Shaping Binary Metal Nanocrystals Through Epitaxial Seeded Growth

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Heteroepitaxy in gas-phase deposition has been extensively studied for the development of functional heterostructures and devices

The same degree of control is necessary to fully realize the potential of heterostructure formation in solution

The majority of efforts towards solution-phase heterostructure growth have focused on chalcogenide or oxide interfaces, or the integration of a metallic component with a chalcogenide or oxide structure

Fully metallic heterostructures with controlled shape and interfaces are less well studied. Shape control of individual metallic nanoparticles, on the other hand, has been extensively studied and can provide a starting point for the development of shaped heterostructures

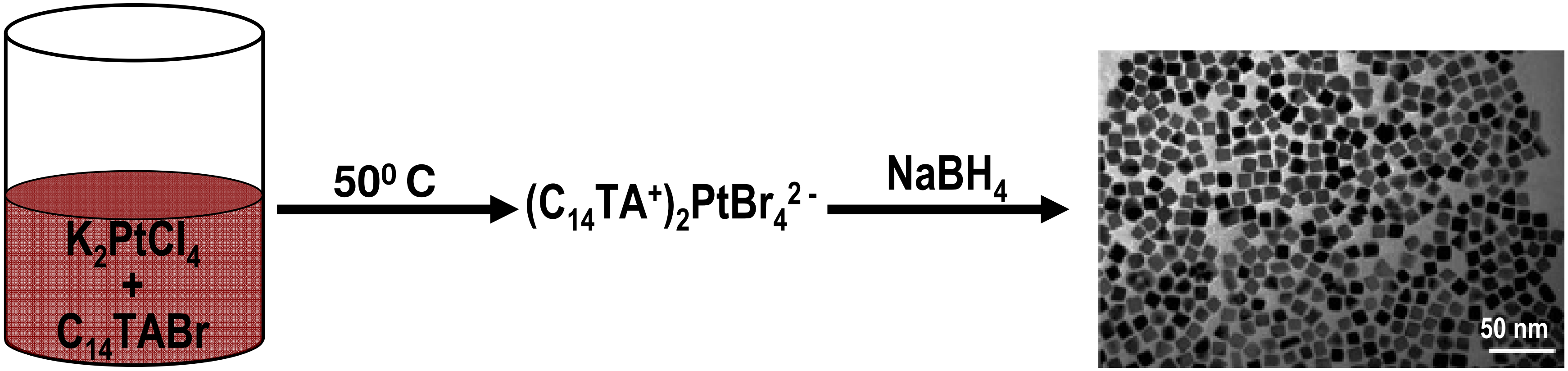
It explored the synthetic design of heterostructures with controlled morphology

Overgrowth of a different material on well-faceted seeds, allows for the use of the defined seed morphology to control nucleation and growth of the secondary structure

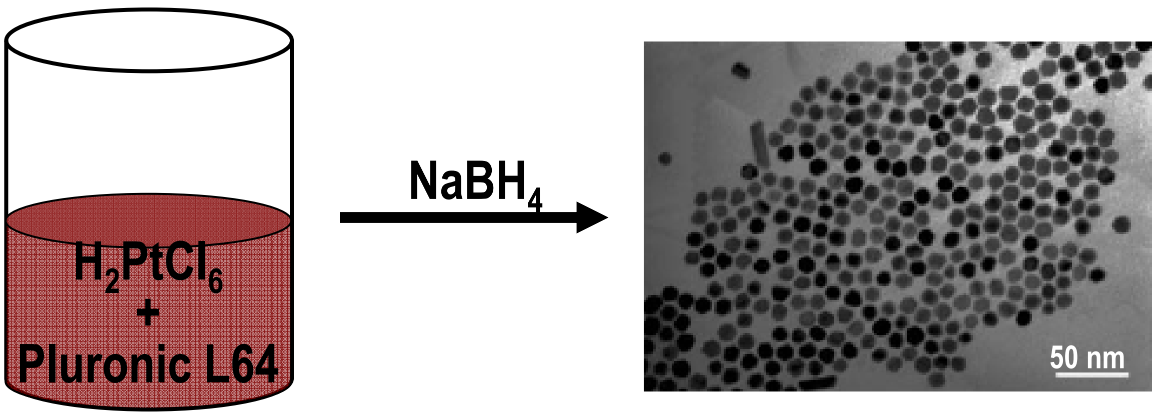
The highly faceted cubic Pt seeds which direct the epitaxial overgrowth of a secondary metal and demonstrated the concept of lattice-matched Pd to produce conformal shape-controlled core–shell particles, and extended it to lattice-mismatched Au to give anisotropic growth

