

## **Co<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub> hybrid flower-like microspheres: a strong synergistic peroxidase-mimicking artificial enzyme with high sensitivity for glucose detection**

**Deshetti Jampaiah,<sup>†a</sup> T. Srinivasa Reddy,<sup>†a</sup> Victoria E. Coyle,<sup>a</sup> Ayman Nafady,<sup>b c</sup> and Suresh K. Bhargava<sup>a\*</sup>**

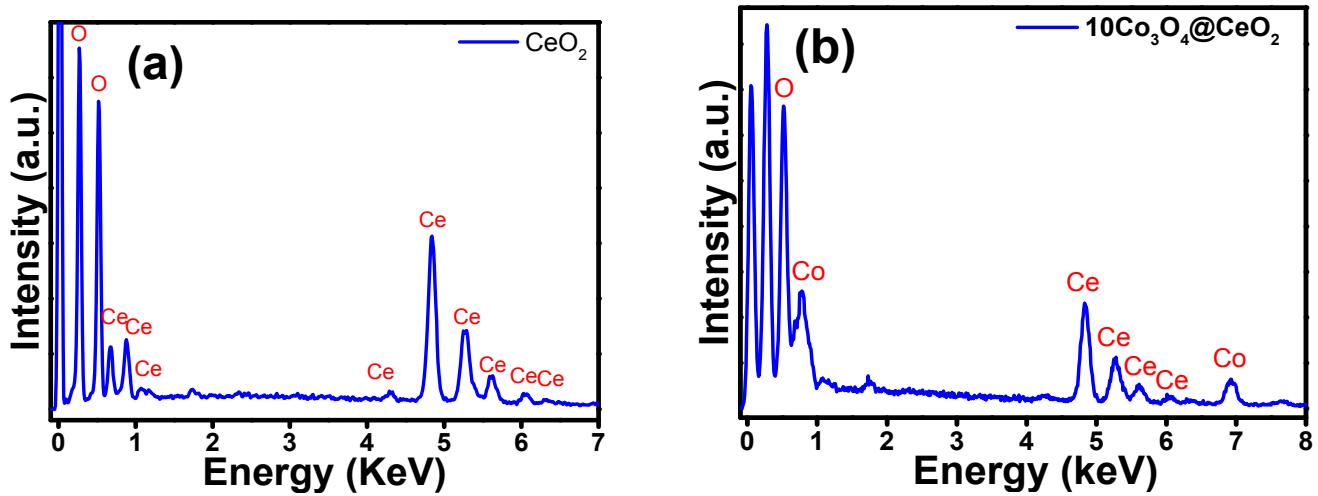
<sup>a</sup>*Centre for Advanced Materials & Industrial Chemistry (CAMIC), School of Applied Sciences, RMIT University, GPO BOX 2476, Melbourne–3001, Australia. E-mail: suresh.bhargava@rmit.edu.in; Tel: +61 3 9925 3365*

<sup>b</sup>*Chemistry Department, College of Science, King Saud University, Riyadh, Saudi Arabia*

<sup>c</sup>*Chemistry Department, Faculty of Science, Sohag University, Sohag 82524, Egypt*

