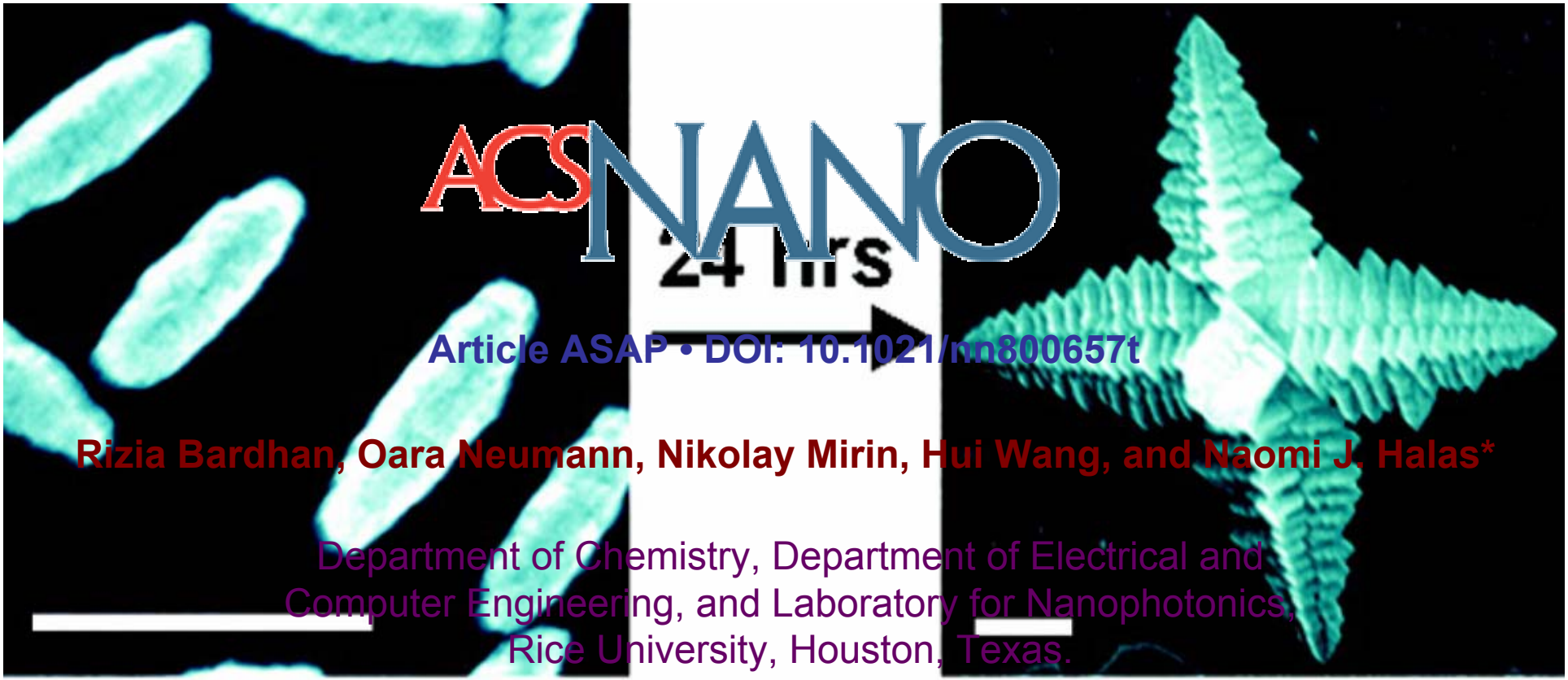
Au Nanorice Assemble Electrolytically into Mesostars



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Introduction

- Anisotropic nanoparticles — Size and shape dependent physical and chemical properties.
- Applications in diverse areas — SERS, optical devises, electronics, etc.

Present work

- Formation of mesoscale star-shaped particles with a hierarchical substructure when an aqueous suspension of nanorice particles is subjected to electrolysis.

Experimental

Various steps

1. Synthesis of spindle-shaped α-Fe_2O_3 particles

Reacting 100 mL of an aqueous mixture containing 2.0 x 10^{-2} M $FeCl_3$ and 4 x 10^{-4} M KH_2PO_4 at 100 °C for 72 h.

2. Functionalization of spindle-shaped α-Fe_2O_3 with organosilane molecules (APTES) to generate an amine-terminated surface.

Mixing 500 µL of APTES with 5 mL of ethanolic solution of α-Fe_2O_3 particles for 12 h under vigorous stirring.

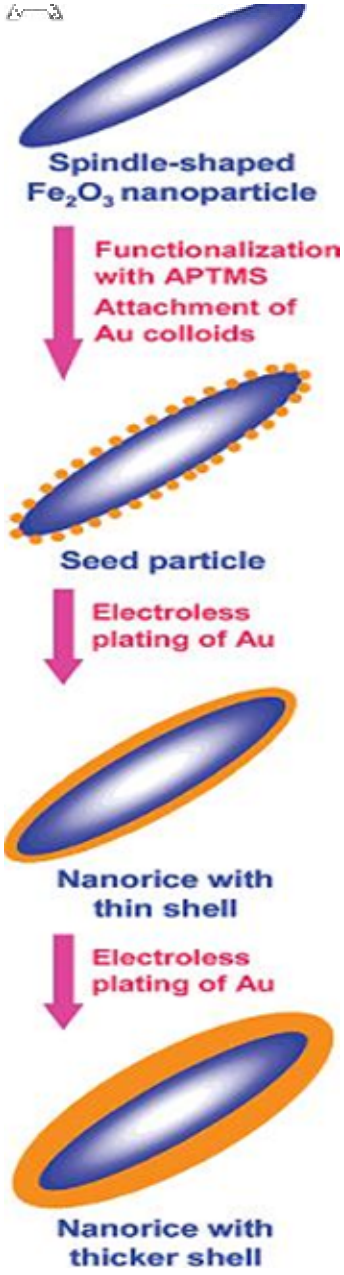
3. These functionalized nanoparticles were decorated with small gold colloid (2-3 nm) (tetrakis hydroxymethyl phosphonium chloride (THPC) capped) prepared by the method reported by Duff et al.

