Gold Aerogel supported on Graphitic Carbon Nitride: an Efficient Electrocatalyst for Oxygen Reduction Reaction and Hydrogen Evolution Reaction

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Material

Formamide (HCONH₂, HPLC grade), hydrogen tetrachloroaurate(III) (HAuCl₄.x H2O, 99.999%), 10% Platinum on graphitized carbon (Pt/C) was bought from Sigma-Aldrich. Sulfuric acid (H₂SO₄, 98%) and potassium hydroxide (KOH), lead nitrate (Pb(NO₃)₂) was purchased from Merck (Germany) and sodium borohydride (NaBH₄) was taken from Spectrochem (India). These all chemicals were used as they received without further purification. N₂ and O₂ gases (99.99 % purity) were purchased from Sigma Aldrich. Mili-Q water was obtained from ultra filtration system (Mili-Q, Milipore) with the measured conductivity 35 mho cm⁻¹ at 25^{0} C.

Characterizations

For microwave synthesis of g-C₃N₄ MAS-II microwave synthesizer from SINEO Microwave Chemistry Technology Company (Shanghai, China) was used. Ultrasound was carried out by SINEO UWave-1000 (Shanghai, China) with 28 kHz frequency. The surface morphology was investigated by Transmission Electron Microscopy (TEM, FEI, Technai G2 2010, operated at 200 kV). High Resolution TEM (HRTEM) was also taken using same instrument. TEM samples were prepared by drop casting a drop and dried at air around 450C. For TEM 10 μ l of 4x10⁻⁵ mg/l solution was drop casted in a TEM grid. The powder x-ray diffraction pattern (p-XRD) experiment was performed by Bruker DAVINCI D8 ADVANCE diffractometer equipped with Cu K α radiation ($\lambda 0.15406$ nm). Field-emission scanning electron microscope (FESEM) system (Carl Zeiss, Germany make, Model: *Sigma*) was used for taking FESEM images. Electrochemical measurements were performed with a conventional three electrode system, glassy carbon as a working electrode, platinum wire as a counter electrode and Ag/AgCl as a reference electrode by using an Electrochemical Workstation (Autolab, Metrohm, PGSTAT 320N), equipped with rotating disk electrode (RDE). In order to reduce noise due to oxygen flow a smoothing was applied in chronoamperometric responses in ORR. For converting potential Ag/AgCl reference electrode to RHE reference the general formula $E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl} +$ $E^{0}_{Ag/AgCl}$ + 0.059 pH was used, where $E_{Ag/AgCl}$ is the working potential $E^{0}_{Ag/AgCl}$ = 0.1976 at 25°C. pH of the working solution was measured by Hanna (HI 2209) pH meter. Thermo gravimetric analysis (TGA) was carried out by TA Instrument (Model: Discovery TGA). ICP-OES (Optima 2100 DV, PerkinElmer) was used to find out the exact amount of Au present in catalysts. The UV-Vis spectra were recorded in Perkin-Elmer (model: Lamda-750) UV-Vis spectrometer. XPS measurements were done using VG Microtech where monochromatic Mg K_{α} X-ray was the source. FT-IR spectrum was performed by using Perkin Elmer RXI FT-IR spectrophotometer.

Determination of nanoparticle size from p-XRD pattern:

The size of AuNPs in the composite could be determined from the following Debye–Scherrer Equation by determining the width of the (111) Bragg reflection.

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Where *L* is the mean size of the ordered (crystalline) domains, *K* is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite, λ is the X-ray wavelength (0.154 nm), *B* is the line broadening at half the maximum intensity (FWHM) in radians.



Figure S1. (a) TEM images of AuNPs-CN_x formed from ultrasound treatment of HAuCl₄ with CN_x (inset: particle size distribution graph, particle size are in the range of 1 nm - 2.5 nm). (b, c) TEM images of Au-CN_x composite (formed from ultrasonic treatment on 0.162 mmol of HAuCl₄ and 0.10 mmol of NaBH₄) showing highly dispersed AuNPs of less than 1 nm on CN_x sheet in Figure S1b and few nano chains on S1c. (d, e) TEM images of Au-aerogel-CN_x formed when 0.162 mmol HAuCl₄ and 0.53 mmol NaBH₄ was used and (f) TEM images showing 6-8 nm AuNPs distributed on CN_x sheet. (g, h) TEM images of Au-aerogel-CN_x formed of HAuCl₄ and 0.79 mmol of NaBH₄ was used. (i) HRTEM image of Au-aerogel-CN_x.



Figure S2. TGA curves of Au-aerogel(1)-CN_x, Au-aerogel(2)-CN_x, AuNPs-CN_x and CN_x.



Figure S3. FT-IR spectra of CN_x (red line), AuNPs- CN_x (green line) and Au-aerogel- CN_x (blue line). Freshly prepared g- CN_x and solid, obtained from evaporation of aqueous dispersion of Au-aerogel- CN_x and AuNPs- CN_x were used for FT-IR measurement.



Figure S4. FT-IR spectra of (a) freshly prepared Au-aerogel- CN_x (blue line) and solid obtained from evaporation of water dispersion of Au-aerogel- CN_x (red line). (b) Freshly prepared AuNPs - CN_x (purple line) and solid, obtained from evaporation of water dispersion of AuNPs - CN_x (green line).



