Supplementary Information (SI)

Simultaneous growth of spherical, bipyramidal and wires of gold nanostructures on solid and solution phases: SERS and electrocatalytic applications

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Experimental details

Materials

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄.3H₂O), Hexadecyltrimethylammonium bromide (CTAB), 4-aminothiophenol (4-ATP) and ascorbic acid (AA) were purchased from Aldrich and were used as received. Sulfuric acid (H₂SO₄), sodium dihydrogen phosphate (NaH₂PO₄), disodium hydrogen phosphate (Na₂HPO₄.2H₂O), orthophosphoric acid (H₃PO₄), hydrogen peroxide (H₂O₂) and sodium hydroxide (NaOH) were purchased from Merck and were used as received. 0.2 M phosphate buffer (PB) solution was prepared using NaH₂PO₄ and Na₂HPO₄. Double distilled water was used to prepare the solutions used in the present work. All other chemical reagents were of analytical grade and were used without further purification.

Instrumentation

Absorption spectral measurements were carried out using Perkin-Elmer lambda 35 and JASCO V-550 UV-visible spectrophotometer. Electrochemical measurements were performed in a conventional two-compartment three electrode cell with indium-tin-oxide (ITO) plate as a working electrode, a platinum wire as counter electrode and NaCl saturated Ag/AgCl electrode as a reference electrode. The measurements were carried out with CHI model 643B (Austin, TX, USA) Electrochemical analyzer. All the electrochemical experiments were carried out under N₂ gas atmosphere at room temperature. Raman measurements were carried out at Bruker Senterra dispersive Raman microscope with laser excitation wavelength of 516 nm. Surface enhanced Raman spectra were recorded at a Horiba JY LabRAM HR800 Raman spectrometer coupled with microscope in reflectance mode with 633 nm excitation laser sources and a spectral resolution of 0.3 cm⁻¹. The laser beam was focused on a spot with a diameter of approximately 1 μ m using a 50× microscope objective. High resolution transmission electron microscopy (HR-TEM) images were obtained from a JEOL JEM 3010 operating at 200 kV. The samples were prepared by dropping 2 μ L of the growth solution containing AuNS on to a carbon-coated copper grid. X-ray diffraction analysis was carried out with a Rigaku X-ray diffraction unit using Ni-filtered Cu K α (λ = 1.5406) radiation. Scanning electron microscope (SEM) measurements were carried at VEGA3 TESCAN, USA. Energy dispersive X-ray analysis and line scanning analysis were carried out using Bruker Nano, Germany.

Results and Discussions



Figure S1. UV-vis absorption spectra obtained for the growth solution (a) before and (b-g) after electrochemical seeding of (b) 1, (c) 2, (d) 3, (e) 6, (f) 9 and (g) 12 h.



Figure S2. SEM images obtained for AuNS grown ITO substrate at the immersion time of 3 h in the growth solution.



Figure S3. SAED pattern obtained of AuNS grown in the growth solution.



Figure S4. EDAX spectrum of AuNS grown ITO substrate.



Figure S5. Nyquist plots for (a) bare ITO and (b-d) AuNS of spherical, bipyramidal and wires grown ITO substrates in 1 mM K_3 [Fe(CN)₆] in 0.2 M PB solution (pH 7) at scanning frequencies from 0.01 to 100000 Hz. Inset: Equivalent electrical circuit used for fitting the impedance spectra.



Figure S6. CVs obtained for (a) bare and (b-d) spherical, bipyramidal and wires of AuNS grown ITO substrates in 0.2 M PB solution (pH 7) at a scan rate of 50 mV s⁻¹.



Figure S7. CVs obtained for 0.5 mM HP at ITO/Au-wires in 0.2 M PB solution (pH 7.2) at different scan rates (10-100 mV s⁻¹). **Inset:** Plot of reduction current vs. square root of scan rate.



Figure S8. SEM images obtained for Au-bipyramidals (a) before and (b) after electrochemical reduction of HP.

Table S1. Impedance spectral data

Description	Deres ITO	ITO/AuNS				
Parameter	Bare IIO	Spherical	Bipyramidal	Wires		
$R_{s}(k\Omega)$	32.85	31.89	30.75	32.39		
C (µF)	2.30 × 10 ⁻⁶	6.92 × 10 ⁻⁶	1.13 × 10 ⁻⁵	3.72 × 10 ⁻⁵		
$R_{CT}(k\Omega)$	7.66	5.41	3.31	2.06		
k_{et} (cm s ⁻¹)	3.47×10^{-5}	4.91×10^{-5}	8.05×10^{-5}	1.29×10^{-4}		

Table	S2.	Comparison	of	SERS	activity	of	Au-nanowires	modified	substrate	with	the
existin	g Au	ı substrates									

AuNS	Probe molecule	Concentration of probe molecule	Average EF	Ref
Au nanorods	4-ATP	1 × 10 ⁻⁶ M	1.7×10^{5}	[10]
Au-film on PVP ^a	4-ATP	1 × 10 ⁻³ M	6.0×10^{3}	[36]
AuNPs	4-ATP	$1 \times 10^{-3} \mathrm{M}$	2.0×10^{5}	[37]
Au nanorods	4-ATP	$1 \times 10^{-4} \mathrm{M}$	4.0×10^{5}	[38]
AgNPs/4-ATP/Au nanorods sandwich	4-ATP	$1 \times 10^{-4} \mathrm{M}$	3.2×10^{8}	[38]
AuNPs-CPAM ^b paper	4-ATP	1 × 10 ⁻³ M	8.9 × 10 ⁸	[39]
Au nanowires	4-ATP	1 × 10 ⁻⁶ M	9.7×10^{5}	This work

^apolyvinylpyridine, ^bcationic polyacrylamides