Nano Malzemeler
Aşağıdan Yukarı Üretim

Nanomalzemelerin Üretimi

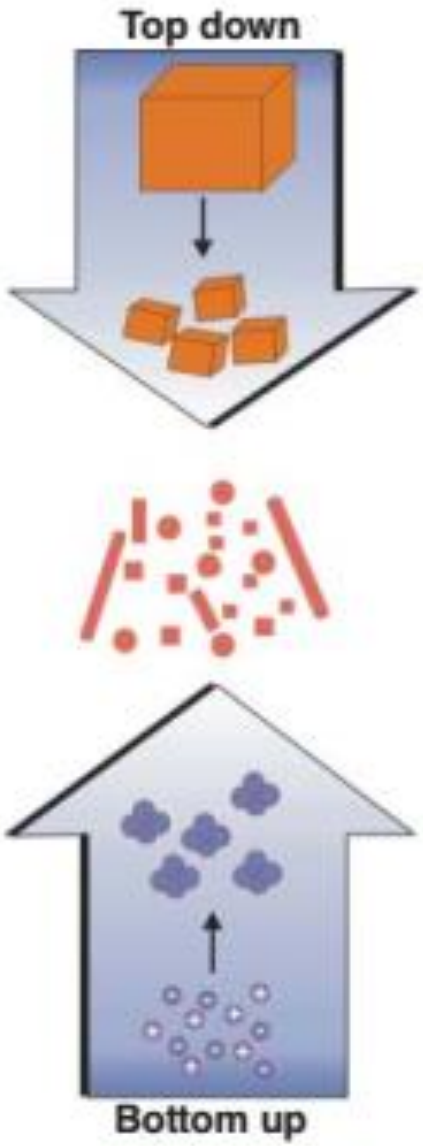


Figure 2.1 "Top-down" and "bottom-up" approaches for the synthesis of nanomaterials.

Aşağıdan Yukarı Üretim (Bottom-Up)

Kimyasal buhar biriktirme (chemical vapor deposition, CVD)
Kimyasal buhar yoğunlaştırma (chemical vapor condensation, CVC)
Moleküler ışın epitaksisi (molecular beam epitaxy, MBE)
Arklı plazma (Plasma Arcing)

Islak kimyasal yöntemler (Wet chemical methods)

- Yer değiştirme reaksiyonları
- Kimyasal indirgeme yöntemi
- Hidrotermal/Solvotermal yöntemler
- Tersinir tanecik yöntemi
- Sol-gel
- Sonokimyasal yöntem
- Biyomimetrik yöntemler

Kimyasal Buhar Biriktirme (CVD)

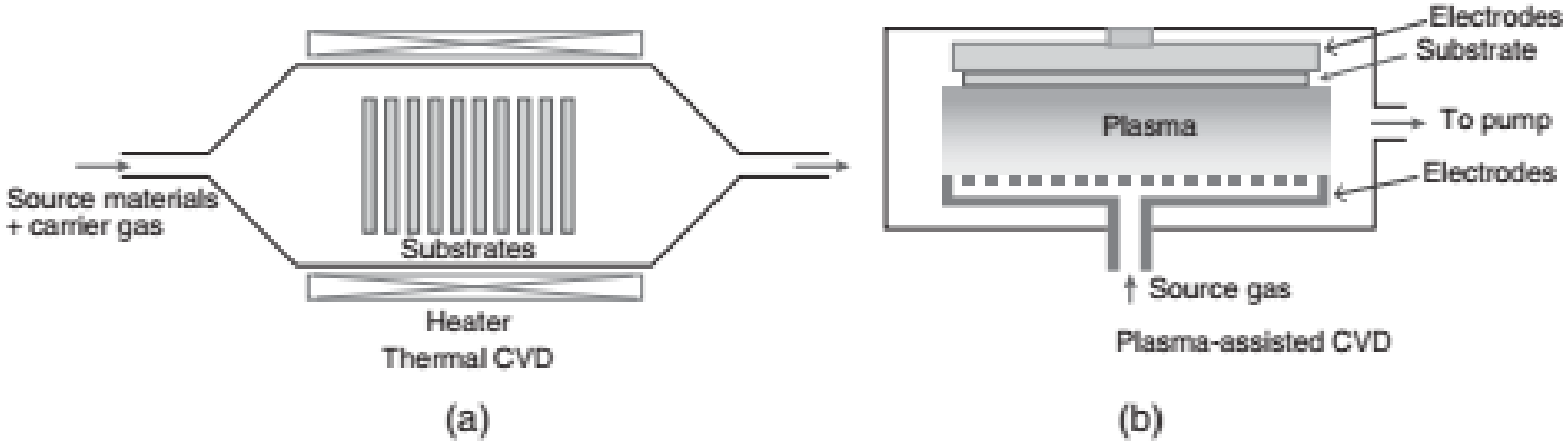


Figure 2.12 Schematic representation of chemical vapor deposition: (a) thermal and (b) plasma assisted. From Ref. [14].

Gazın parçalanması ısı etkisiyle ve/veya plazma ile yapılabilmekte
CVD, PVD gibi yöne bağlı olmayan ya da gördüğü yeri kaplama gibi bir dezavantaj içermemektedir.
Plazma ile gerçekleşen proses, proses sıcaklığının düşmesine yardımcı olmaktadır.

Kimyasal Buhar Biriktirme (CVD)

Silisyum nitrür: entegre devrelerde yalıtkan ve kimyasal bariyer olarak kullanılmaktadır.
İnce film silisyum nitrür yüksek hidrojen içerirse (%8), iç yapıda oluşan yüksek çekme gerilmeleri kaplamanın altlıktan ayrılmasına neden olabilir.
Silisyum nitrür, bu ölçeklerdeki diğer izolasyon malzemelerine göre en yüksek direnç ve dielektrik dayanımına sahiptir.