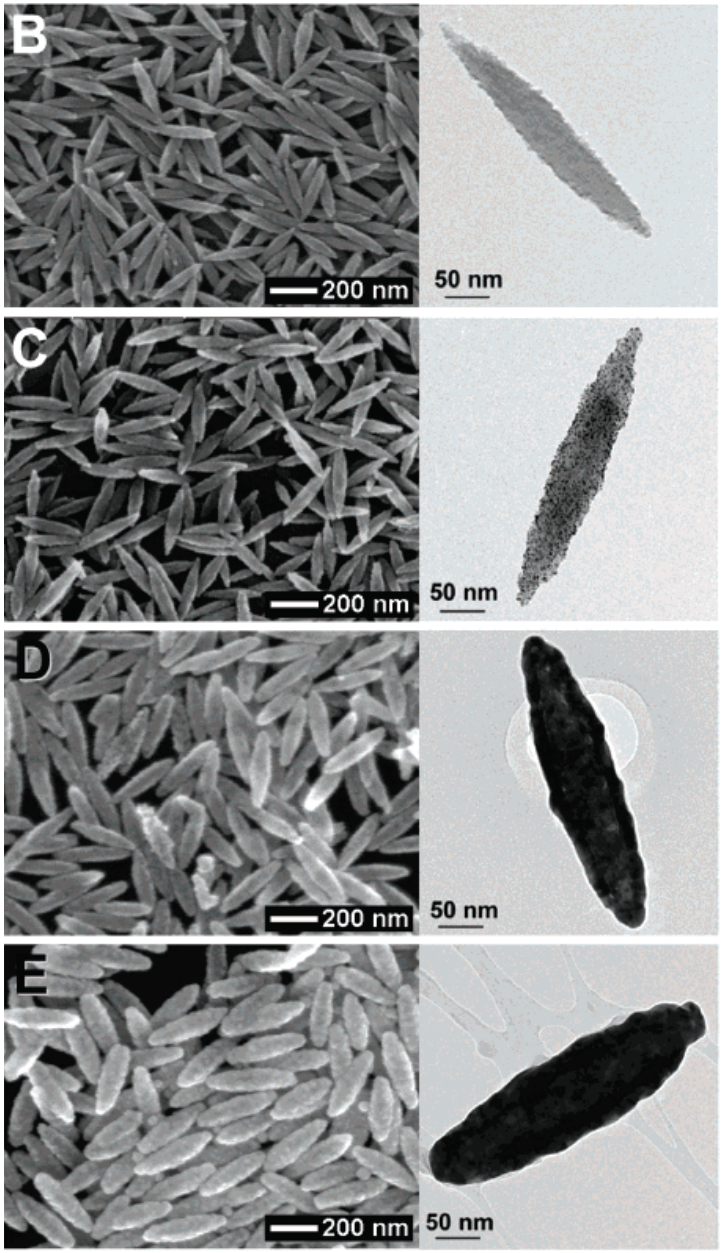
4. Nanorice particles were fabricated via seed-catalyzed reduction of $AuCl_4^-$ ions by formaldehyde in aqueous solutions at room temperature.

Experimental

$FeCl_3$ (2.0 x 10^{-2} M)
+
4 KH_2PO_4 (x 10^{-4} M)

100 °C
72 h.

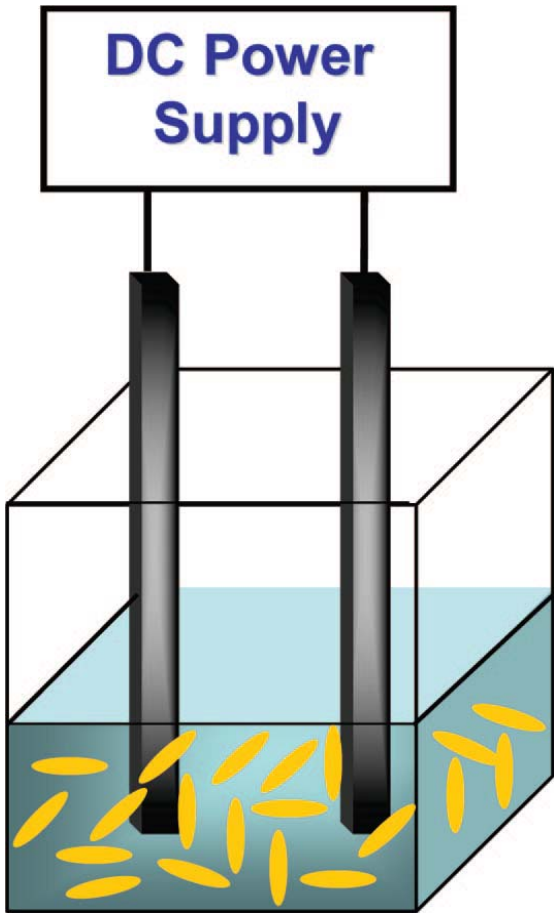




The nanorice particles utilized in these experiments consisted of hematite cores with a longitudinal diameter of 340±25 nm and a transverse diameter of 54± 6 nm, coated with a 22 ± 3 nm Au shell.

