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Tunable optical features from self-organized rhodium nanostructures

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Manipulating the surface to tune plasmonic emission is an exciting fundamental challenge and here we report on the development of unique morphology-dependant optical features of Rh nanostructures prepared by an equilibrium procedure. The emergence of surface plasmon peaks at 375 nm and 474 nm, respectively, is ascribed to truncated and smooth surface of nanospheres in contrast to the absence of surface plasmon for bulk Rh(0) in the visible range. Smaller sized, high surface area domains with well developed, faceted organization are responsible for the promising characteristics of these Rh nanospheres which might be especially useful for potential catalytic, field emission and magnetic applications. © *2010 American Institute of Physics.*
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After the landmark report from Gans, surface plasmon resonance (SPR) of anisotropic nanostructures has attracted tremendous attention toward the understanding of shape dependent optical properties.[1] However, the spherical nanoparticles per se could be envisaged to elicit a more uniform response as a result of their plasmonic field enhancement to a perturbation. Conversely, the departure from sphericity due to asymmetry in the field of nanoparticles or presence of disordered (anisotropic) morphology can have a "diffuse" response resulting in a splitting of their dipole absorbance in to multiple bands.[2,3] These advances in the understanding of surface plasmon behavior of nanoparticles have indeed, provided several promising solutions for the confinement of light below their diffraction limit enabling[4,5] several technological breakthroughs including chemical and biochemical sensors,[6] plasmonics,[7] solar cells and lighting,[8] cancer treatments,[9] near-field optical microscopy,[10] etc. For example, the optical properties of Au and Ag nanostructures have been known for nearly 150 years, culminating in the niche application of their SPR in various fields. In contrast, the optical properties of Rh nanoparticles remain relatively unexplored. The location of the SPR peak of Rh nanoparticles in the UV region not only gives them an interesting brown-black color but makes it much more difficult also to probe, mainly because of less absorption of light at this wavelength.[2,11] In disparity to this, on the basis of discrete dipole approximation, Xia *et al.* proposed a weak and broad SPR signal at ~380 nm for Rh multipods in the deep UV region.[12] Indeed, different morphologies of Rh via seeded Polyol route, have been reported revealing shape and capping dependent SPR features.[13] More recently, Rh nanotubes have also exhibited interesting broad SPR at 500 nm.[14] All these results reflect that the picture of the SPR of Rh is still not clear necessitating more investigations.

Synthesis of these Rh nanostructures briefly involves, the immersion of an Al foil (99.99% purity with thickness 75 μm after etching) having a bilateral area (2 cm^2) as the substrate in 1 mM aq. RhCl$_3$.[15] Time dependent studies were carried out after optimizing various experimental parameters such as concentration, temperature and exposed aluminum area. *In situ* UV-visible experiments were performed using the above-mentioned procedure for understanding the growth kinetics. Further, to see the effect of Cl$^-$ ions on the absorption peaks of *in situ* formed Rh nanospheres, we have investigated SPR after the addition of 0.5 M RhCl$_3$ and 0.5 M HCl both separately and also together. Lack of any significant change in the optical features clearly confirms that Cl$^-$ do not have any major role in the SPR absorption.

Figures 1(a) and 1(b) clearly indicate that Rh spherical aggregates are made up of individual nanoparticles with a size of approximately 3 nm. This is verified from different samples by high resolution transmission electron microscopy (HRTEM) images shown in Ref. 21 [Figs. I(a)–I(d)]. Most of the particles ($<$10 nm) however show distinctive SPR peaks that are strongly dependent on their size, shape, and structure. With this background, since in the present case the Rh nanospheres are made up approximately 3 nm particles, their assembly is also expected to show SPR. Accordingly, we could also conveniently monitor the optical features of Rh nanostructures during galvanic replacement between Rh^{3+} and Al using time dependent UV analysis.

Figure 2 illustrates the emergence of two surface plasmon peaks at 375 nm and 474 nm, respectively, due to the difference in the surface roughness of these nanospheres, as can be evident from the associated transmission electron microscopy (TEM) images. Interestingly, with time the intensity of both peaks (absorbance) increase to reach a critical value before its further diminution due to coalescence. The increase in the absorbance of the solution associated with both the peaks upto 10 min may be attributed to the fact that initially, the number of nucleating sites are presumably available for reduction facilitating the formation of more nano-
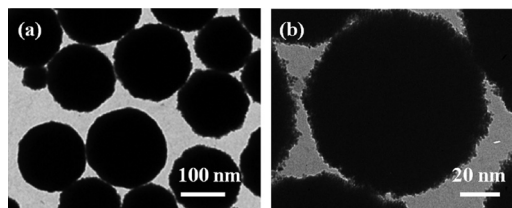

FIG. 1. [(a) and (b)] Bright field TEM of Rh nanospheres (~150 nm) at different magnifications revealing the assembly of smaller particles of approximately 3 nm.