**\*Corresponding Author:**

E-mail: suresh.bhargava@rmit.edu.in; Tel: +61 3 9925 3365



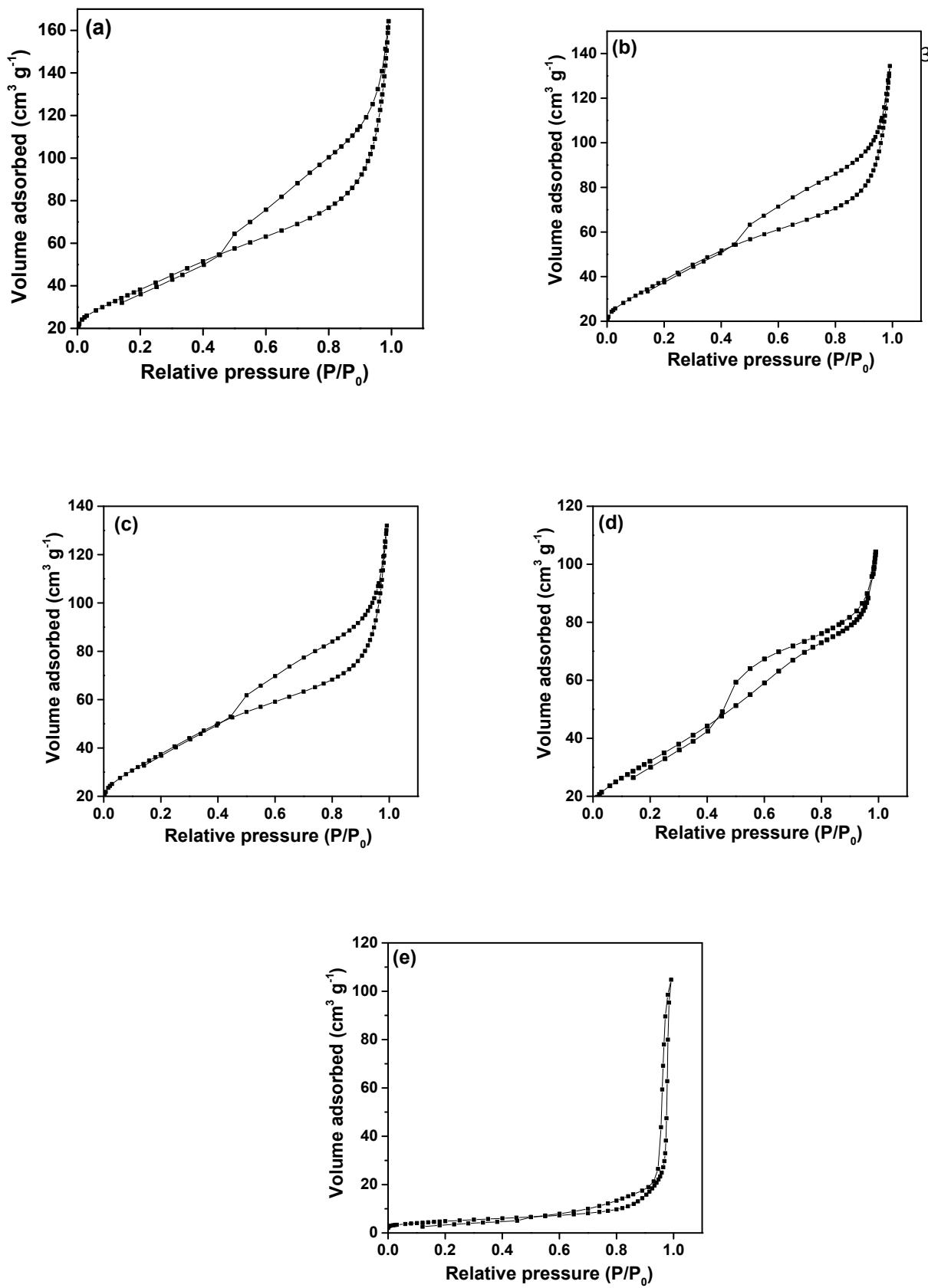
**Fig. S1** SEM-EDX spectra for the (a)  $\text{CeO}_2$ , and (b)  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  hybrid microspheres.