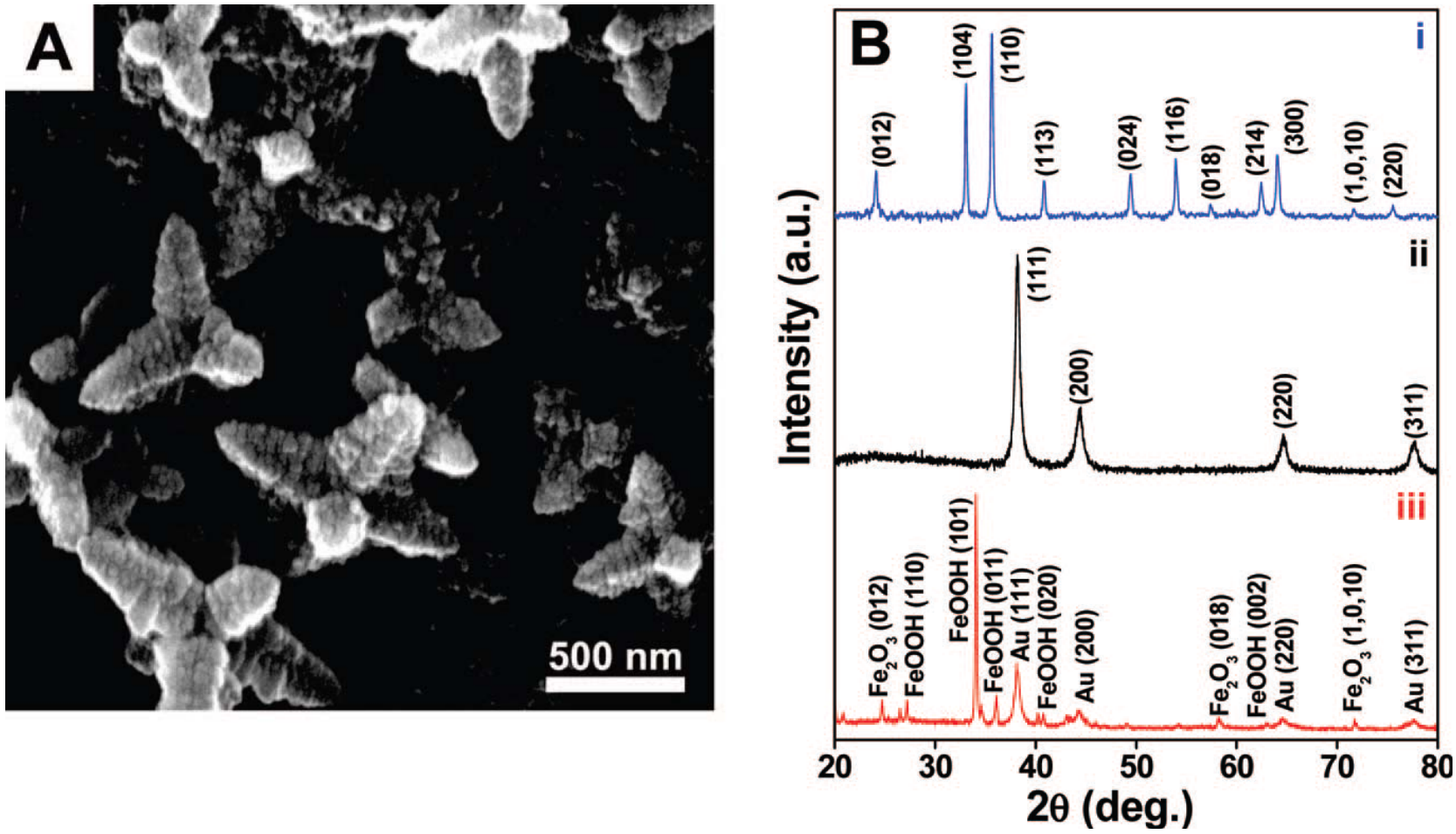
Nano Lett.,**2006,** *6*, 827.

