

Novel porous silica encapsulated Au nanoreactors as peroxidase mimic for one pot glucose detection

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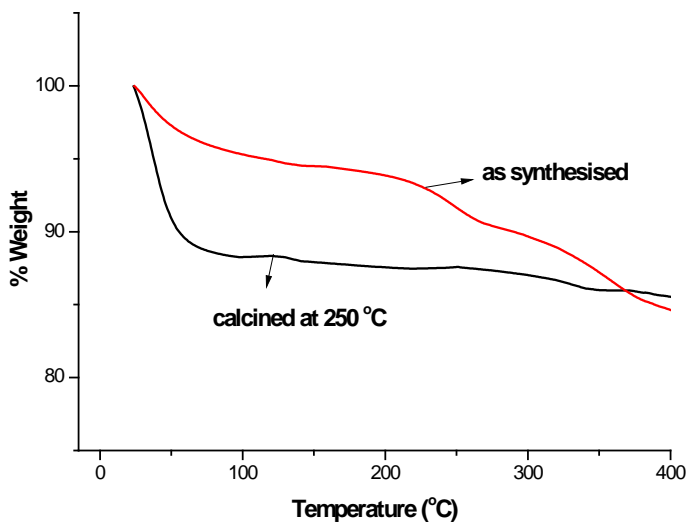
Synthesis of Au@p-SiO₂:

Synthesis of thiol stabilised gold nanoclusters. 8.5 mL of a stock solution of HAuCl₄ in acetonitrile (10 mM) was mixed with 20 mL of acetonitrile. Thiol (0.593 g, 1.6 mmol) in 2 mL of methanol was added to this mixture. The mixture was stirred for 30 min. 100 μL NaBH₄ solution (1.58 M) in methanol was added and stirring was continued for 45 min. All the steps were carried out at ice-cooled condition. 30 mL water was added to gold nanocluster solution. Acetonitrile was removed in vacuo. Aqueous solution of gold nanocluster was purified by dialysis using cellulose membrane. The concentration of this final solution was found to be 2 mM by elemental analysis.

Synthesis of silica encapsulated gold nanoclusters. 500 μL the above gold nanocluster solution was mixed with a 1:4 mixture of water:ethanol (10 mL). 30-40 μL NaOH solution (0.1 M) and 10-15 μL tetraethyl orthosilicate (98 wt% Aldrich) were added to this mixture and stirred at room temperature for 2 d. Silica encapsulated gold nanoclusters were separated from the reaction medium by centrifuging at 14000 rpm and redispersing in water several times.

Synthesis of Au nanoparticles encapsulated in porous silica. The above silica encapsulated Au cluster solution was dried at 100 °C and calcined at 250 °C under air at a ramp rate of 1 °min⁻¹.

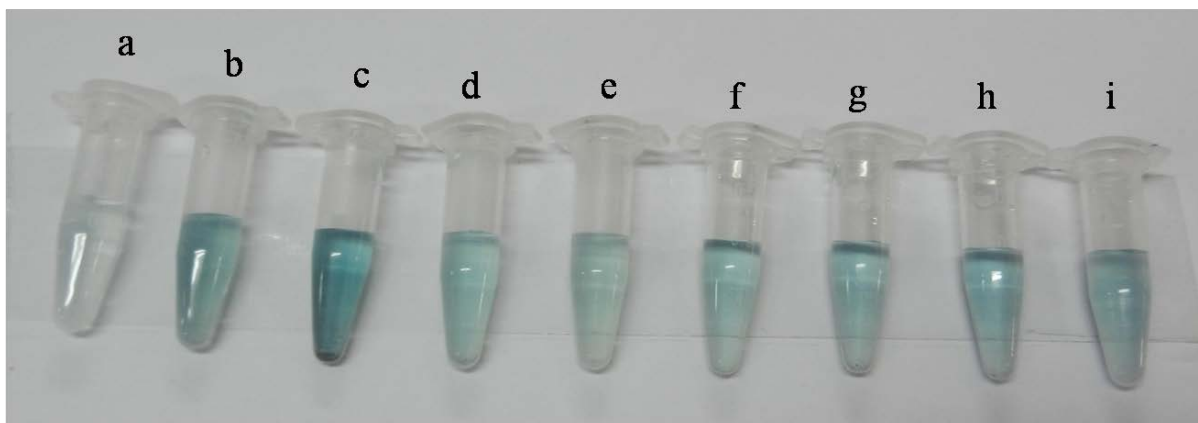
TGA Analysis of the as synthesized and the sample calcined at 250 °C. The decrease in weight at 50 °C corresponds to water which is adsorbed due to the porosity.



Comparison of the Michaelis constant (K_m) between Au@p-SiO₂, other nanoparticles and HRP

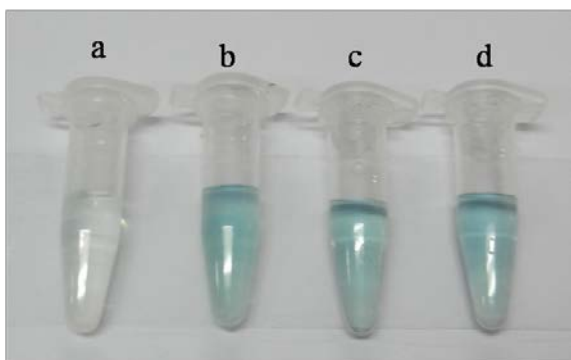
Catalyst	Substrate	K_m (mM)
Au nanoreactor	TMB	8.70
	H ₂ O ₂	0.156
HRP	TMB	0.434
	H ₂ O ₂	3.70
Fe ₃ O ₄ MNPs	TMB	0.098
	H ₂ O ₂	154
CuO Nps	TMB	0.013
	H ₂ O ₂	85.6

Stability and activity of Au@p-SiO₂ after treatment at various temperatures and pH values.