**Table S1**

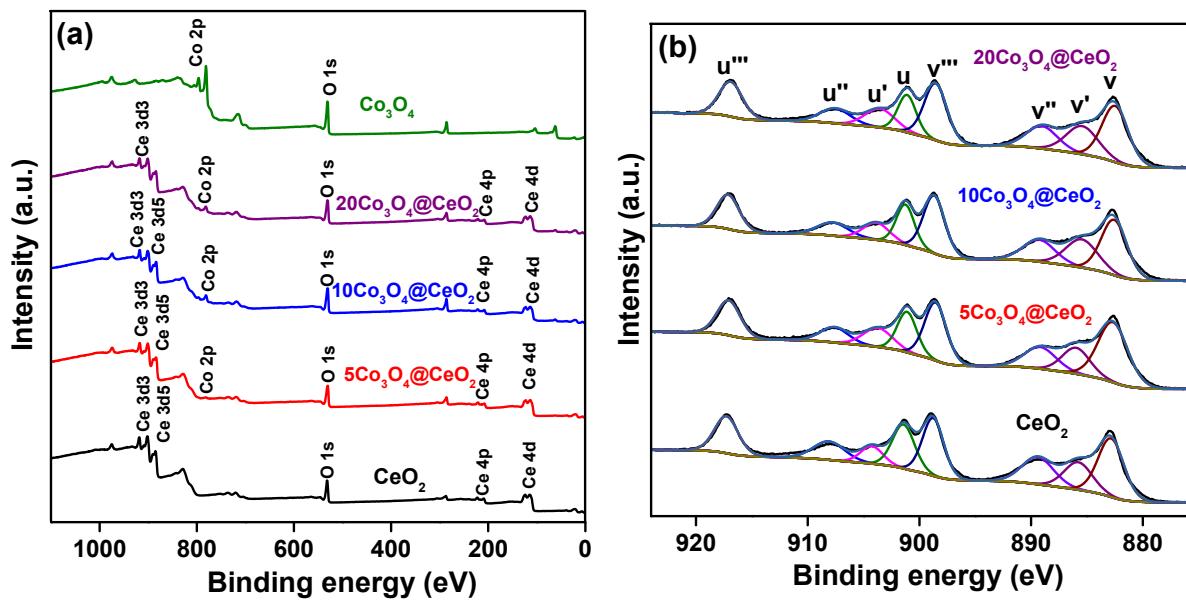
The content of Co values of  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  hybrid microspheres.

| Catalyst                               | Designed Content of Co (wt%) | Calculated Content of Co (wt%) <sup>a</sup> |
|--|------------------------------|---|
| $10\text{Co}_3\text{O}_4@\text{CeO}_2$ | 10                           | 9.95  |

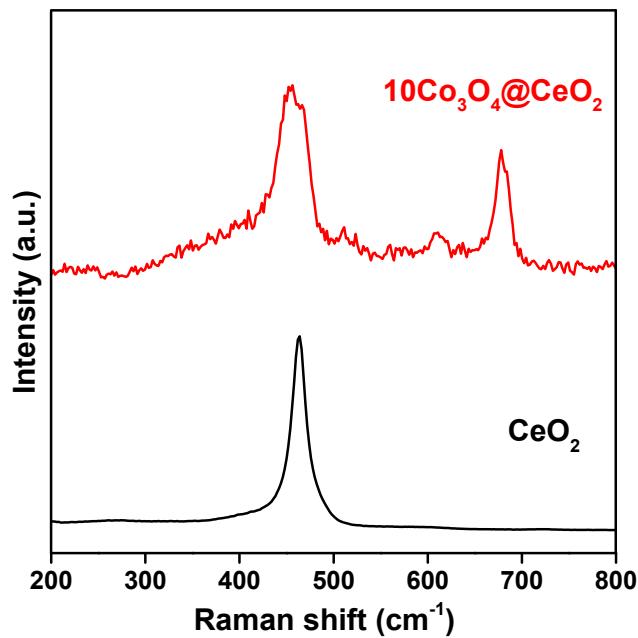
<sup>a</sup>The metal content was tested by ICP-AES analysis.