Experimental

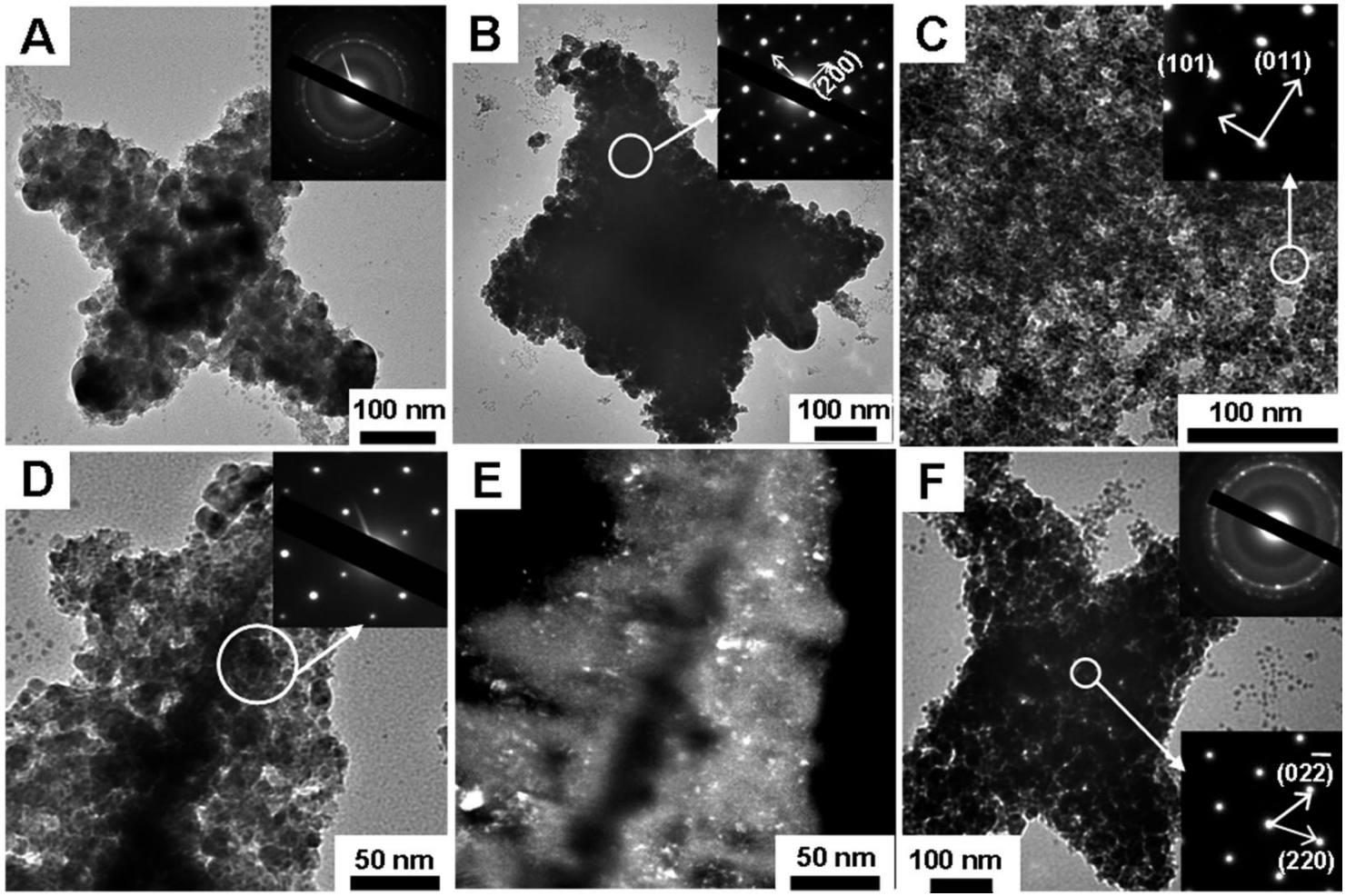


Applied potential --- 5 V
Time --- 24 h

Schematic representation of experimental set-up showing a DC power supply connected between two Pt electrodes (gray bars), separated by 0.014 m, immersed in aqueous Au nanorice solution.