The seed with faceted nanocrystals may have significant potential towards the development of shape-controlled heterostructures with defined interfaces

I. Synthesis of Seed Particles

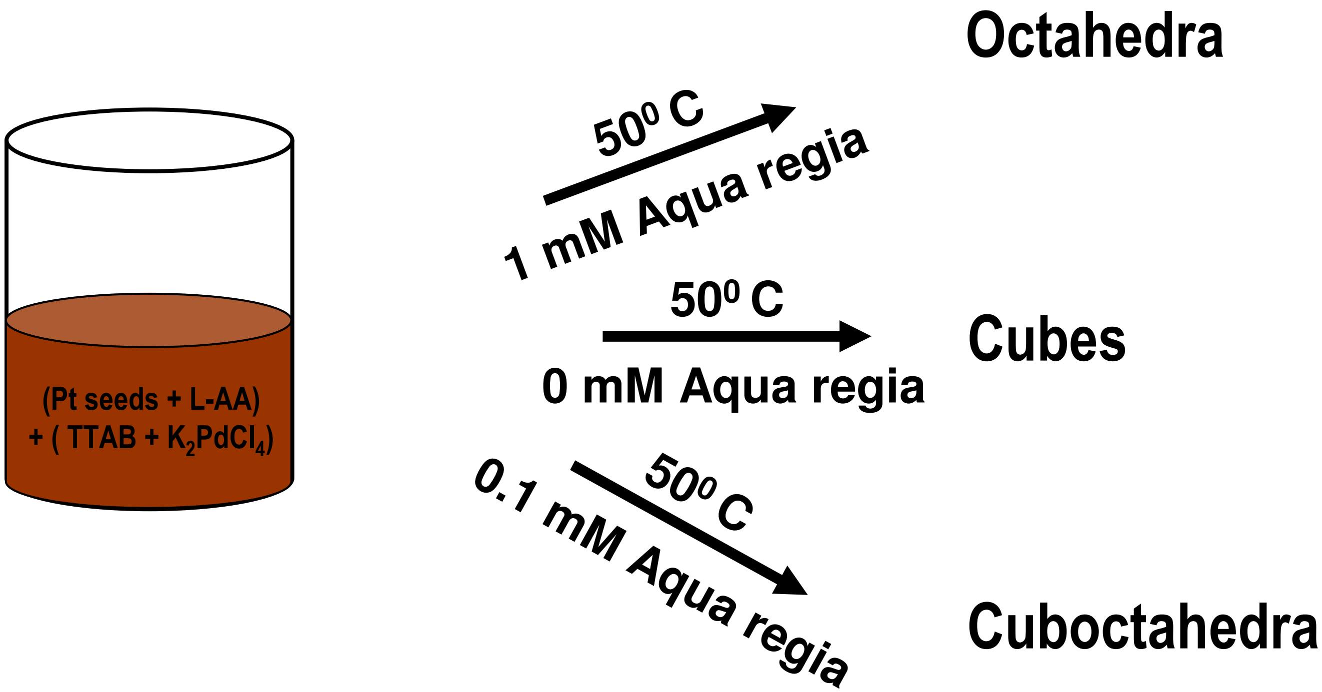


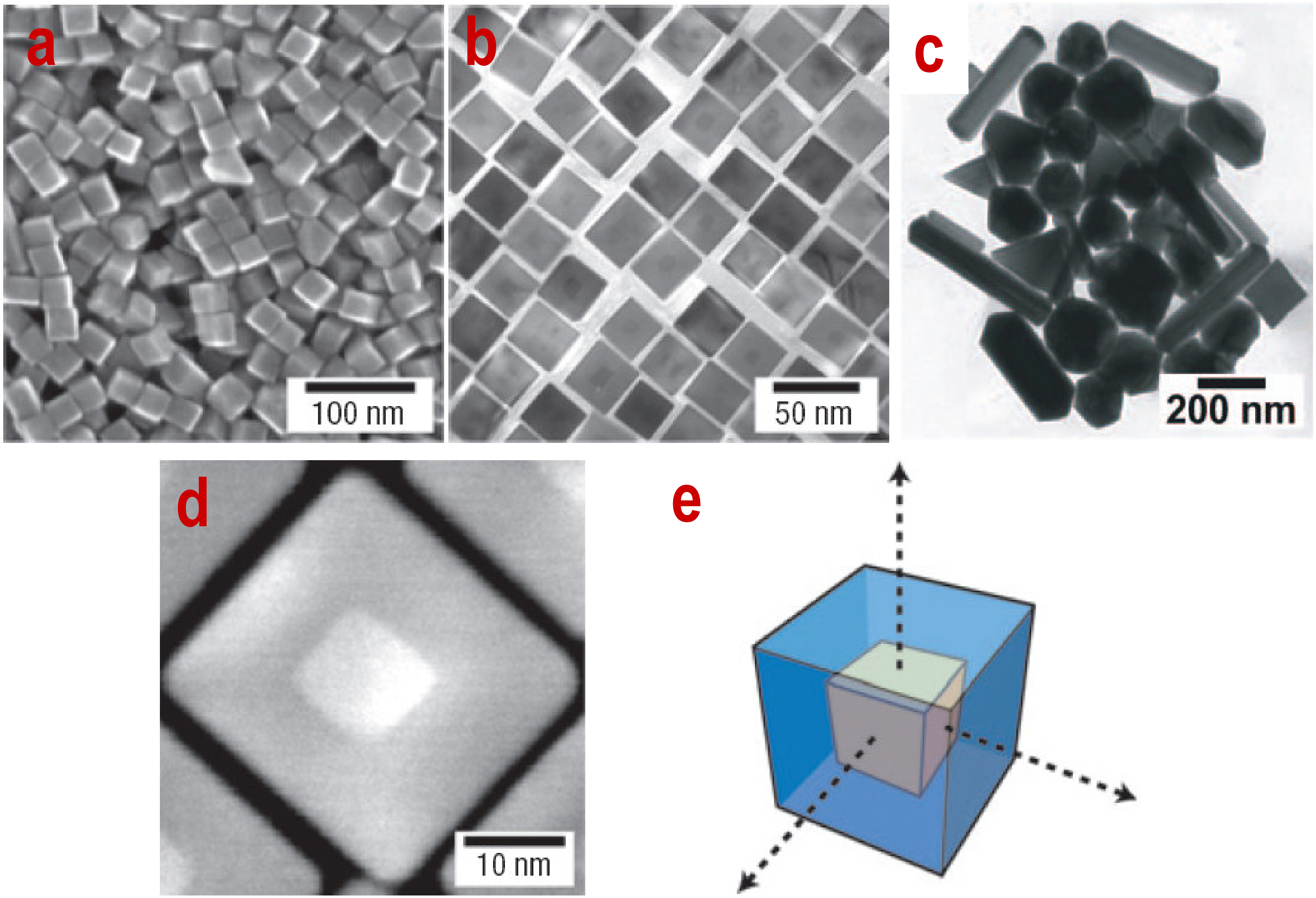
(13.4 nm face diagonal and 9.5 nm edge length)