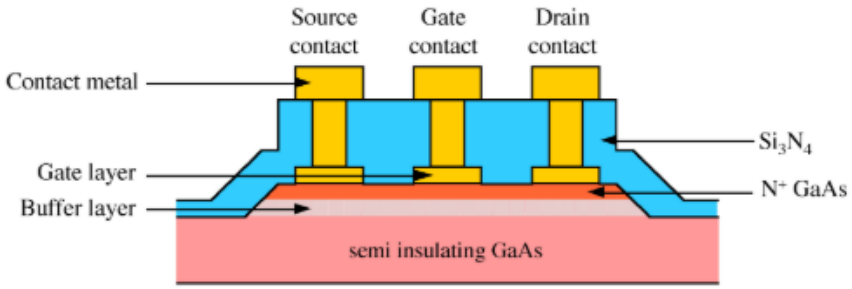


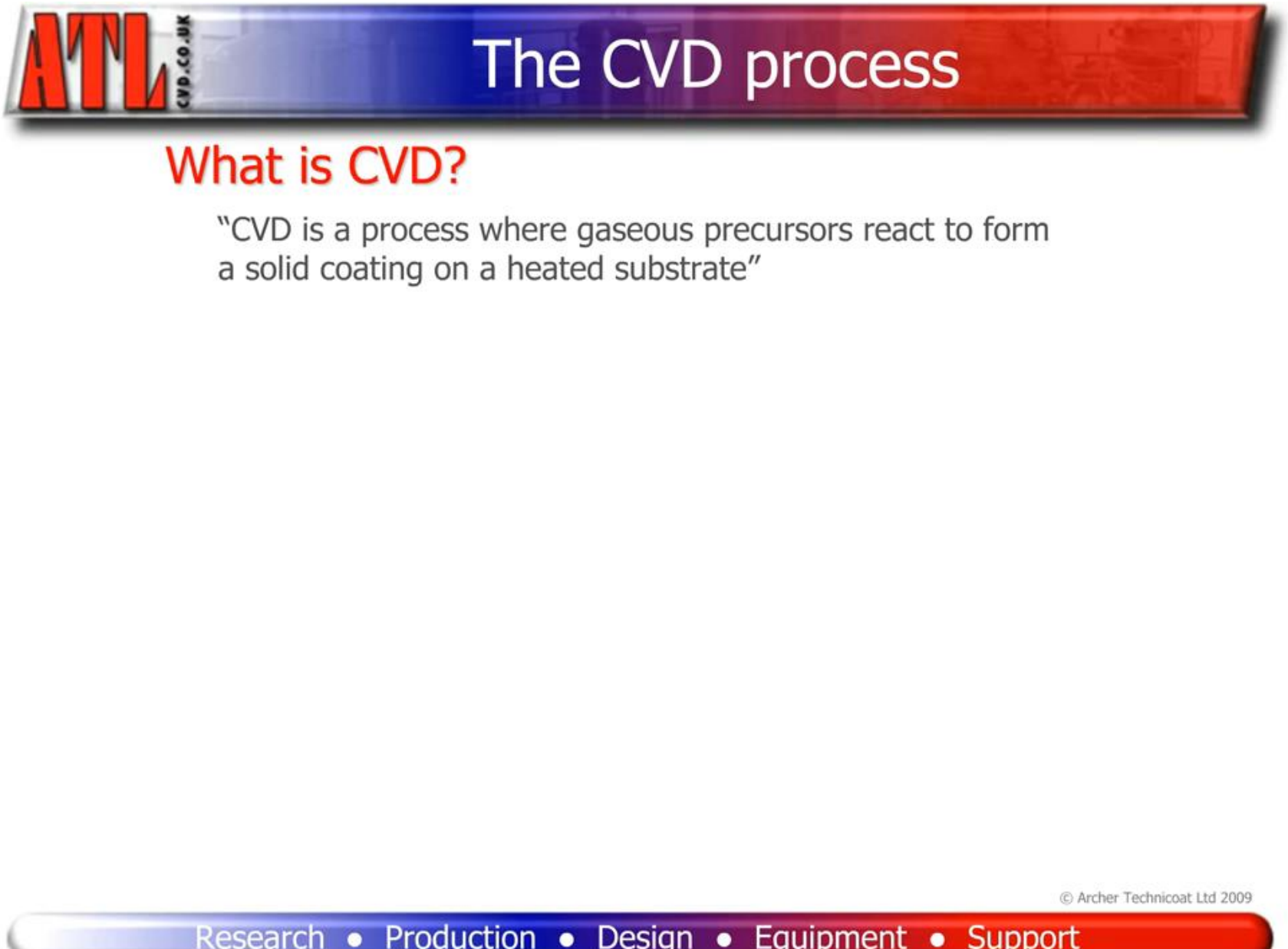
Figure 1. Schematic diagrams of a GaAs metal-semiconductor field effect transistor (MESFET). Adapted from A. R. Barron, in *CVD of Nonmetals*, Ed. W. S. Rees, Jr., Wiley, NY (1996).

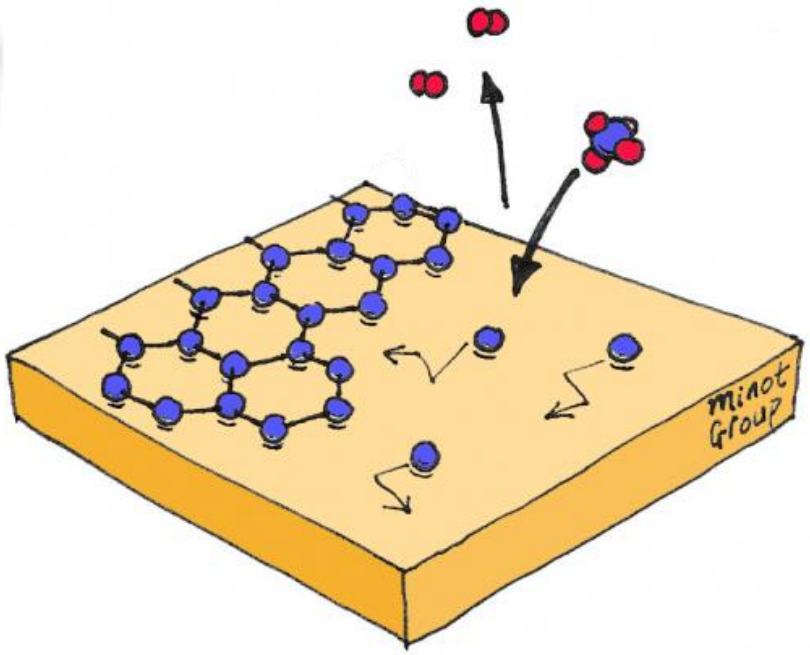
Deposition	LPCVD	PECVD
Growth temperature (°C)	700 - 800	250 - 350
Composition	$Si_3N_4(H)$	SiN_xH_y
Si/N ratio	0.75	0.8 - 1.2
Atom% H	4 - 8	20 - 25
Dielectric constant	6 - 7	6 - 9
Refractive index	2.01	1.8 - 2.5
Resistivity (Ω.cm)	1016	106 - 1015
Band gap (eV)	5	4 - 5

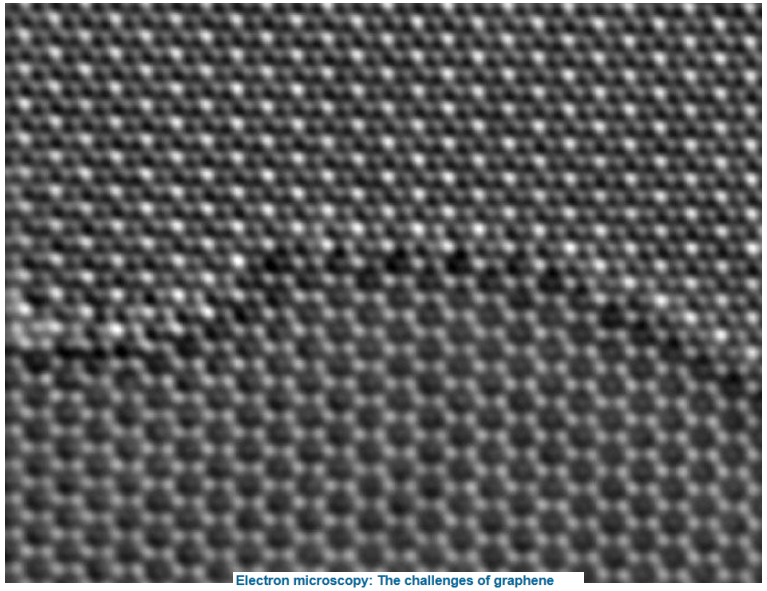
$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$$

$$3SiCl_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$

Kimyasal Buhar Biriktirme (CVD)

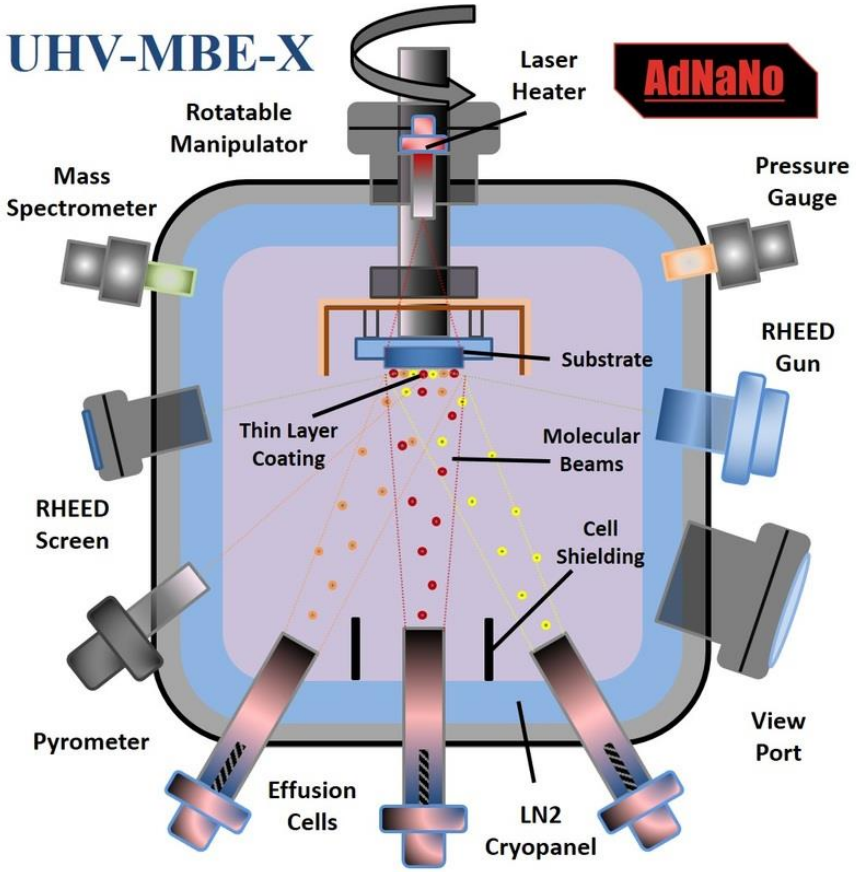






Electron microscopy: The challenges of graphene
Knut W. Urban
Nature Materials **10**, 165–166 (2011) | doi:10.1038/nmat2964

