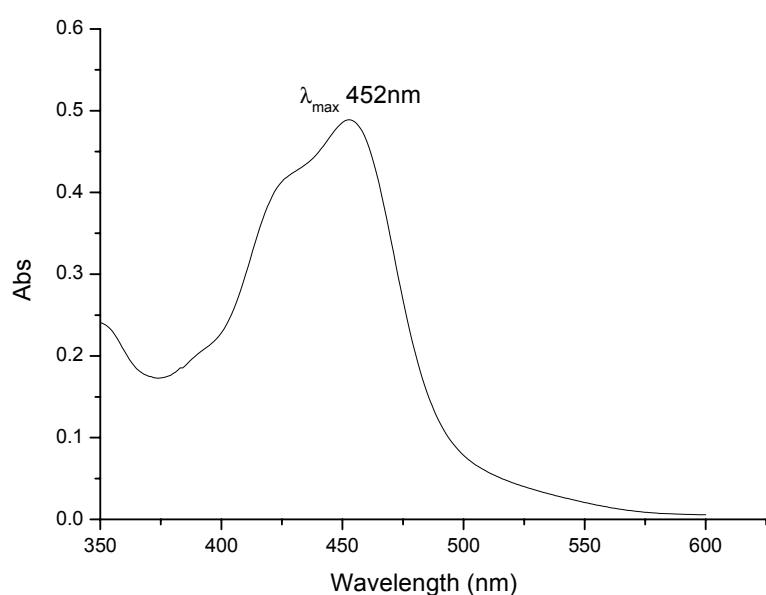
The presence of O<sub>2</sub> in the evolved gas was determined, firstly by successful use of the traditional glowing splint test on gas collected after lime water removal of any CO<sub>2</sub> contaminant. A methylene blue dye solution was then also used as confirmation of the presence of a high level of O<sub>2</sub> in the evolved gases.<sup>21</sup>



Electronic Supporting Information Fig. S1. Image of Sephadex powders as dried beads coated with nanoparticles of (a) Co<sub>3</sub>O<sub>4</sub>; (b) Fe<sub>3</sub>O<sub>4</sub>; (c) Mn<sub>3</sub>O<sub>4</sub>.

Sample (Mr)	Wt% of metal oxide in prepared polymer/metal oxide
Dex(6k)- $\text{Co}_3\text{O}_4$	2.95
Dex(70k)- $\text{Co}_3\text{O}_4$	2.84
Dex(500k)- $\text{Co}_3\text{O}_4$	2.1
Dex(6k)- $\text{Fe}_3\text{O}_4$	20
Dex(70k)- $\text{Fe}_3\text{O}_4$	12.6
CMdex(~15k) $-\text{Co}_3\text{O}_4$	7.05
Sephadex- $\text{Co}_3\text{O}_4$	2.1
Sephadex- $\text{Fe}_3\text{O}_4$	26.7
Sephadex- $\text{Mn}_3\text{O}_4$	1

Electronic Supporting Information Fig. S2. TGA data for prepared biopolymer stabilized metal oxides and nanoparticle coated Sephadex beads showing different wt% of  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  or  $\text{Mn}_3\text{O}_4$  present in the dried dextran/ metal oxide. A weight of sample for the water oxidation reactions was used such that 9mg of the metal oxide was present.



Electronic Supporting Information Fig. S3. Uv-vis absorption spectrum of a 70k dextran- $\text{Co}_3\text{O}_4$  photocatalytic water oxidation reaction mixture (pH 5.8), showing the absorption maximum of the  $[\text{Ru}(\text{bpy})_3]^{3+}$  photosensitizer at 452nm.