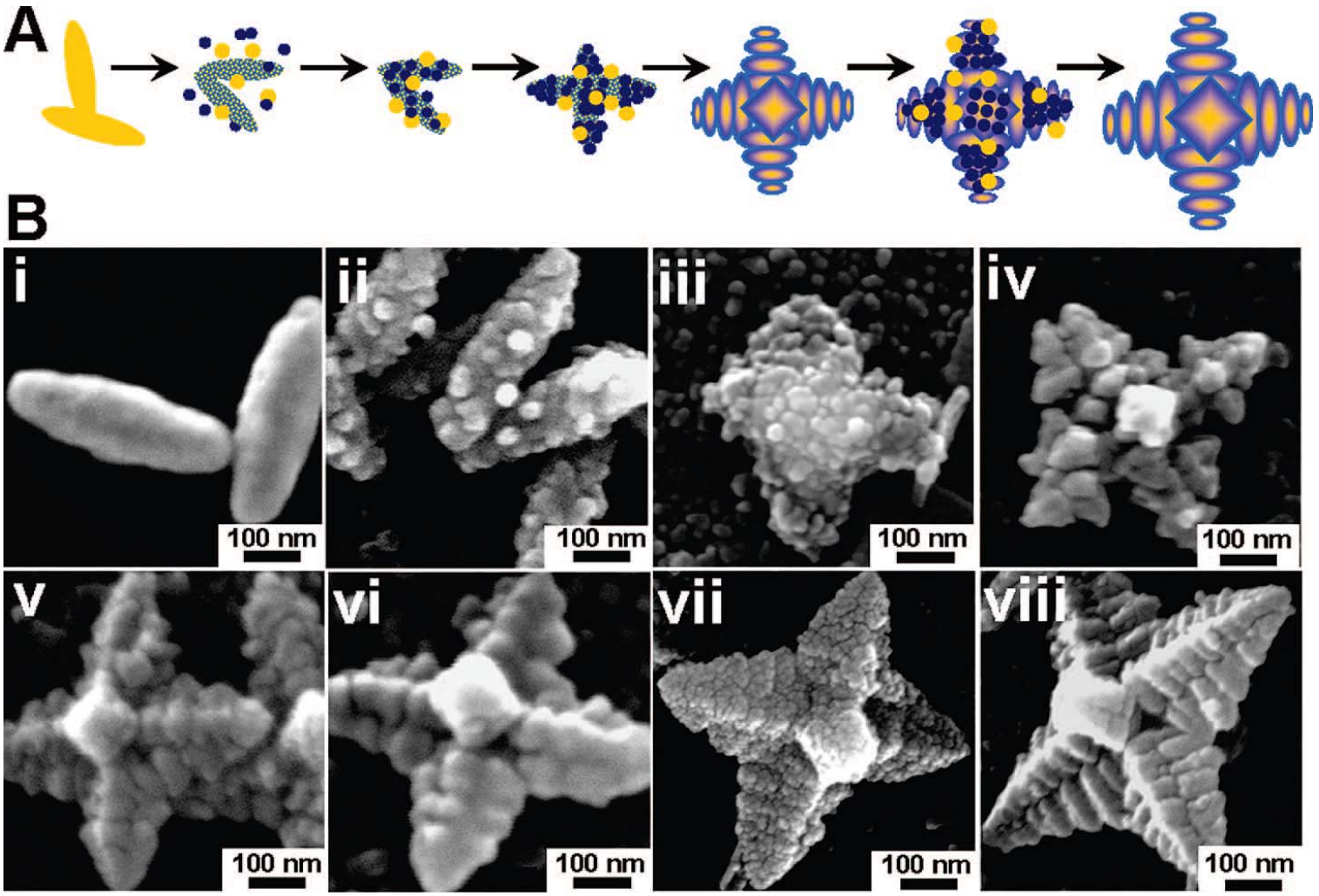


(A) SEM image of Mesostars. (B) XRD spectra of (i) α-Fe_2O_3 cores, (ii) nanorice (showing Au peaks), and (iii) mesostars.



(A) a star-shaped structure obtained after 6 h of electrolysis and ED pattern showing polycrystalline rings provided as inset, (B) a mesostar formed after 24 h of electrolysis and corresponding SAED pattern representing α-FeOOH single crystalline domain, (C) an α-FeOOH nanocrystals observed in solution and SAED pattern showing single crystalline domain, (D) tip of a mesostar and corresponding SAED pattern representing α-FeOOH single crystalline area, (E) dark field image of mesostar tip corresponding to panel D, and (F) mesostar obtained after 24 h of electrolysis

Proposed mechanism



The mesostars were formed in the bulk of solution.

The conversion yield was 50%.

(A) Schematic representation of mesostar formation mechanism. (B) SEM images supporting the mesostar formation mechanism starting with (i) nanorice, (ii) 2 h of electrolysis, (iii) 4, (iv) 6, (v) 8, (vi) 10, (vii) 12, and (viii) 24 h.

$$\text{Cathode}: 2H_2O_{(1)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq)}$$