Moleküler Işın Epitaksisi (MBE)



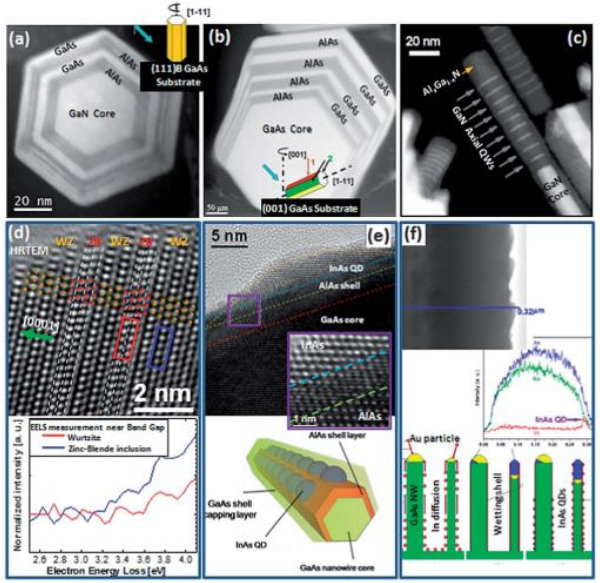
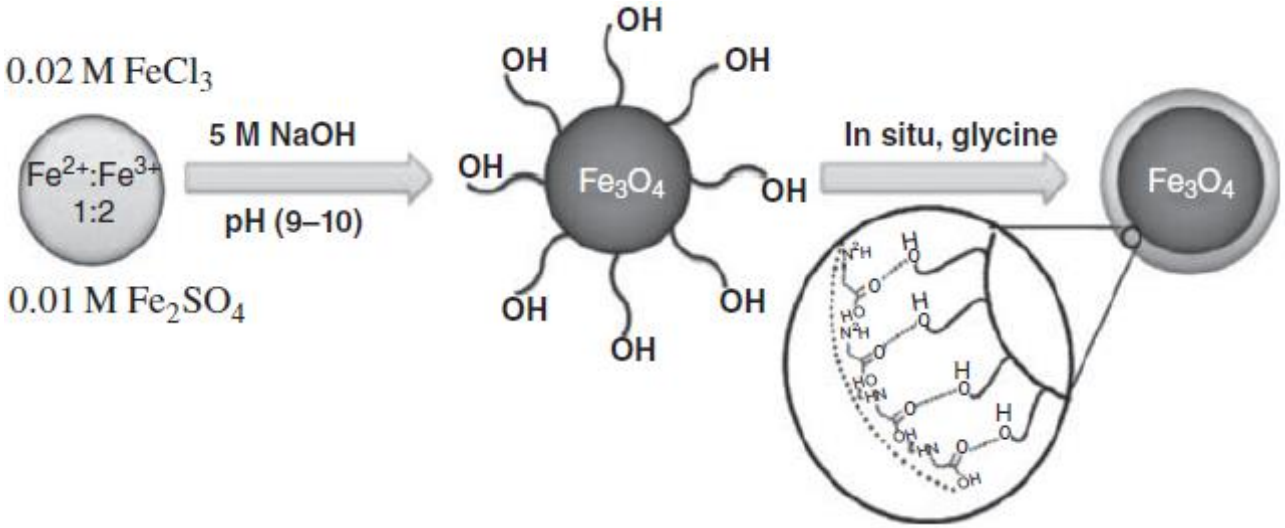


Fig. 1 (a) Radial MQWs in a multishell GaAs–AlAs grown on (111)B GaAs. (b) Radial MQWs in a multishell GaAs–AlAs grown on (001)GaAs. (c) Axial GaN QWRs separated by $Al_xGa_{1-x}N$ barriers in GaN–$Al_xGa_{1-x}N$ NWs. Copyright 2011 by the American Physical Society.[31] e-Tomography HAADF STEM reconstructed models of the radial and axial QWs can be also found elsewhere.[29,32] (d) ZB domains within a WZ GaN NW, acting as QWs. (e) InAs QD on the surface of a {110}-faceted GaAs–AlAs NW. Adapted with permission from ref. 92. Copyright 2010 American Chemical Society. (f) InAs QDs on the surface of a {112}-faceted GaAs–AlAs NW. Reprinted with permission from ref. 93. Copyright 2012 American Chemical Society.

- ✓ Yüksek vakumda, molekül demetinin ısıtılmış altlık üzerinde tek kristal olarak biriktirilmesi
- ✓ Tek bir atomik katman birikim yapabilme
- ✓ Kristal büyümesinin ve kontaminasyonun yüksek kontrolü
- ✓ LED, lazer diyotları, transistörler, bilgisayarlarda okuma/yazma parçalarının uçları…

Yerdeğiştirme reaksiyonları



Box 2.4 Synthesis of metal chalcogenides.

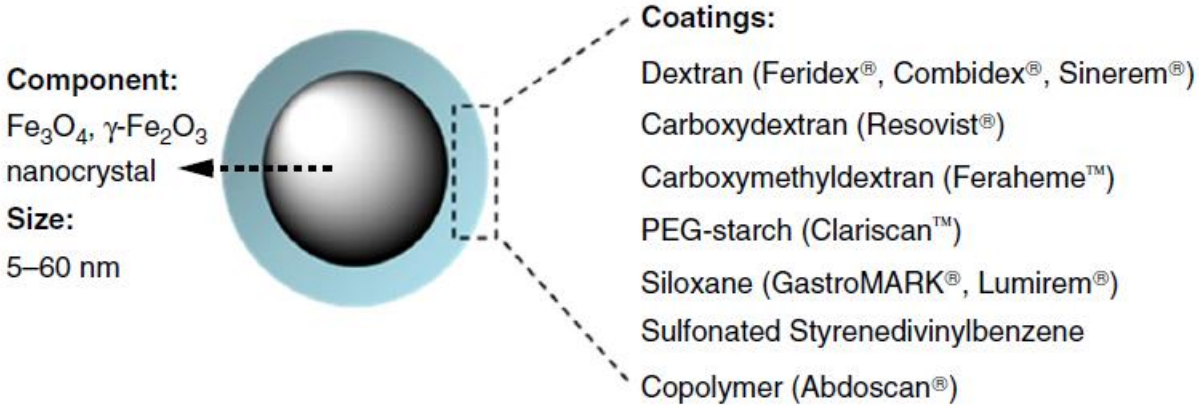
Chalcogen is added to the metal precursor solution in a hot coordinating solvent.

CdE (E = S, Se or Te) NPs: Chalcogen is added to the Cd precursor (dimethyl Cd, Cd oxide, carbonate, or acetate) in a hot coordinating solvent (e.g., tri-*n*-octylphosphine oxide, TOPO). High temperature is maintained for fast particle nucleation followed by lowering the temperature for slow particle growth.

Doped ZnS NPs: ZnS nanophosphors doped with halides, Cu^{+}-halides, Cu^{+}-Al^{3+}, Cu^{+}-Al^{3+}-Mn^{2+}, or Mn^{2+} can be prepared by the colloidal precipitation method at room temperature.

In a typical synthesis, aqueous copper(II) acetate solution is added to aqueous $ZnSO_4$ solution; to the resulting Zn^{2+}-Cu^{2+} precursor, Na_2SO_3 is added; SO_2 gas generated during this process reduces Cu^{2+} to Cu^{+}; and followed by the addition of solution of Mn^{2+}/Al^{3+}/F^{-}/Cl^{-}/Br^{-}/I^{-}) and PVP solution. Finally, Na_2S solution is added, leading to the precipitation of doped ZnS nanoparticles.

Superparamagnetic Iron oxide nanoparticles: clinically approved or in clinical test



- ✓ **Partikül boyutu, partikül dağılımı, kristalinite, morfolji kontrolü yüksek**
- ✓ **Konsantrasyon, sıcaklık, pH, zaman, eklenen diğer reaktantlar prosesi doğrudan etkilemekte**
- ✓ **Partiküllerin müyüme mekanizması çoğunlukla difüzyon veya Ostwald olgunlaşması ile gerçekleşmekte**
- ✓ **Metal oksiteler, metal kalkojenitler, netalik nanopartiküller üretmek mümkün**

Yer değiştirme reaksiyonları

WARNING:

This experiment uses toxic and carcinogenic reagents and directly handles extremely hot liquids. Gloves, protective clothing and a fume hood should be used. This should be performed by, or under the direct supervision of, an experienced chemist.