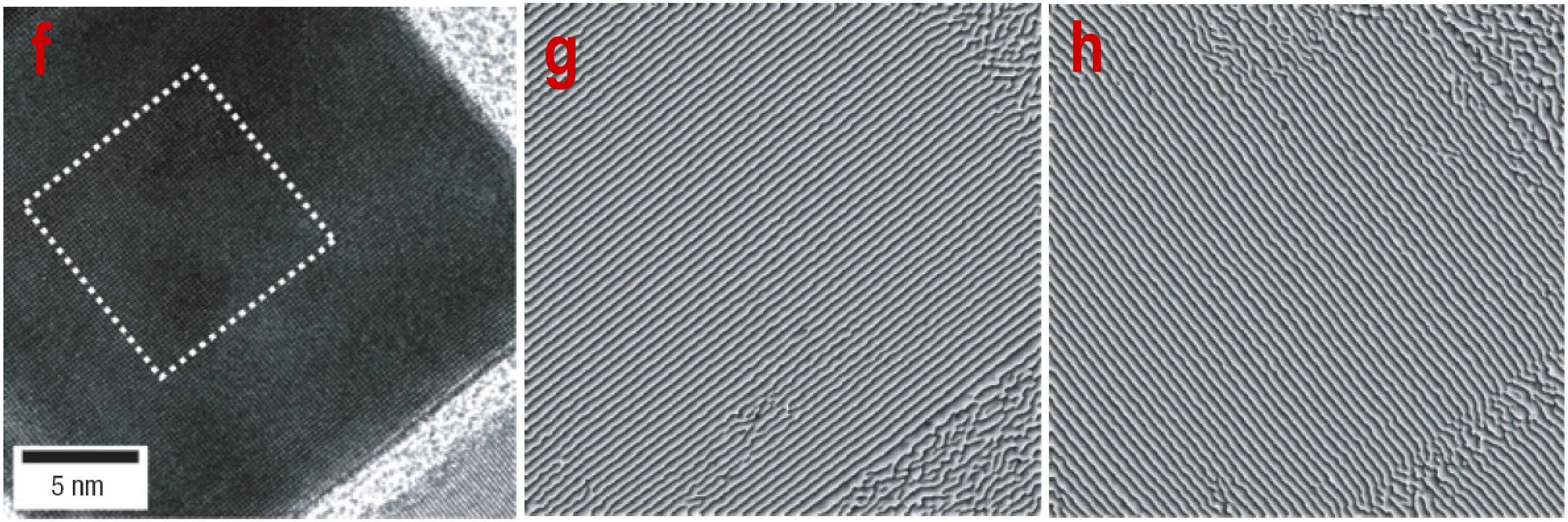


3.5 nm

II. Epitaxial Overgrowth of Lattice-matched Core-shell Structure




a
100 nm
b
50 nm
c
200 nm
d
10 nm
e

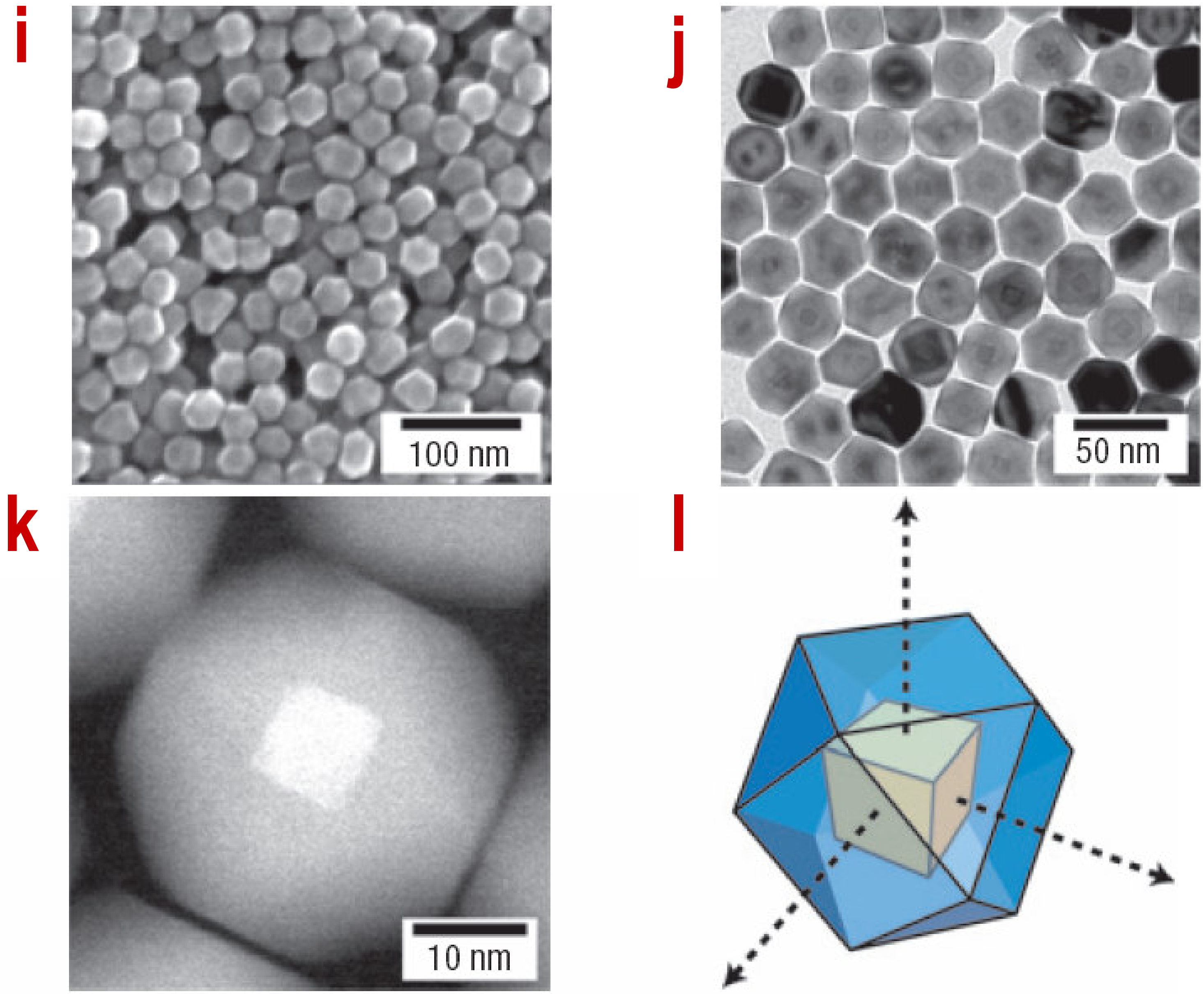


Phase constructions of a Pt/Pd cube showing a coherent and epitaxial interface between the cubic Pt core and Pd shell. f–h, The (002) and (020) reflections from the Fourier transform of the HRTEM image (f) were used to construct the corresponding moire images (g,h), which indicate that there are no visible distortions through the expected Pt/Pd boundaries, shown by the dotted line in f.