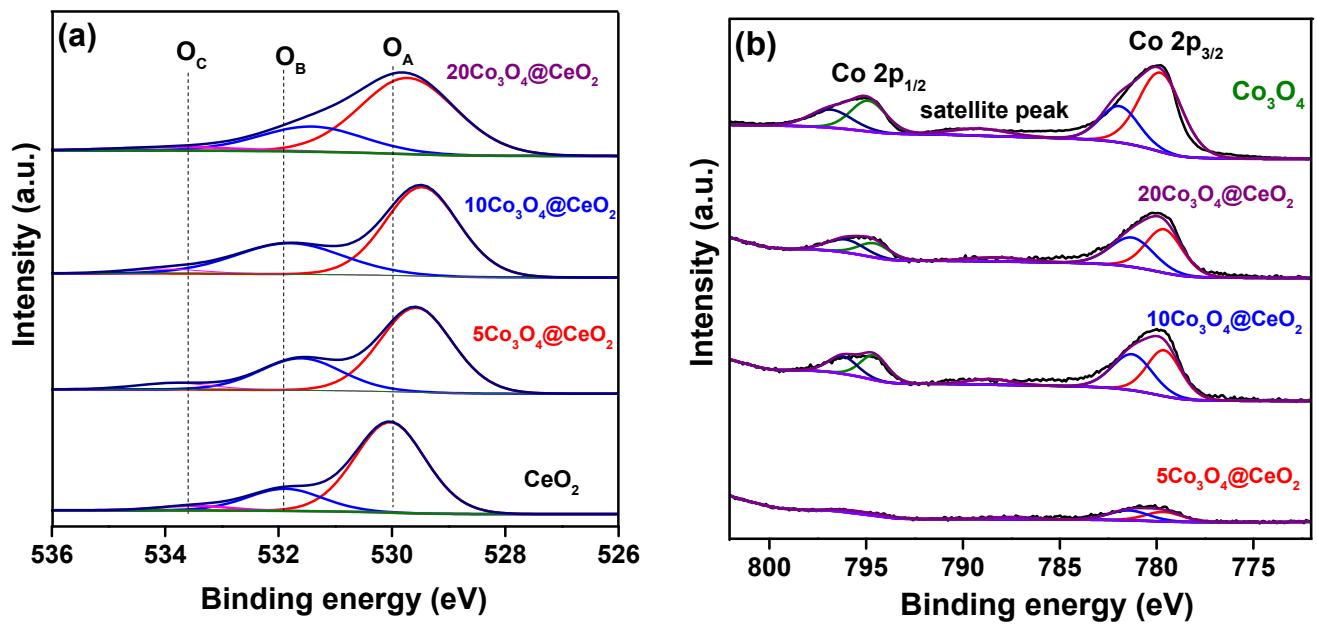
**Fig. S2** Nitrogen adsorption–desorption isotherms for the (a)  $\text{CeO}_2$ , and (b)  $5\text{Co}_3\text{O}_4@\text{CeO}_2$  (c)  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  (d) $20\text{Co}_3\text{O}_4@\text{CeO}_2$  and (e)  $\text{Co}_3\text{O}_4$  catalysts.