Kimyasal indirgeme reaksiyonları

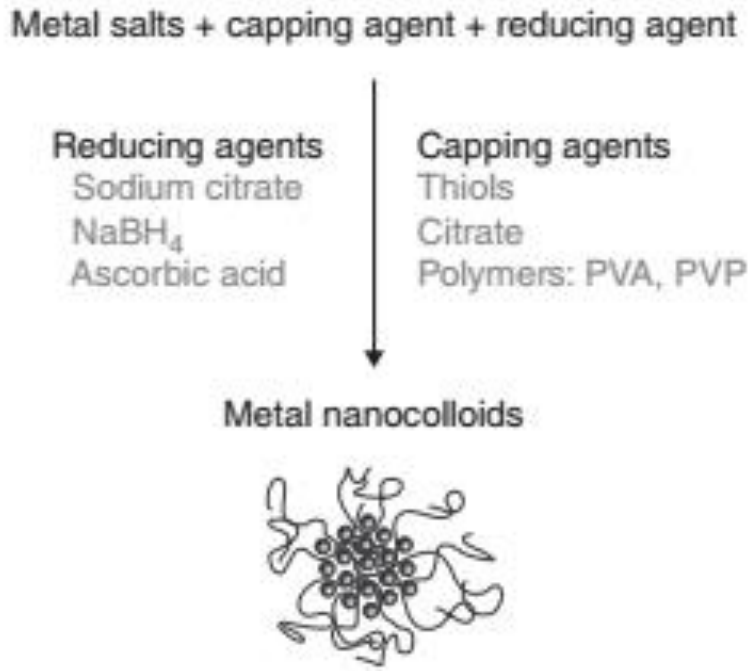


Figure 2.13 Schematic representation of chemical reduction method for nanosynthesis.

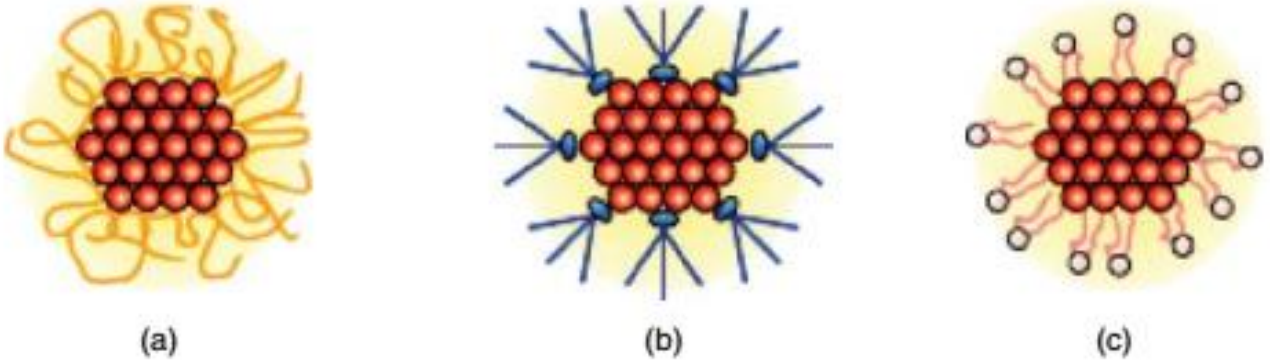
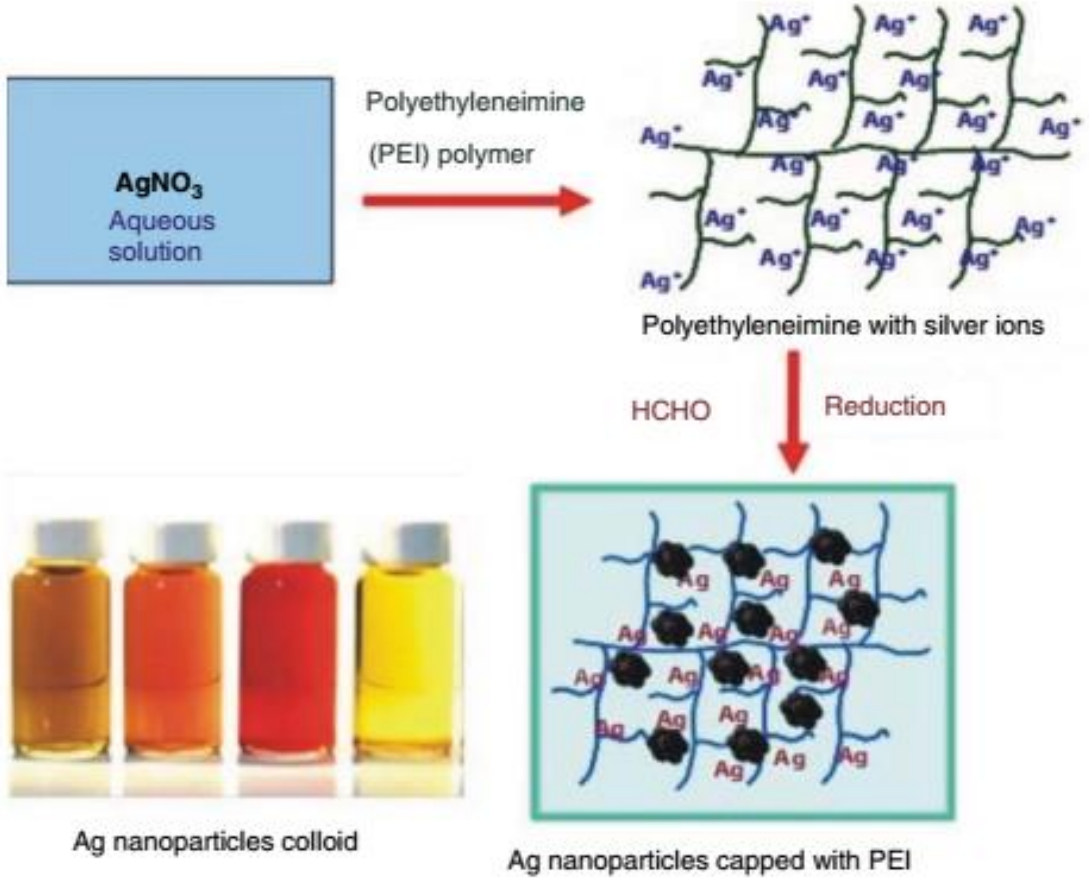


Figure 2.14 Schematic representation different capping agents (a) polymer; (b) organic ligand, and (c) micelle. (*See color plate section for the color representation of this figure.*)