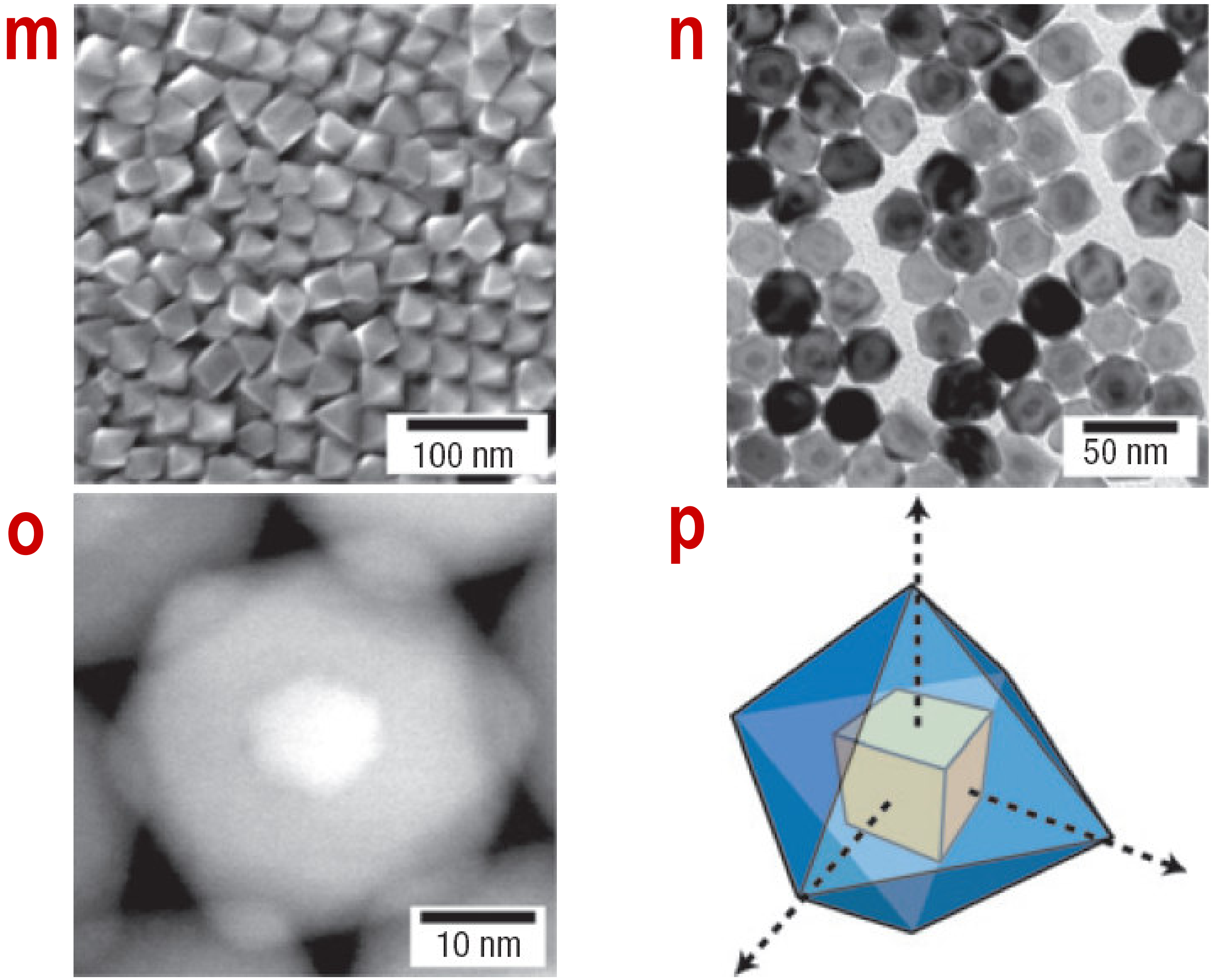
$$NO_2 \longrightarrow NO + O$$

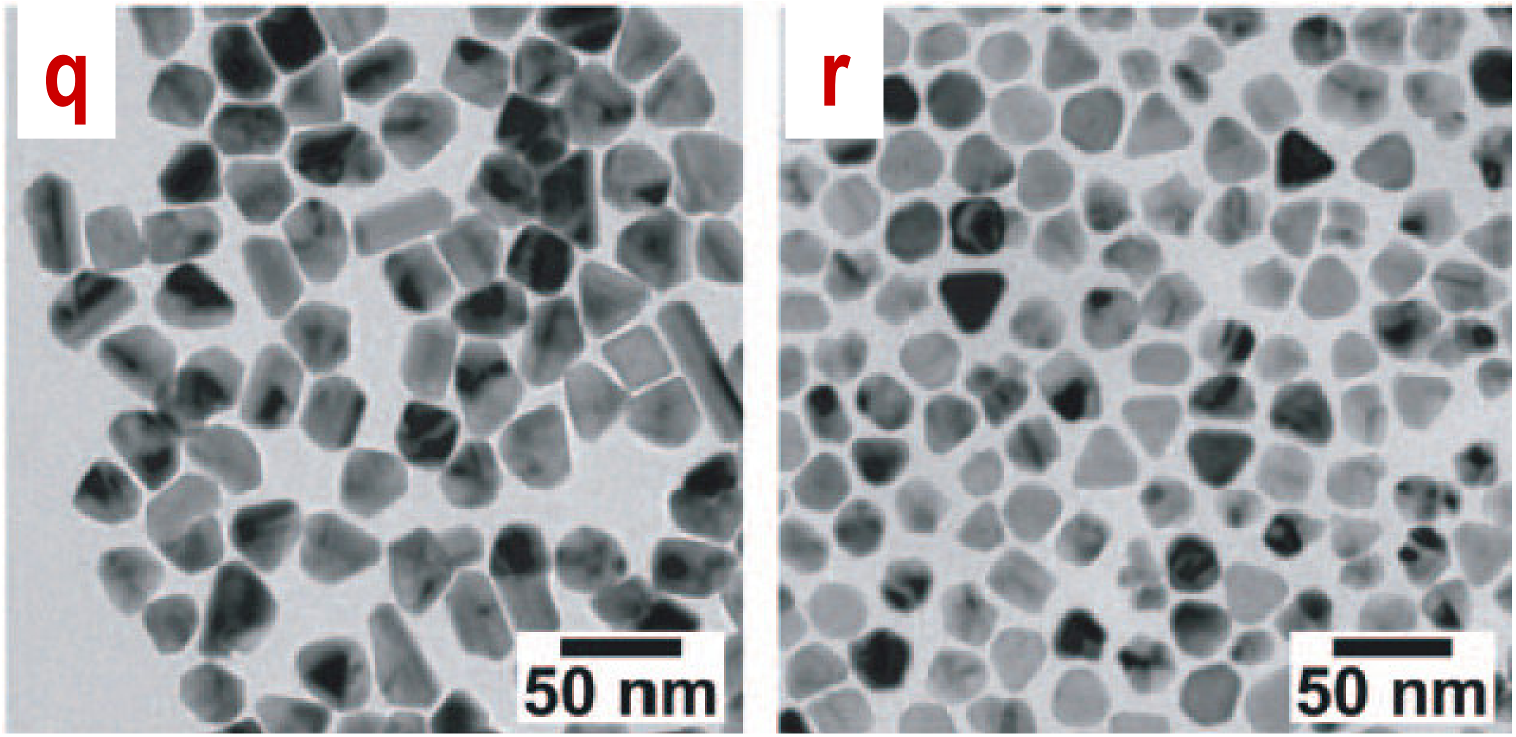
The NO desorbs between 230 and 300 K leaving behind adsorbed oxygen, which may interact selectively with the Pd surfaces of the growing particles

By adding NO_2, it is able to vary the growth rates along the (100) and (111) directions to give cuboctahedrally (36.4nm body diagonal) and octahedrally shaped Pd shells (34.6nm measured two-dimensional projection of the body diagonal, 40.8nm calculated body diagonal)



i
j
100 nm
50 nm
k
l
10 nm


m
100 nm
n
50 nm
o
10 nm
p



The TEM images in (q) and (r) show that Pd overgrowth on small Pt seeds (3.5 nm) in the presence of 1 mM HNO3 and 1 mM aqua-regia, respectively, does not allow for controlled growth along the {100} and {111} directions as seen for the cubic Pt seeds to give cubes and octahedra.