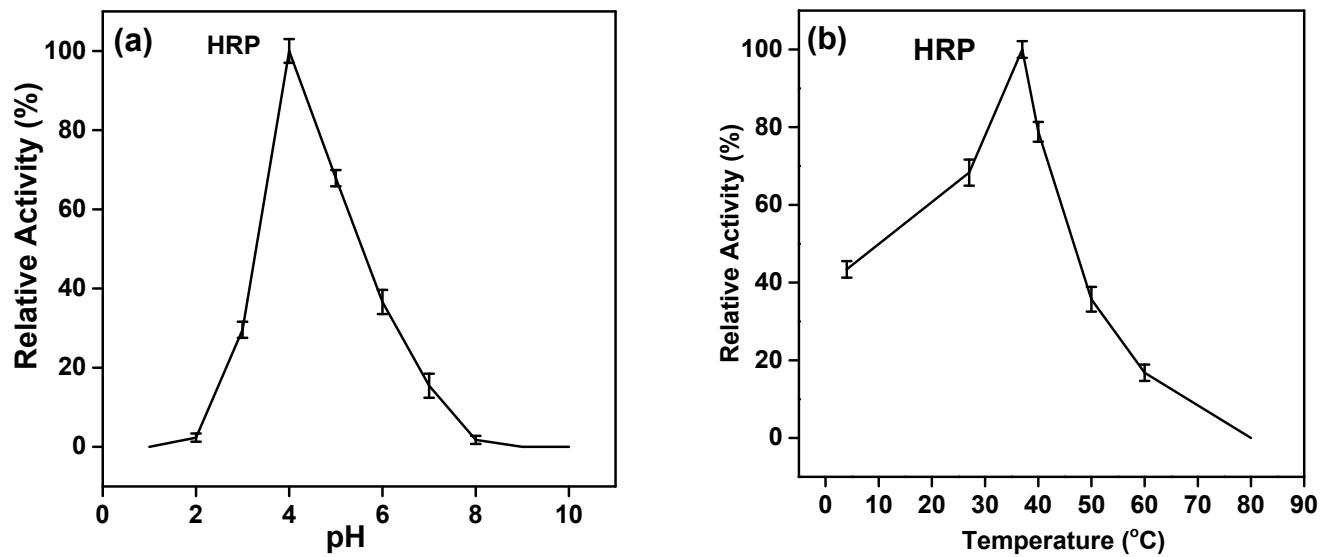
**Fig. S3** XPS spectra of CeO<sub>2</sub>, 5Co<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub>, 10Co<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub>, 20Co<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub>, and Co<sub>3</sub>O<sub>4</sub> catalysts (a) survey scan, (b) Ce 3d.



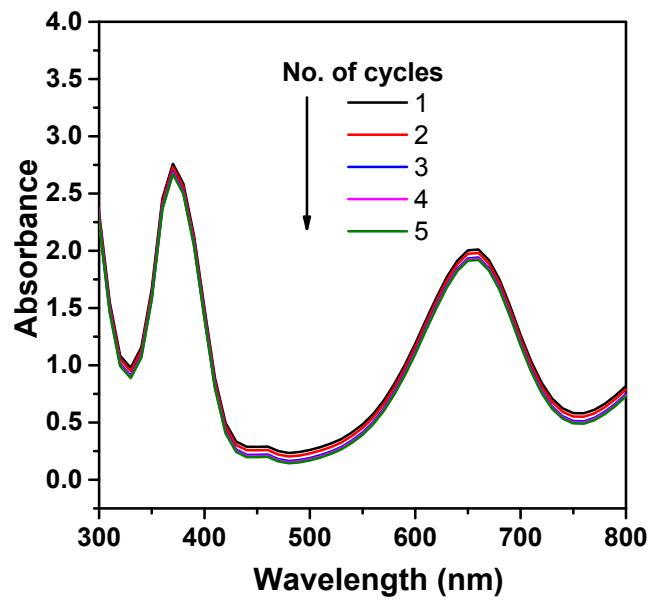
**Fig. S4** Raman spectra of the CeO<sub>2</sub> and 10Co<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub> microspheres.