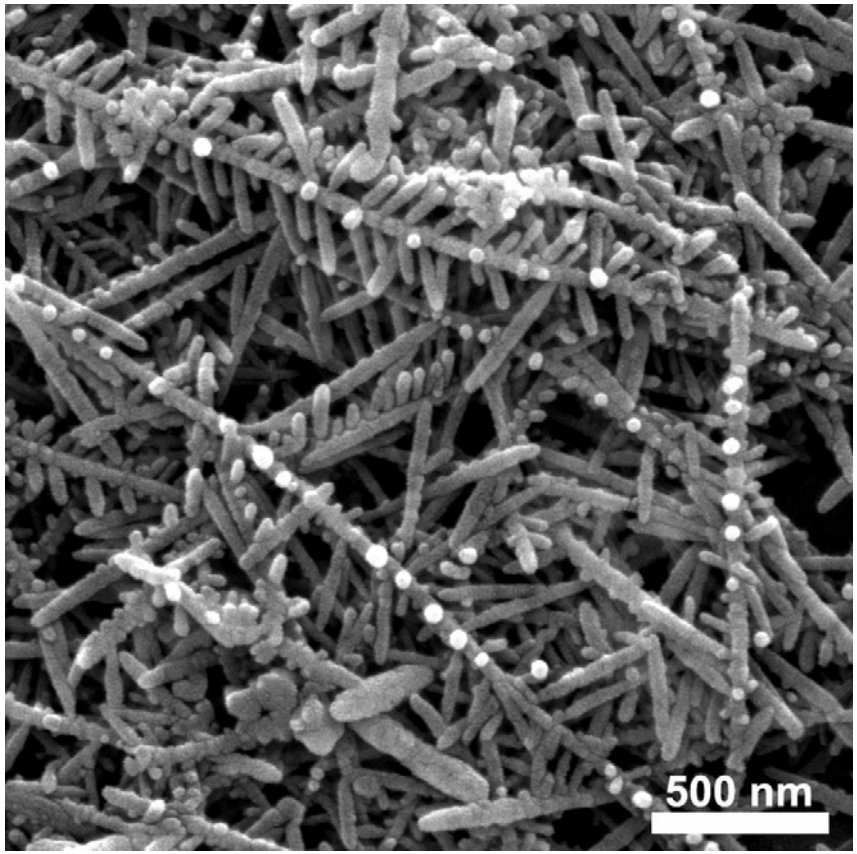
$$E_{red} = 0.00V \quad (1)$$

$$\text{Anode}: 4OH^-_{(aq)} \rightarrow O_{2\,(g)} + 2H_2O_{(1)} + 4e^-$$

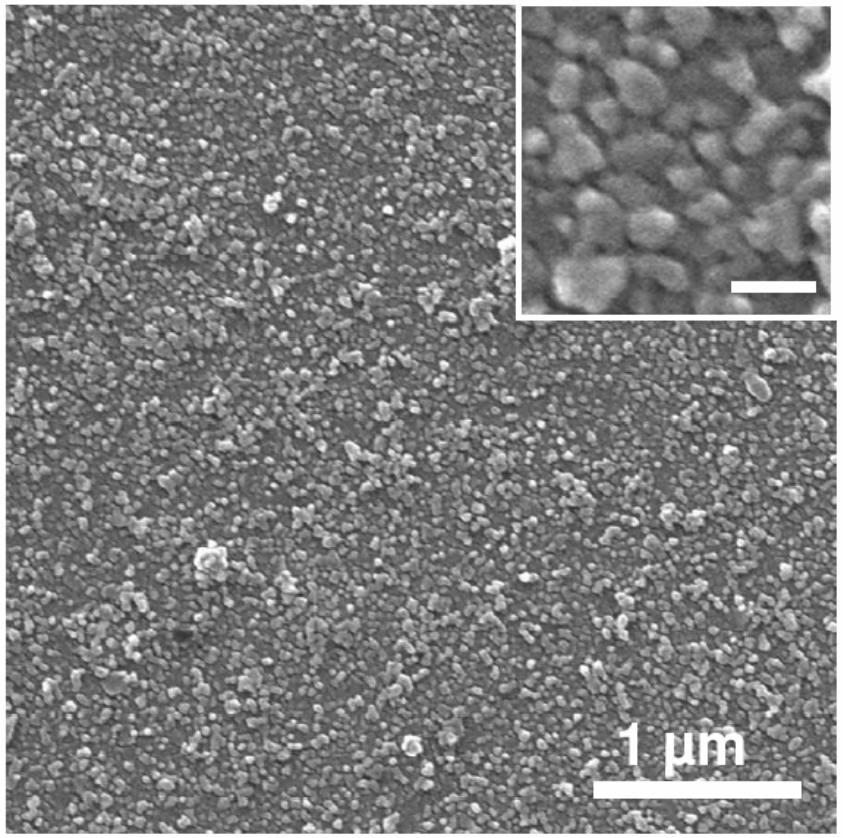
$$E_{ox} = -1.23V. \quad (2)$$

$$2Fe_2O_3 \cdot H_2O + 2OH^- + 2H^+ \rightarrow 4FeOOH + O_2 + 2H_2 \quad (3)$$

The formation of mesostars could have occurred because of the assembly of FeOOH nanocrystals along the most convenient polarizable axis in the DC-field as well as the weak interparticle magnetic interaction between the FeOOH nanocrystals.

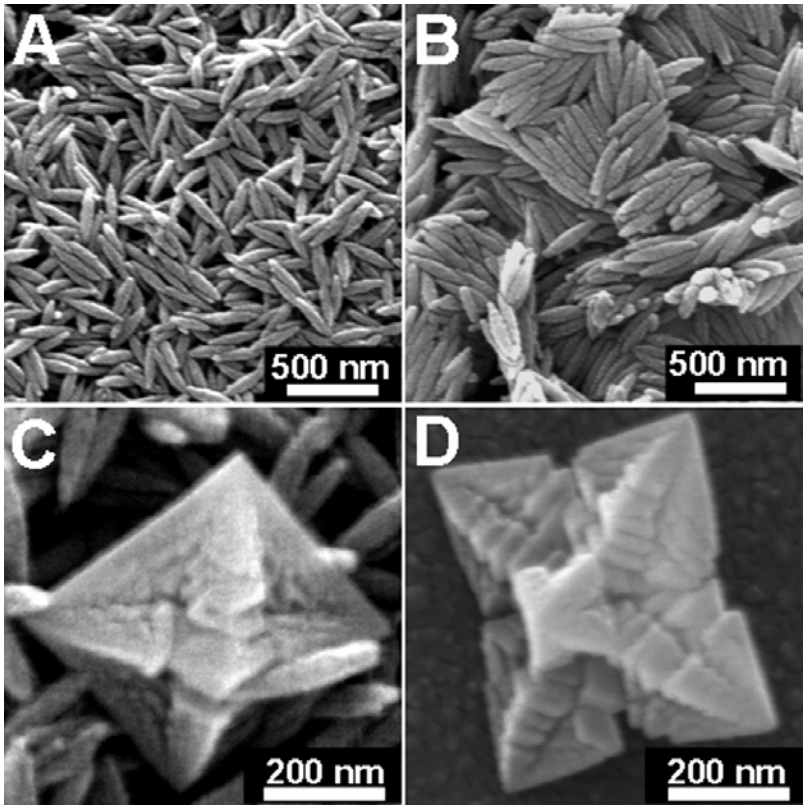


SEM image of long chain branched structures obtained at 5 V in addition to the mesostars