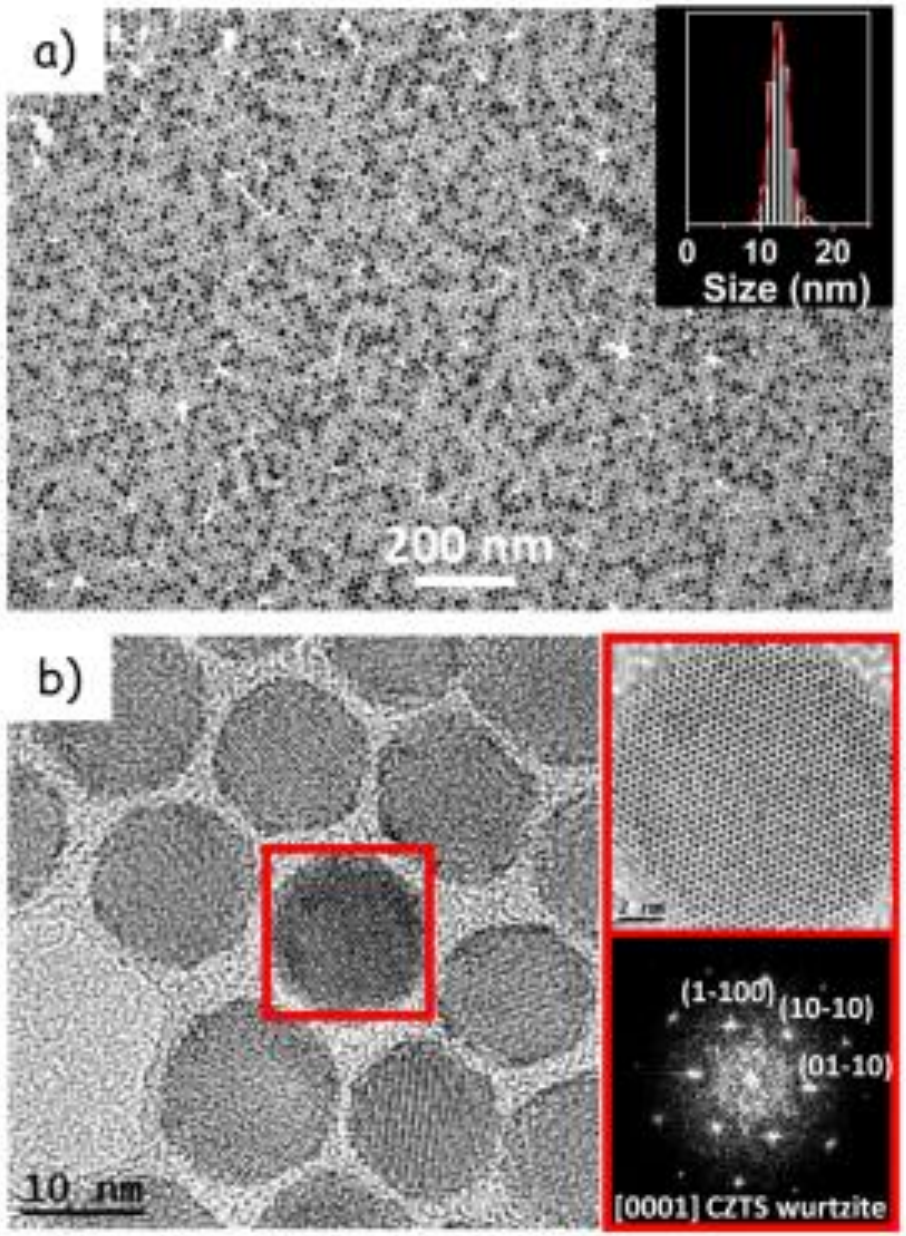
Kimyasal indirgeme reaksiyonları

Box 2.6 Preparation of silver nanoparticles.

In a typical synthesis, 0.85 g of $AgNO_3$ was dissolved in 100 ml of aqueous solution of 0.85 wt% polyethyleneimine (PEI, M_w 600,000–1,000,000) and homogenized by stirring for 2 min. It is followed by the addition of 1 ml of 35% solution of formaldehyde and mixing the resultant solution well. Light yellow color appeared after 2 min, indicating the nucleation and growth of Ag NPs.



Box 2.6 Preparation of Ag NPs by reduction method. Manoth et al. [16] © 2008. With permission of Elsevier. (*See color plate section for the color representation of this figure.*)



Kimyasal indirgeme reaksiyonları

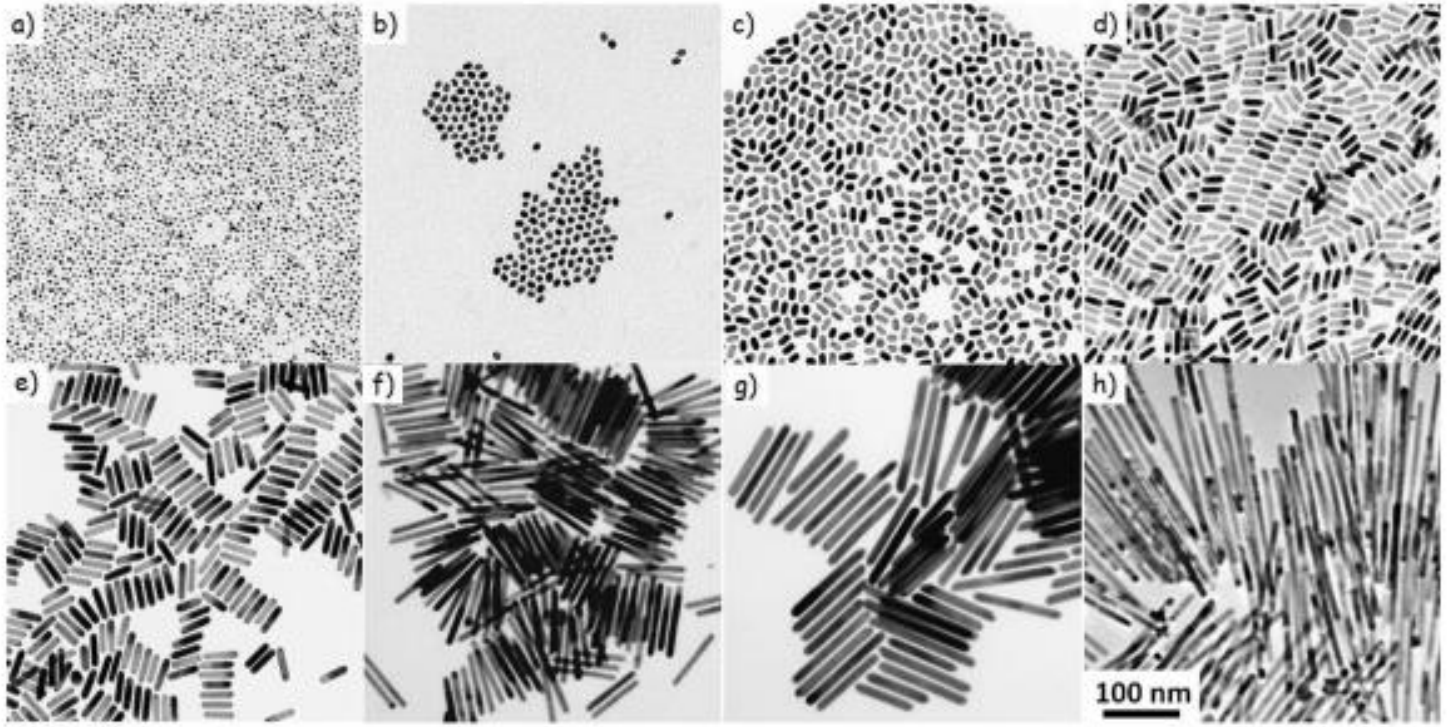
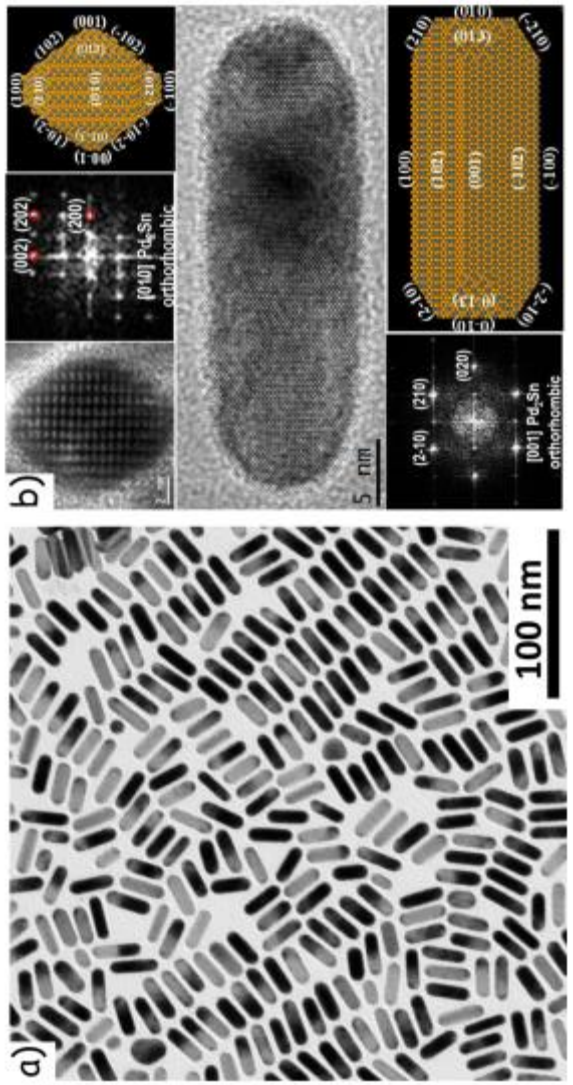
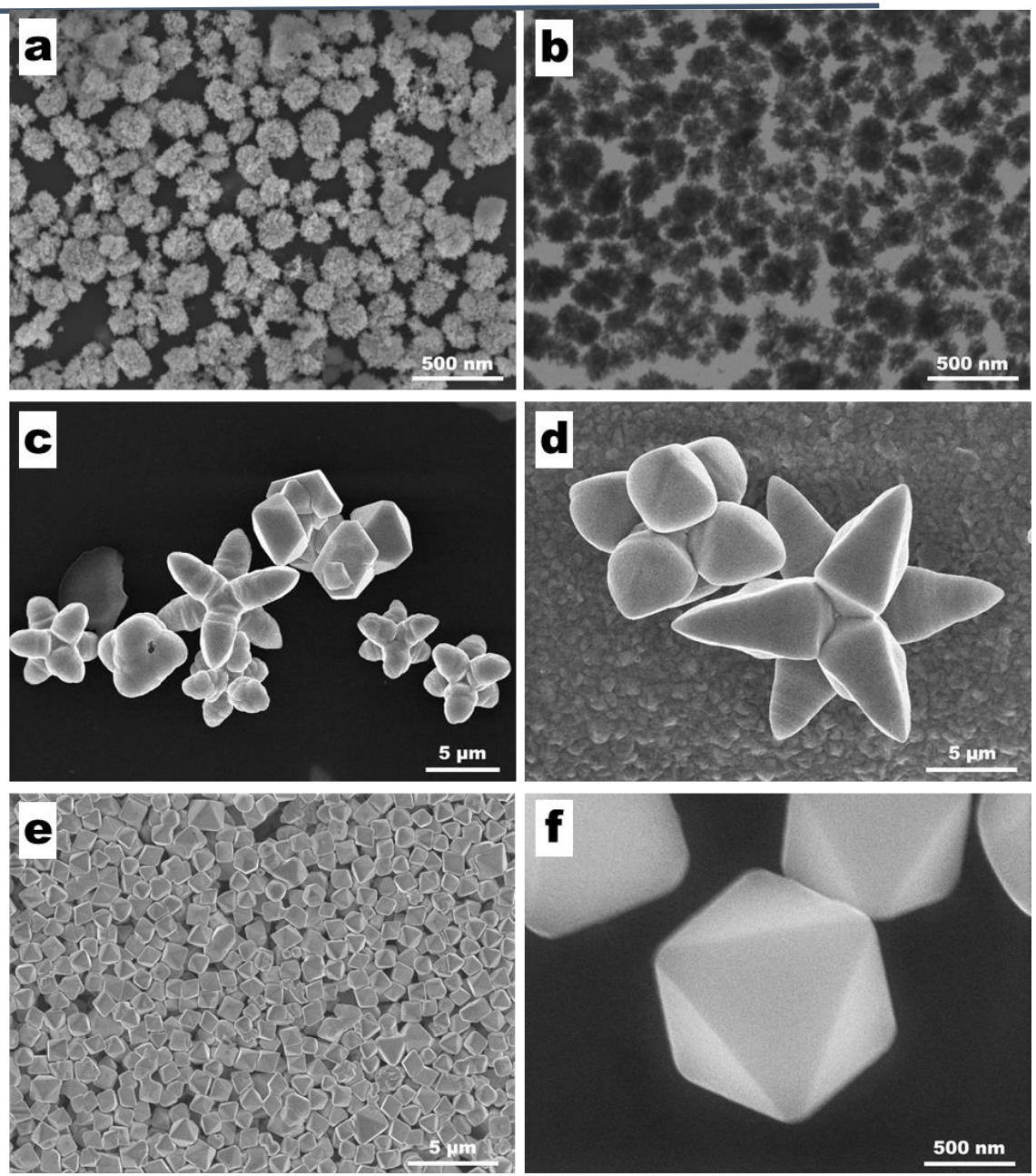