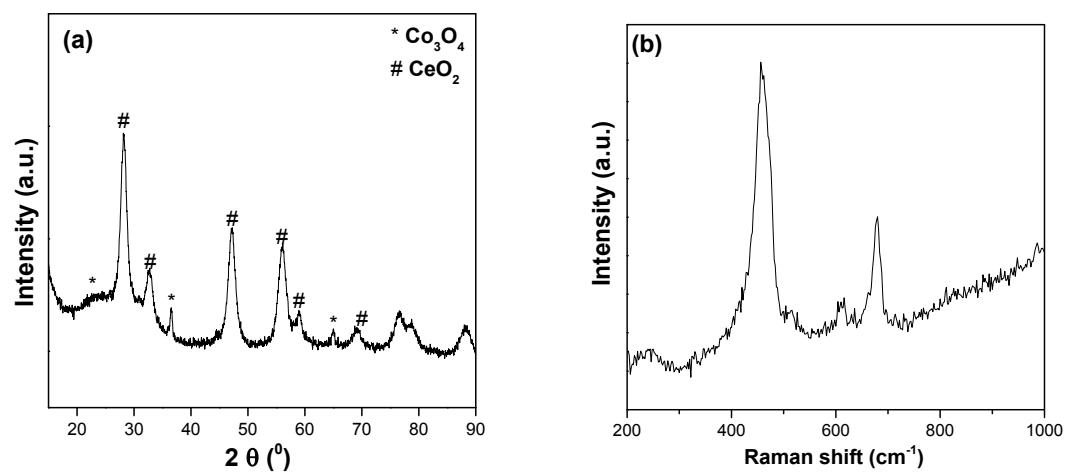
**Fig. S5** XPS spectra of  $\text{CeO}_2$ ,  $5\text{Co}_3\text{O}_4@\text{CeO}_2$ ,  $10\text{Co}_3\text{O}_4@\text{CeO}_2$ ,  $20\text{Co}_3\text{O}_4@\text{CeO}_2$ , and  $\text{Co}_3\text{O}_4$  samples (a) O 1s, (b) Co 2p.



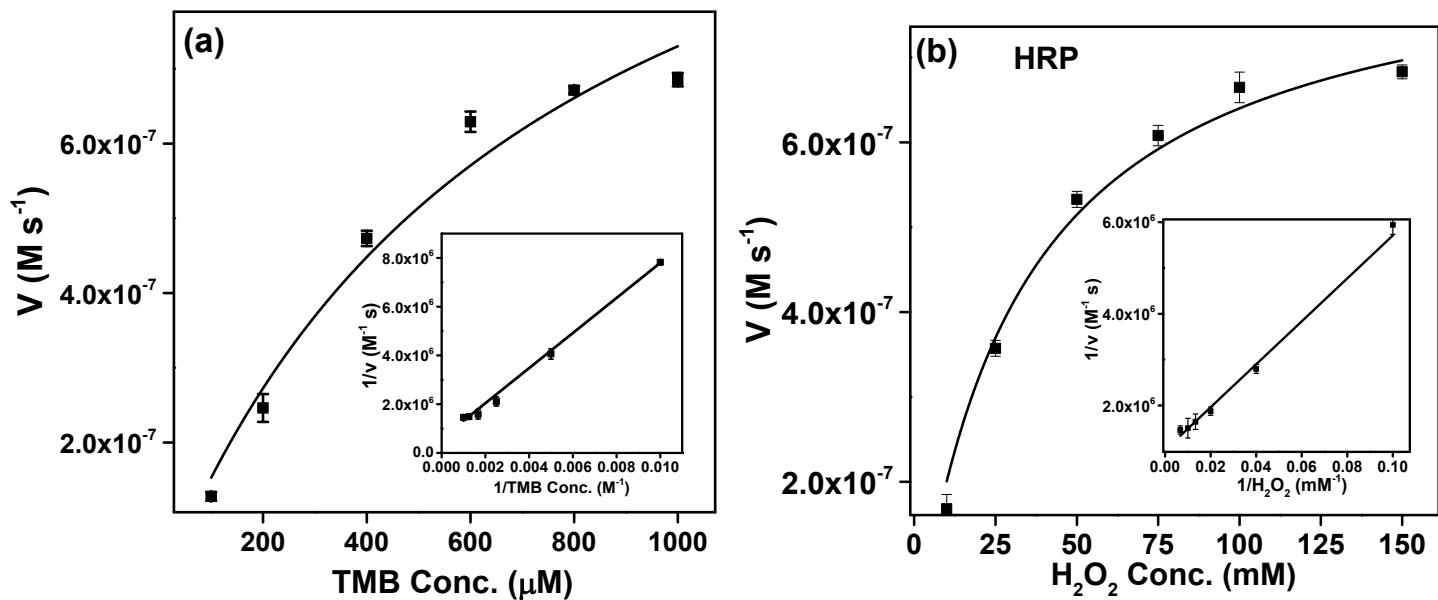
**Fig.S6** The peroxidase-like activity of HRP is dependent on (a) pH, (b) temperature.