III. Epitaxial Overgrowth of Lattice-mismatched Anisotropic Growth

Growth of anisotropic Au Rods

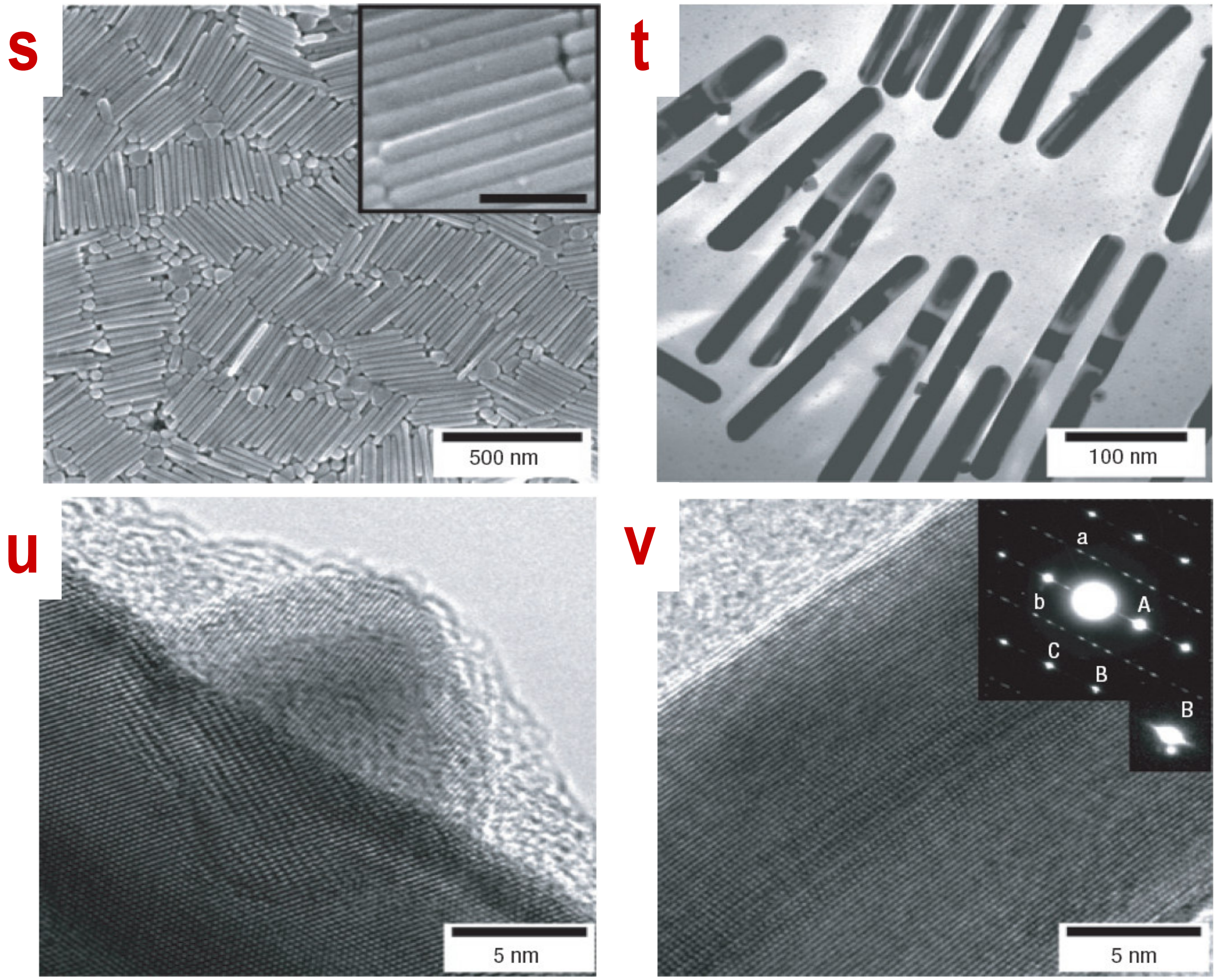
(I) 5 ml growth solution containing

100 mM TTAB

+ 0.25 mM HAuCl4

+ 0.5 mM L-AA

(II) Addition cubic Pt seeds (25 μl) to the above growth solution



Epitaxial overgrowth of lattice-mismatched Au on cubic Pt seeds to give anisotropic growth of Au rods. s, SEM image of Au rods nucleated from cubic Pt seeds. **t**, TEM image of multiple rods indicating that a single Pt cube is associated with each Au rod. **u**, HRTEM image showing a single Pt cube partially embedded in the side of a Au rod. **v**, The length of the rod, viewed down the (112)/(100) zone with continuous {111} fringes running parallel to the long axis, and the corresponding selected-area electron diffraction pattern.

Summary

The controlled epitaxial overgrowth of a secondary metal on well-faceted cubic Pt seeds.

Both conformal shape-controlled overgrowth as well as anisotropic overgrowth depending on the degree of lattice mismatch.

This concept could be applied to other material systems (for example, Rh, FePt and CoPt), creating novel heterostructures for catalysis, optical and magnetic applications where shape control plays a crucial role.