Figure 2. TEM micrographs of Pd_2Sn NPs with different aspect ratios (AR): (a) 4.3 ± 0.2 nm, AR = 1; (b) 9 ± 1 nm × 6.8 ± 0.6 nm, AR = 1.3; (c) 15 ± 1 nm × 7 ± 1 nm, AR = 2.1; (d) 24 ± 2 nm × 7 ± 1 nm, AR = 3.4; (e) 44 ± 4 nm × 10 ± 2 nm, AR = 4.4, (f) 98 ± 8 nm × 9 ± 1 nm, AR = 10.8; (g) 130 ± 10 nm × 24 ± 4 nm, AR = 5.4; and (h) 290 ± 20 nm × 12 ± 3 nm, AR = 24.2.



Hidrotermal Sentez

Hidrotermal Sentez İçin Otoklav Ekipmanları

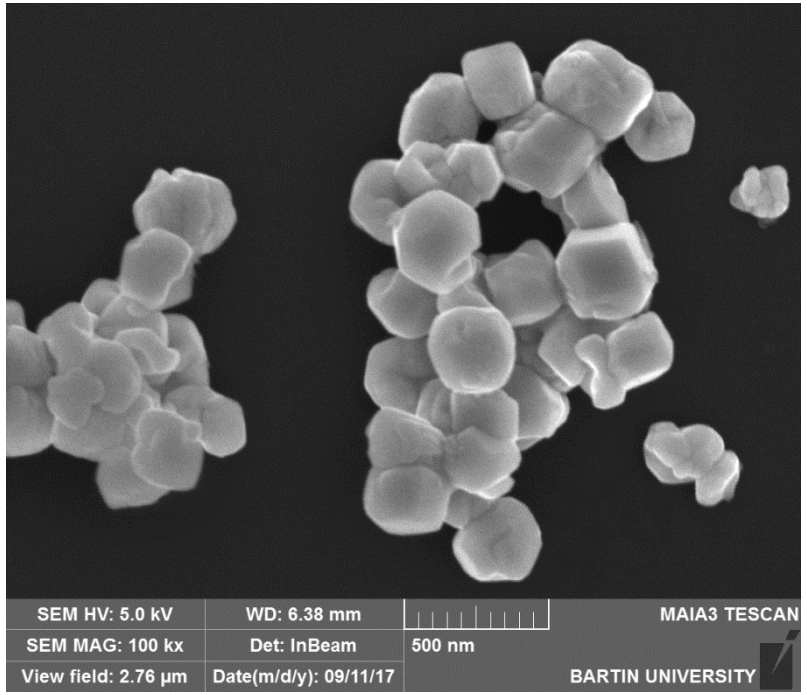


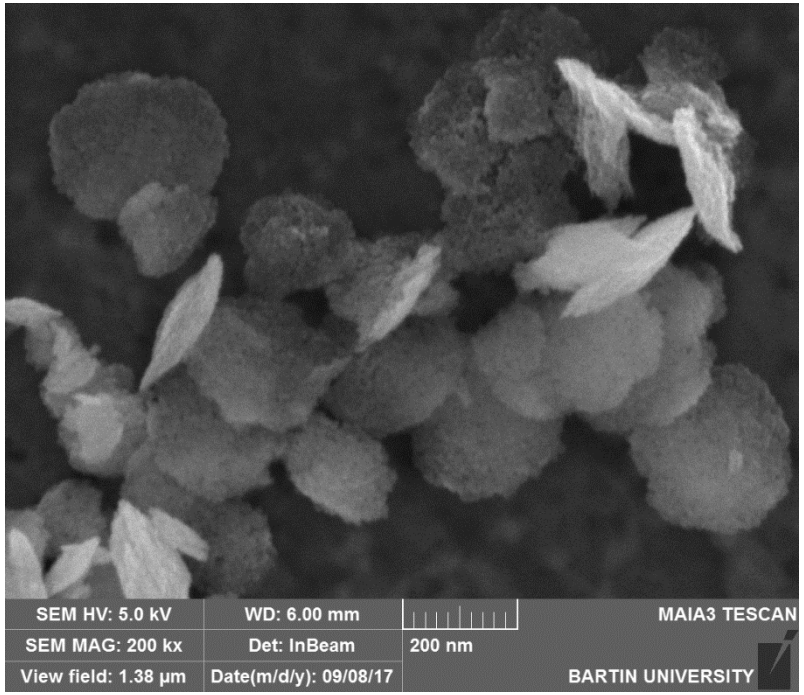
Ortam sıcaklığından yüksek sıcaklık ve ortam basıncından yüksek basınçlarda gerçekleşen sentez işlemine hidrotermal sentez denir.