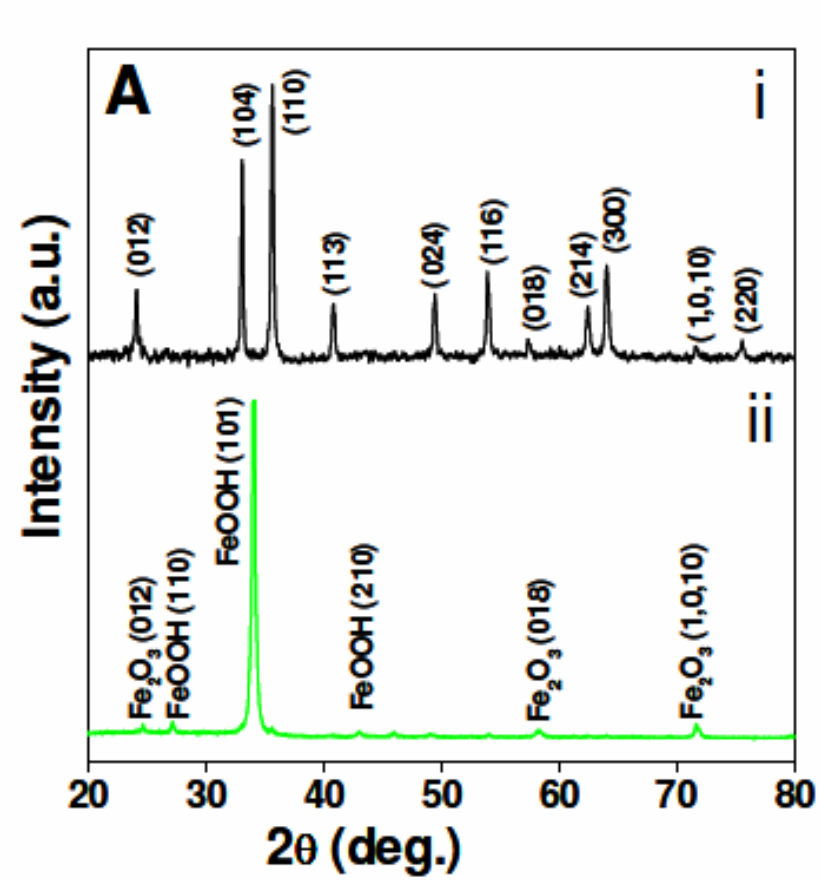


SEM image of one electrode utilized in the electrolytic cell is shown

Role of Au



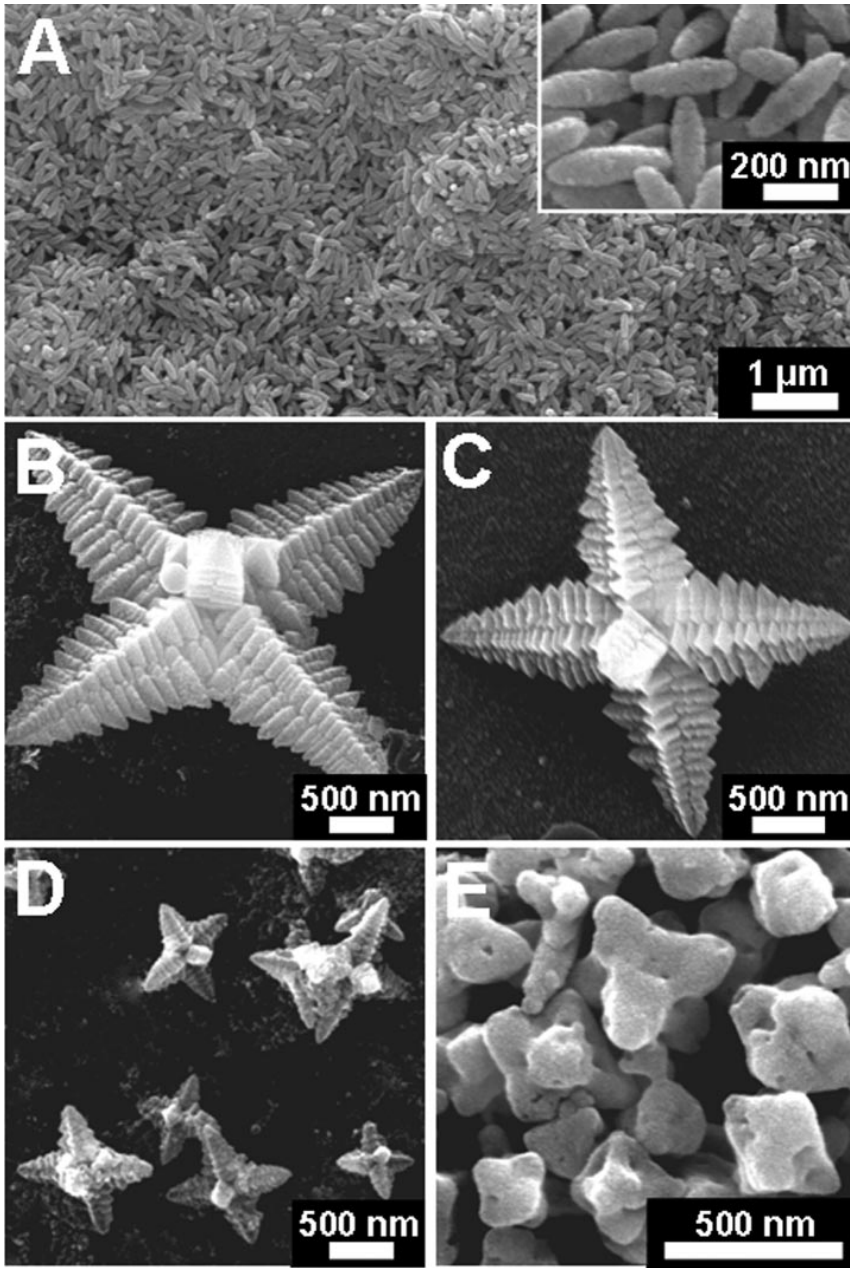
SEM images of (A) α-Fe_2O_3 cores, (B) assembled α-Fe_2O_3 cores formed after 10 hrs of applying 5 V, (C) pyramidal mesostructures formed after 14 hrs, (D) larger pyramidal mesostructures formed after 24 hrs