Figure S5. (a, b) The deconvulated spectra of C1s and N1s XPS spectra of CN_x . (c) Comparison of N1s XPS spectra of g-CN_x, AuNPs-CN_x, Au-aerogel-CN_x.



Figure S6. CVs curve for 0.5 mM $K_4[Fe(CN)_6]^{3-/4-}$ redox couple in 0.05 M H_2SO_4 at different scan rate and corresponding current vs square root of scan rate plot of (a, b) Au-aerogel-CN_x (c, d) AuNPs-CN_x and (e, f) bare GCE.

Table T1. Electrochemical parameters deduced from Figure S6 such as ΔE_p and slope of cathodic and
anodic current of Au-aerogel-CN_x, AuNPs-CN_x and bare GCE.

Catalyst	$\Delta E_{p} (mV)$	Slope (i _a)	Slope (i _c)	
		$(\mu A/Vsec^{-1})^{1/2}$	$(\mu A/(Vsec^{-1})^{1/2})$	
Au-aerogel-	62	94 ($R^2 = 0.985$)	$-68 (R^2 = 0.990)$	
CN _x				
AuNPs-CN _x	66	$64 (R^2 = 0.993)$	$-32 (R^2 = 0.997)$	
GCE	75	$28 (R^2 = 0.999)$	$-20 (R^2 = 0.997)$	

 Table T2. ECSA of different catalysts in acidic and basic medium.

Catalyst	$A_r cm^2$	A _r cm ²	
	(Acidic)	(Basic)	
AuNPs-CN _x	0.14	0.07	
Au-aerogel(1)-	1.17	0.6	
CN _x			
Au-aerogel(2)-	1.05	0.5	
CN_x			
AuE	0.17	0.1	



Figure S7. ORR polarisation curves of (a) AuNPs- CN_x/GCE , (b) Au-aerogel(1)- CN_x/GCE , (c) Au-aerogel(2)- CN_x/GCE at different rotation speed at 0.5 M oxygen saturated KOH solution at a scan speed 100 mV sec⁻¹ with Au loading of 0.130 mg cm⁻².

Koutecky-Levich (K-L) equation:

$$1/j = 1/j_k + 1/j_d = -1/nFkC^{0_2} - 1/B\omega^{1/2}$$

Where j is the measured current density, j_k , j_d is the kinetic and diffusion limited current density. ω is the electrode rotating rate. B can be determined from the slope of K-L plot and theoretically can be obtained from the following equation

$$\mathbf{B} = 0.62 \ nF(D^{o_2})^{2/3} v^{-1/6} C^{o_2}$$

where Faraday constant (F= 96485 C mol⁻¹) and n is the number of electron transferred per O₂ molecule, in 0.5 M KOH diffusion coefficient (D^{0_2}) of O₂ (1.9 x 10⁻⁵ cm² s⁻¹), kinetic viscosity (v = 0.01 cm² s⁻¹) and C^{0_2} is the bulk concentration of O₂ (1.2 x 10⁻⁶ mol cm⁻³).

For 0.5 M H₂SO₄ diffusion coefficient (D^{o_2}) is 1.8 x 10⁻⁵ cm² s⁻¹, v = 0.01 cm²s⁻¹ and C^{o_2} = 1.13 x10⁻⁶ mol cm⁻³.

Specific activity and Mass activity determination

The specific activity (SA) and MA (mass activity) were calculated using these equations $SA = I_k / ECSA$ Here I_k is the kinetic current. Mass activity of the electrode were evaluated from equation below

 $MA = I_k / m_{Au}$

Here m_{Au} is the mass of Au on the electrode.



Figure S8. (a) CVs of Pt-C in N₂ saturated (green line), O₂ saturated (blue line) and O₂ saturated 2 M methanol (red line) in 0.5 M KOH solution (b) Au-aerogel-CN_x in N₂ saturated (green line), O₂ saturated (blue line), O₂ saturated 2 M methanol (red line) 0.5 M KOH solution. Scan rate 100 mV/sec (c) Chronoamperometric stability in 0.5 M alkaline medium at Au-aerogel-CN_x, AuNPs-CN_x and 10% Pt-C at 0.7 V(RHE).



Figure S9. CVs of different catalyst at O_2 saturated 0.5 M H_2SO_4 : Au-aerogel(2)-CN_x (red line), Au-aerogel(1) -CN_x (blue line) AuNPs-CN_x (green line), flat Au electrode (purple line) and Au-aerogel(2)-CN_x in N₂ atmosphere. Scan rate100 mV sec⁻¹.



Figure S10. ORR polarisation curves of AuNPs- CN_x/GCE , Au-aerogel(1)- CN_x/GCE , Au-aerogel(2)- CN_x/GCE at different rotation speed at 0.5 M oxygen saturated H₂SO₄ solution at a scan speed 100 mV sec⁻¹ with Au loading of 0.130 mg cm⁻².

Catalyst	A _r	E _{1/2}	SA (0.25 V)	MA	Tafel slope
	(cm ⁻²⁾	(V)	(mA cm ⁻²)	(Ag ⁻¹)	(mV)
				(0.25 V)	
AuNPs-CN _x	0.14	+0.21	0.14	3	150
Au-aerogel(1)	1.17	+0.3	0.15	19	155
-CN _x					
Au-aerogel(2)	1.05	+0.33	0.13	15	160
-CN _x					
Flat Au	0.17	+0.03	-	-	-
electrode					

 Table T3. Different parameter of synthesized catalysts in acidic media.