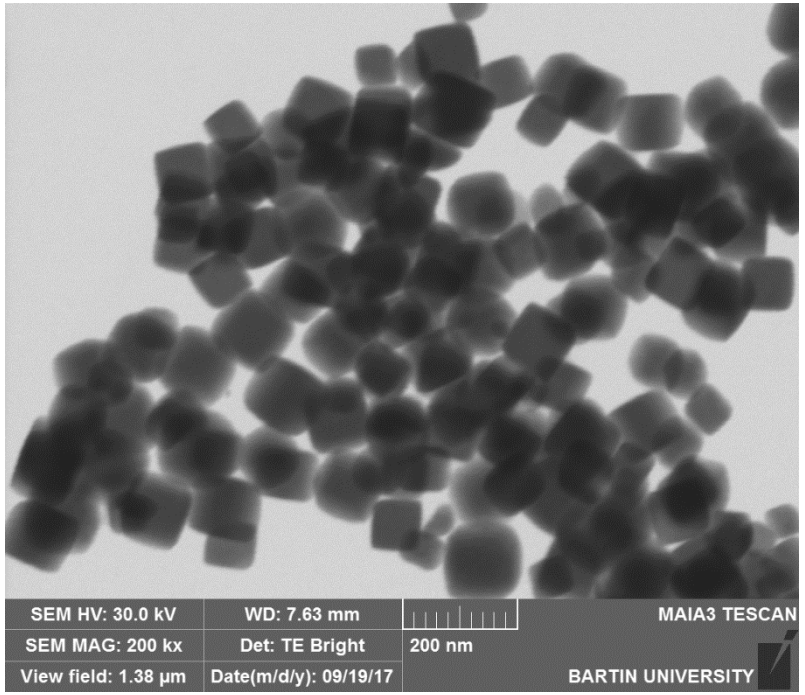
- ✓ Çözeltinin elektrik iletkenliğinde çok yüksek artış
- ✓ Yoğunluğundaki yüksek düşüş
- ✓ Madde taşınımının çok kolay ve hızlı olması
- ✓ Yüksek kristalinite ve tek kristal

Hidrotermal Sentez

Hidrotermal yöntem ile sentezlenmiş hematit nanoyapılar







Sol-Jel Yöntemi

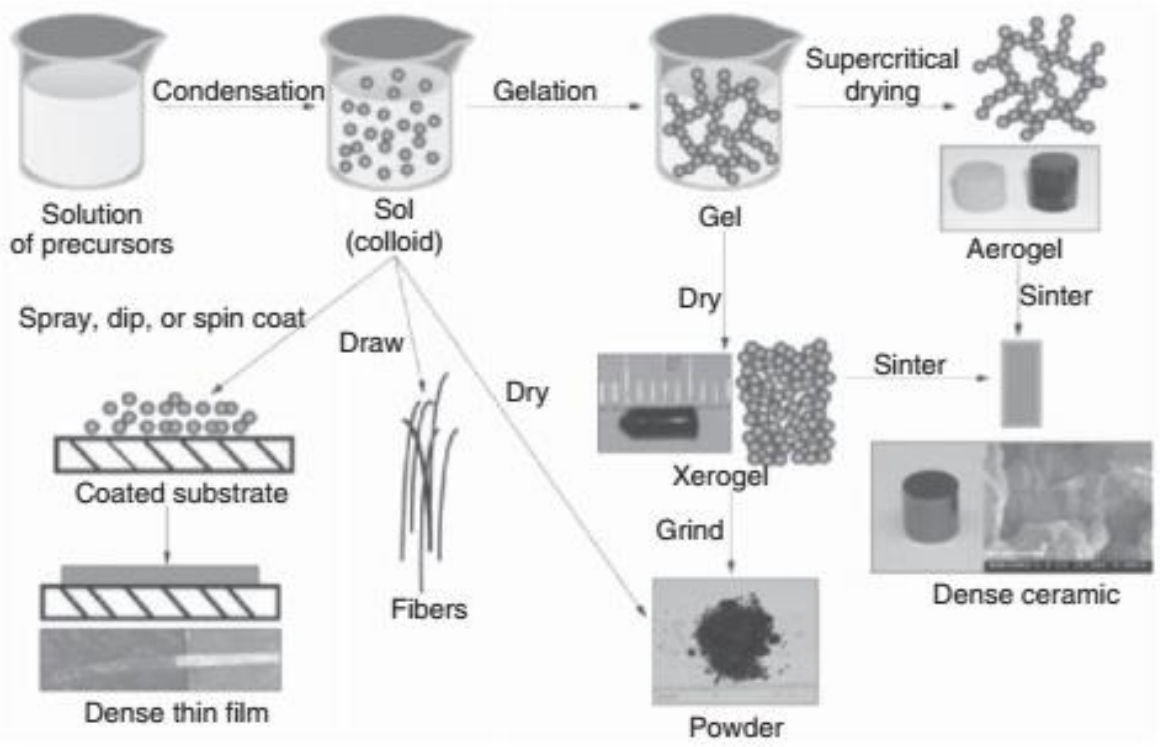
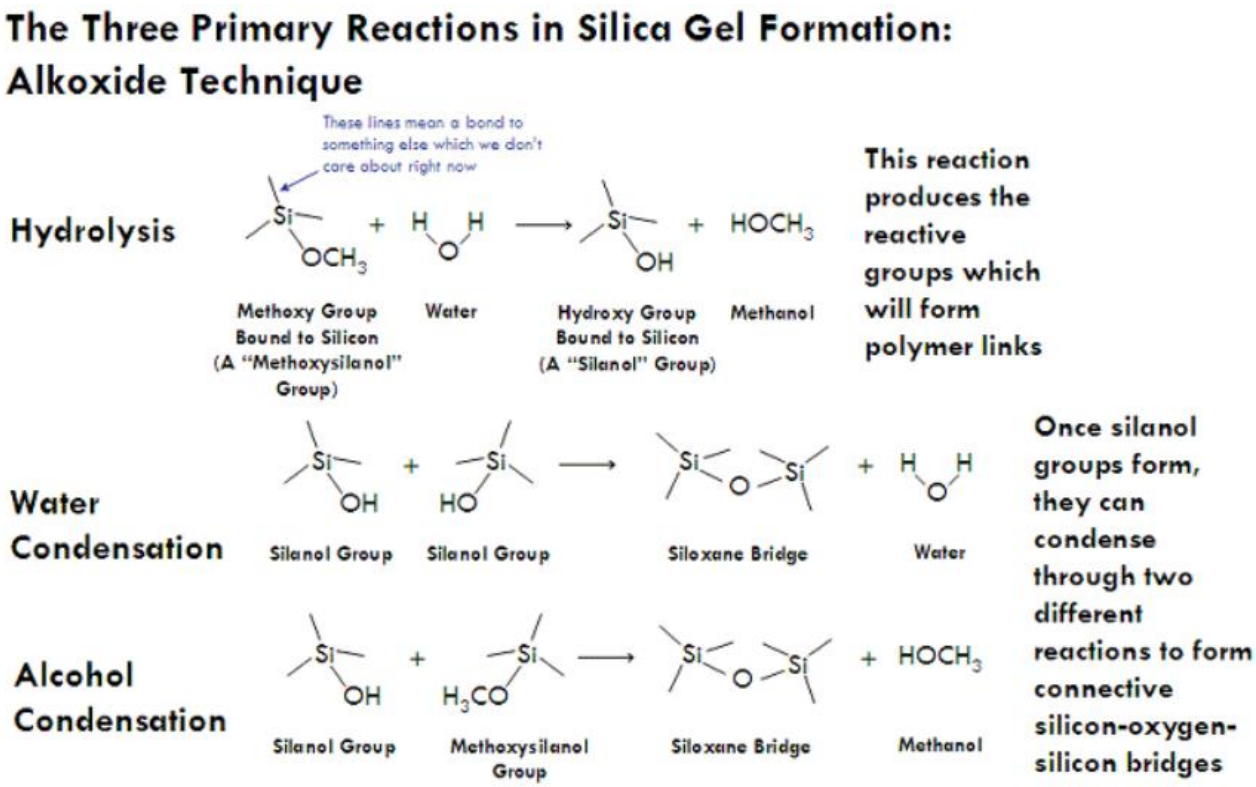


Figure 2.16 Schematic representation of sol–gel process for the synthesis of a variety of nanostructures. Hench and West [19] © 1990. With permission of ACS.



1- Sol hazırlanması: Alkoksit ya da metal tuzlarından hidroliz yöntemi ile kararlı solüsyonlar hazırlanır.

2- Jel hazırlanması: Hidrolizden sonra solüsyon yoğunlaşmaya ve polimerleşmeye (jel) başlar. Bu aşamada parçacık boyutu birkaç nm'ye kadar büyür.

3- Sineresis (sıvı bırakımı): Yaşlandırma işlemi ile jel katılaşır. Bu aşamada oluşan nanoparçacık boyutu büyür.

4- Kurutma: Suyun ve diğer solventlerin uzaklaştırılması. Kalsinasyon ile yüksek sıcaklıklarda da yapılabilir.