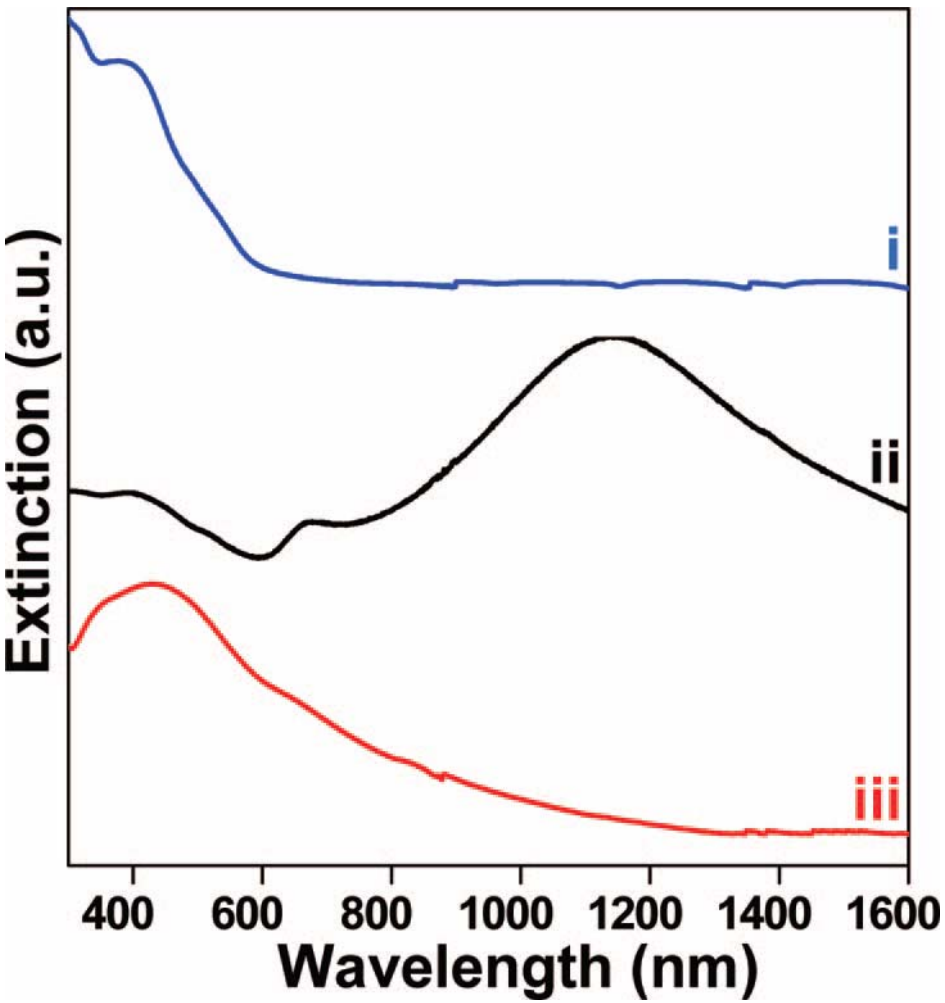
(A) XRD spectra of (i) α-Fe_2O_3 cores, and (ii) pyramidal mesostructures.

Au shell may act as a direct agent in initiating nucleation sites for mesostar formation.

Role of applied voltage



SEM images of mesostructures obtained by varying the voltage while keeping electrolysis time constant at 24 h: (A) aggregated nanorice formed at 0.5 V (B) stars at 2 V; (C) stars obtained at 3 V; (D) mesostars observed at 5 V; and (E) distorted stars observed at 10 V.



Extinction spectra of (i) α-Fe2O3 cores with λ_{max} 390 nm, (ii) nanorice particles with longitudinal plasmon λ_{max} 1100 nm and transverse plasmon max 650 nm, and (iii) mesostars with λ_{max} 430 nm.

Conclusions

❖ Observed the unusual formation of hierarchical mesostars *via* electrolysis of an aqueous suspension of nanorice particles.

❖ The Au α-Fe_2O_3 nanorice particles self-assembled into fractal mesostructures composed of α-Fe_2O_3, α-FeOOH, and Au.

❖ The nucleation of α-FeOOH nanoparticles, followed by oriented attachment of primary particles along specific crystallographic planes is the reason for the formation of the mesostars.

❖ Nanorice particles and mesostars strongly indicate that electrolysis can significantly alter the morphology and constituent material of the nanostructures.

Thanks