Images for TMB oxidation after incubation of the gold nanoreactor at a range of pH.

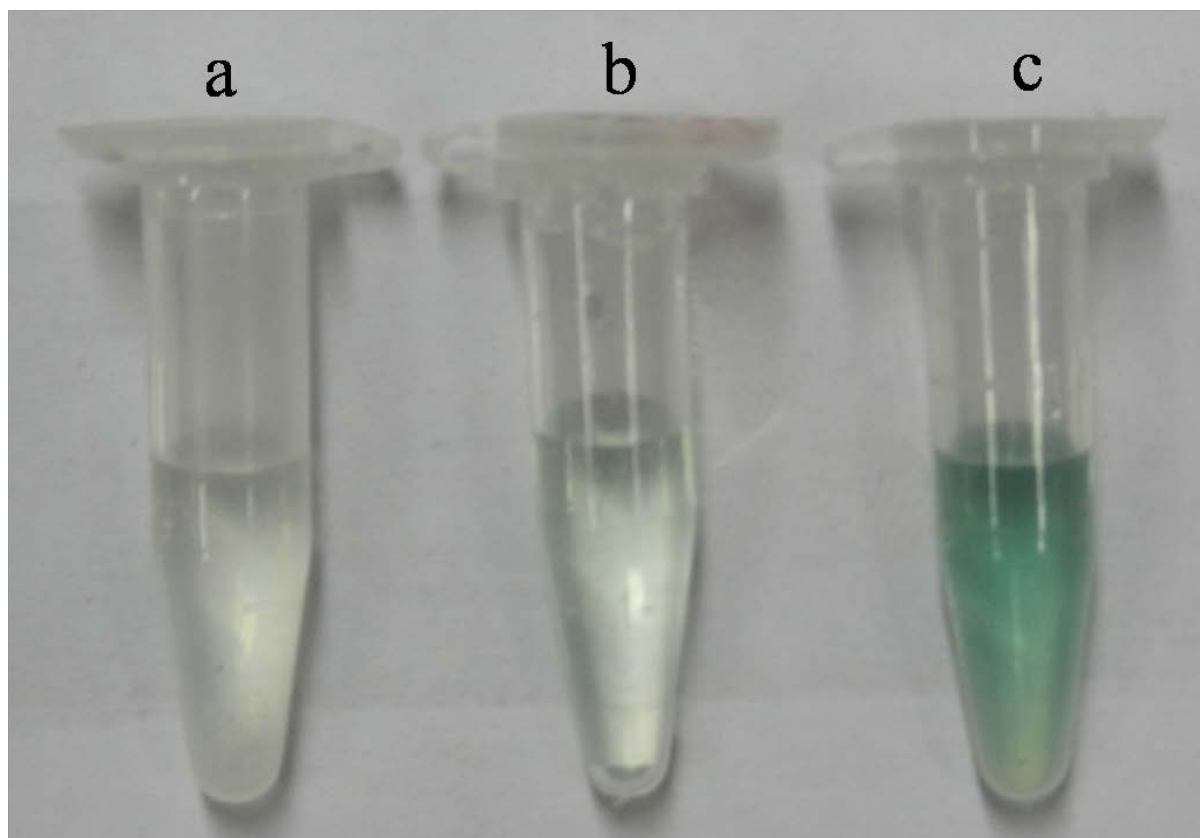
a=without catalyst, 1 mg of catalyst was incubated in 1 mL of (50 mM) phosphate buffer solution of different pH (b=2.5, c=4, d=5, e=6, f=7, g=8, h=9, i=10) for 2 h. Then the catalyst was collected by centrifugation and washed with water. Stock solutions of catalyst were prepared by dispersing the incubated catalysts in 1 mL of water. In a typical experiment 50 μ L of 20 mM TMB in 0.1 N HCl, 25 μ L of stock catalyst solution, 50 μ L of 2 mM H₂O₂ and 200 μ L 160 mM phosphate buffer of pH 4 were added and incubated in 30 °C water bath for 20 min.



Images for TMB oxidation after incubation of the gold nanoreactor at a range of temperature.

a=without catalyst, 1 mg of catalyst was incubated in 1 mL of water at a range of temperature (b=70 °C, c=80 °C, d=90 °C). These incubated catalysts were used for doing TMB oxidation. In a typical experiment 50 μ L of 20 mM TMB in 0.1 N HCl, 25 μ L of stock catalyst solution, 50 μ L of 2 mM H₂O₂ and 200 μ L 160 mM phosphate buffer of pH 4 were added and incubated in 30 °C water bath for 20 min.

Lack of activity of pure silica when compared to Au@p-SiO₂



Images for TMB oxidation using Au nanoreactor and silica

In a typical experiment 294 10 μL 9.41×10^{-4} M TMB 35 μL Au catalyst (stock solution 1mg/mL, for c), no catalyst (for b), 1 mg silica (for a), 350 μL H₂O₂ of 10 mM, 16 μL of 160 mM phosphate buffer of pH 4 were added and incubated in a 40 °C water bath for 10 min. Final pH of the solution was 4.5.

Recyclability study of the catalyst:



In a typical experiment 200 μL 20 mM TMB in 0.1 M HCL, 300 μL 0.1 mM H_2O_2 , 50 μL 500 mM phosphate buffer at pH 4.0 and 0.3 mg catalyst dispersing in 450 μL of double-distilled water were incubated at 40 $^\circ\text{C}$ in a water bath for 20 min. Resulting solution became colourless to blue. Two consecutive reactions were done by using the same catalyst after collecting by centrifugation and giving washing by water.