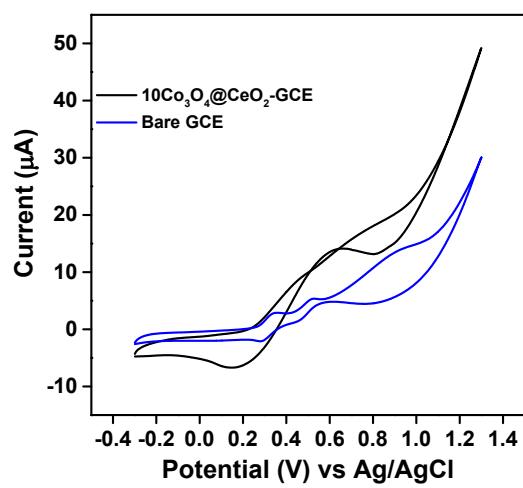
**Fig. S7** Catalytic activity of  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  hybrid microspheres in five successive recycles.



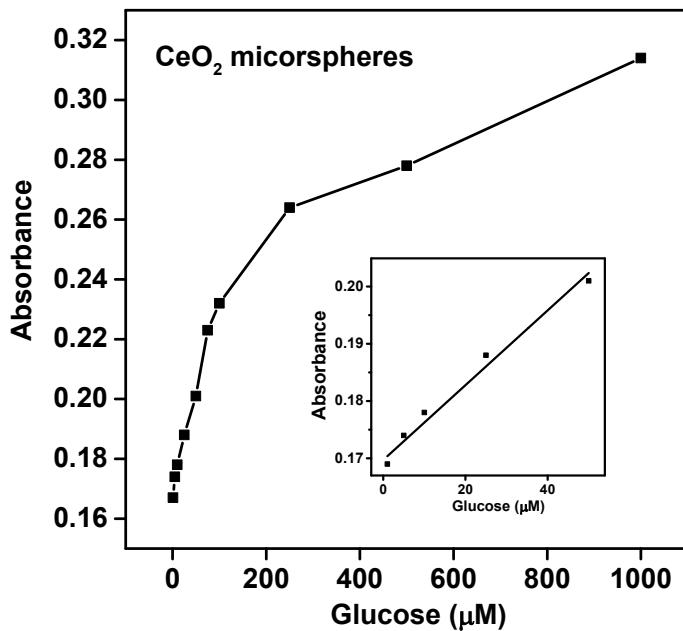
**Fig. S8** (a) Powder XRD patterns and (b) Raman spectra of  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  hybrid microspheres after TMB substrate oxidation.



**Fig. S9** Steady-state kinetic analyses using Michaelis-Menten and Lineweaver-Burk models (insets of figures) for HRP (1.5 ng/mL) by (a) varying the concentrations of TMB (100–1000  $\mu\text{M}$ ) with a fixed amount of  $\text{H}_2\text{O}_2$  (100 mM) and (b) varying the concentrations of  $\text{H}_2\text{O}_2$  (10–150 mM) with a fixed amount of TMB (800  $\mu\text{M}$ ).



**Fig. S10** Cyclic voltammogram curves of a bare glassy carbon electrode (GCE) and GCE modified  $10\text{Co}_3\text{O}_4@\text{CeO}_2$  hybrid microspheres.



**Fig. S11** Glucose concentration response curve for glucose detection using GO<sub>x</sub> and the pure CeO<sub>2</sub> microspheres (inset: linear calibration plot for glucose). The error bars represent the standard deviation of three repeated measurements.