Biyomimetrik Yöntemler

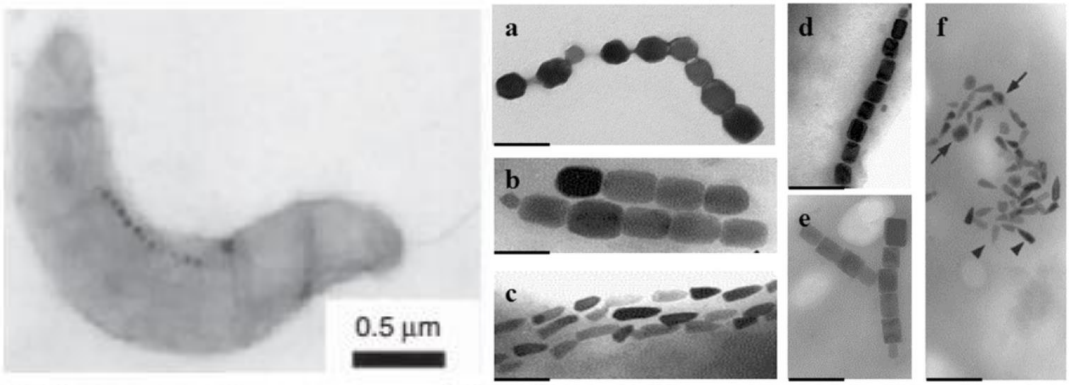


Figure 2.18 Scanning electron micrograph (SEM): (a) magnetotactic bacteria (*Magnetospirillum gryphiswaldense*) cell; (b) magnetite crystals observed at the ends of the chain in magnetotactic bacteria. Bazylinski and Frankel [23] © 2004. With permission of Nature Publishing Group.

Diğer yapay manyetik nanopartikül sentezlerine göre biyo-uyumlu, güvenli ve süperparamanyatik oluşu ile avantaj sağlamaktadır

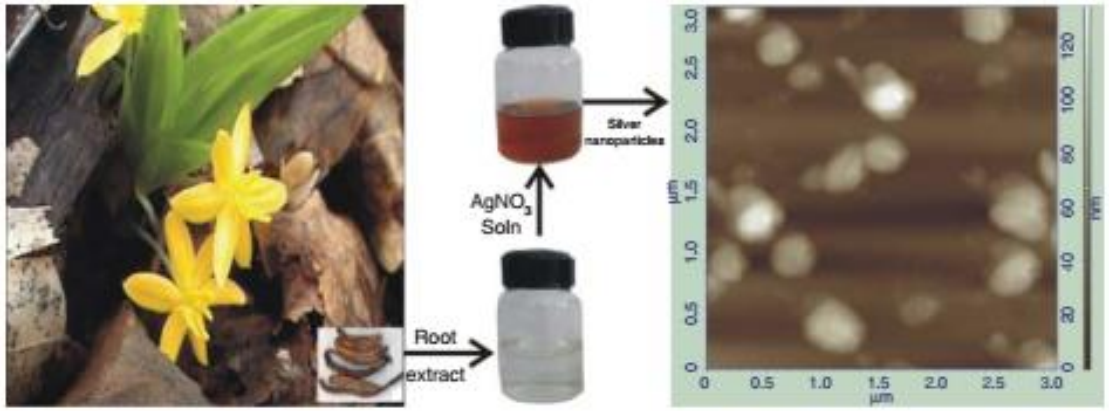
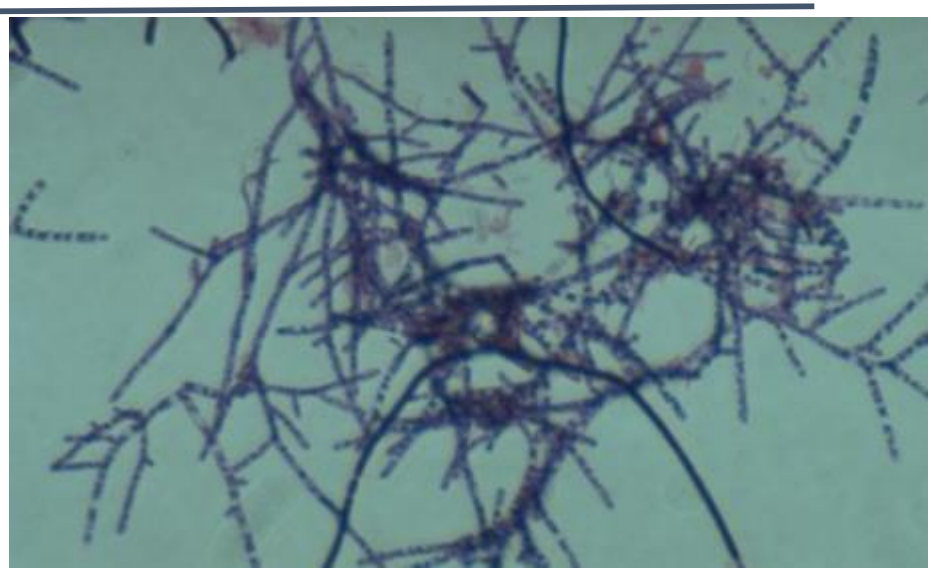


Figure 2.19 Plant *Curculigo orchioides* (inset shows dried root) root extract used for nanosynthesis and AFM image of resultant silver nanoparticles. Courtesy, Dr. Sushma Dave, VIET, Jodhpur, India. (*See color plate section for the color representation of this figure.*)



Actinomycetes are Gram-positive mycelial bacteria, known to produce a wide variety of industrially and medically relevant compounds (antibiotics, chemotherapeutics, fungicides, herbicides and immunosuppressants)

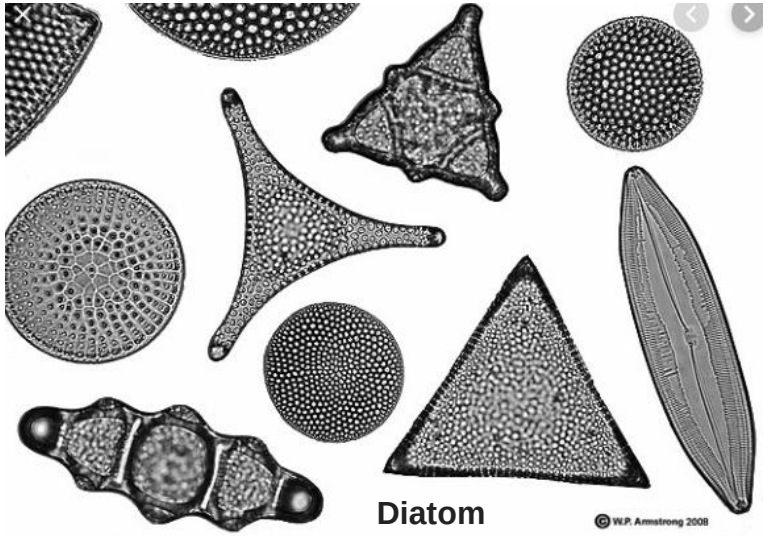


TABLE 2.3 Extracellular Bionanosynthesis of Nanoparticles

Biological Entity	NPs Synthesized (Size
Bacteria	
Pseudomonas aeruginosa	Au (15–30 nm)
Rhodopseudomonas capsulata	Au (10–20 nm)
Bacillus megatherium	Au (02–03 nm)
Bacillus subtilis	Ag (05–60 nm)
Bacillus licheniformis	Ag (50 nm)
Enterobacter cloacae	Ag (50–100 nm)
Escherichia coli	Ag (05–25 nm)
Lactobacillus fermentum	Ag (12 nm)
Klebsiella pneumonia	Ag (50 nm)
Proteus mirabilis	Ag (10–20 nm)
Brevibacterium casei	Ag (50 nm)
Actinomycete	
Thermomnospora sp.	Au (08 nm)
Fungi	
Verticillium sp.	Ag (25 nm)
Fusarium semitectum	Ag (10–60 nm)
Fusarium oxysporum	Ag (20–25 nm)
Phanerochaete chrysosporium	Ag (100 nm)
Aspergillus fumigatus	Ag (05–25 nm)
Aspergillus clavatus	Ag (10–25 nm)
Aspergillus flavus	Ag (07–10 nm)
Fusarium solani	Ag (05–35 nm)
Fusarium oxysporum	Au (20–40 nm)
Trichothecium sp.	Au (5–200 nm)
Colletotrichum sp.	Au (20–40 nm)
Algae	
Sargassum wightii	Au (20–40 nm)
Plant leaves extract	
Pelargoncum gravcolens	Au (20–40 nm)
Cymbopogon flexuosus	Au (0.05–2 nm)
Tamarindus indica	Au (20–40 nm)
Coriandrum sativum	Ag, Au (20–26 nm)