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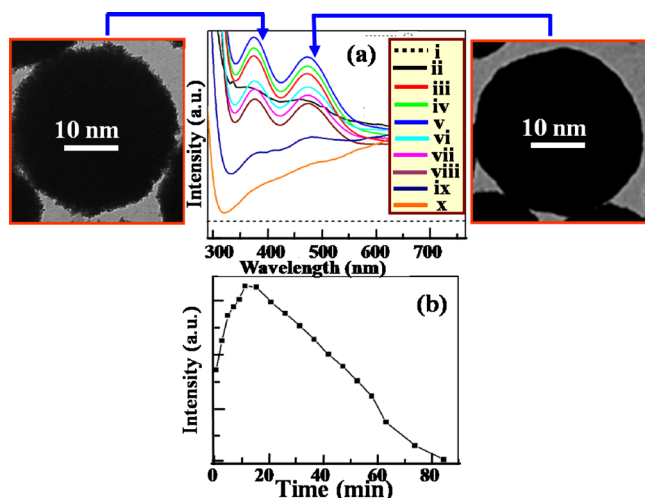
FIG. 2. (Color online) (a) Superimposed *in situ* UV-visible spectra at different stages of the reaction indicating response at 375 nm and 474 nm corresponding to truncated and smooth surfaces, respectively, and (b) variation in the intensity of peak corresponding to 375 nm as a function of time.
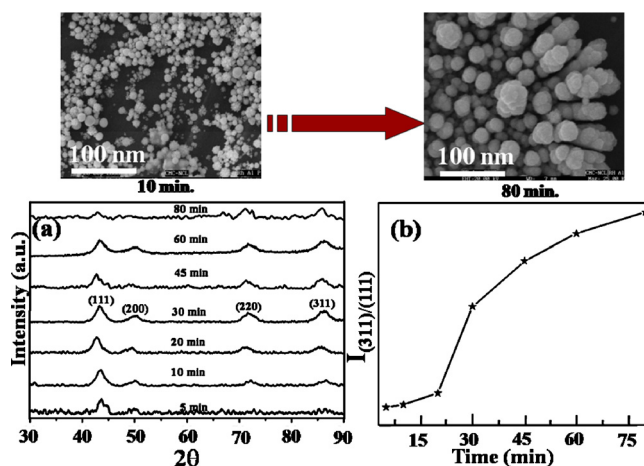

FIG. 3. (Color online) (a) Superimposed XRD pattern for Rh nanospheres collected at different stages between 5 to 80 min and (b) variation in the comparative intensity ratios of (311) : (111) peaks with time.

spheres. However, after 80 min the absorption spectrum becomes relatively featureless, revealing a broad and low absorbance over the visible region, which is also consistent with the black color of the aggregates.

We have confirmed the origin of these two peaks arising from Rh morphological variation by carrying out several separate experiments. Although spherical nanoparticles of Rh are not expected to reveal any SPR response, we observe a strong response ascribed to the difference in the surface roughness of these nanostructures (truncated and smooth). The origin of the absorption peak at 375 nm is due to smooth Rh nanostructures as confirmed by several other reports. For example, Xia *et al.* observed SPR signal at ~380 nm for Rh multipods, along with a blue shift due to surface anisotropy.[12] Similarly a broad absorption at 500 nm was seen for Rh nanotubes and hence our both peaks could arise due to Rh(0) despite possible changes due to anomalous dispersion.[4,5,16] Moreover, the SPR on a planar (smooth) interface show an anomalous behavior around its intrinsic resonance wavelength. For example, McLellan *et al.*[17] have reported an analogous SPR response of sharp and truncated Ag nanocubes ranging from 60–100 nm having a blueshift in SPR bands along with the possibility of *in situ* sharpening of their edges which gives excellent support to our results. In fact, just like the charge transfer between the halide and gold ion can produce a well defined absorption peak in the UV-visible range,[18] Kundu *et al.* have reported strong bands at 374 and 470 nm for Rh due to charge transfer from ligand to metal in the mixed solution of cetyl trimethylammonium bromide (CTAB) and Rh ions.[19] However, this is not the origin of our peaks as independent experiments carried out by using externally added chloride ions (HCl and RhCl₃) have not generated any enhancement in intensity or change in the absorption spectra.

In order to investigate the structural evolution with time, we carried out time dependent x-ray diffraction (XRD) studies focusing on subtle changes in the organization. The growth of nanostructures should at least in principle, start from the lowest energy sites leading to a progressive displacement from the highest energy sites as a function of time. Accordingly, the entire diffraction profile shown in Fig.

3 could be indexed to (111), (200), (220), and (311) planes of Rh which confirms the formation of face-centered cubic structure.[14,20] These findings are in excellent agreement with the data obtained by energy dispersive x-ray (EDX) spectral analysis shown in Ref. 21 (Fig. II).

The above observation indicates a general model of growth, whereby the initially fast reduction in Rh ions favor epitaxial growth into a thermodynamically favorable (111) low energy crystal face. Interestingly, the rate of growth initially in (311) plane is indeed less, although there is an increase with time, indicating the competition between thermodynamics and kinetic factors. For example, typically at 5 min, the reaction is dominated by nonequilibrium conditions so that the growth of nanoparticles occurs at the thermodynamically favorable low energy (111) plane. With time, however, these Rh nanospheres become truncated, shifting to a branched surface above 40 min and finally to nanorods via accelerated additional growth along the (311) direction. Crystallite size of these particles is about 2.5 nm as inferred from the full width and half maximum (FWHM) of the 43.54° peak (2.252 Å), which is in agreement (2.9 ± 0.4 nm) with the corresponding size from TEM images (Ref. 21, Fig. I). Alternatively, nanorods growth can be explained by a mechanism of oriented attachment, where supersaturation of Rh ions on initially nucleated Rh causes steric hindrance between attached aggregates resulting in the formation of a order driven by the rate of adsorption at (311) versus (111) face which is kinetically controlled under these nonequilibrium conditions.

In summary, we have observed optical features for Rh nanospheres obtained by a galvanic displacement with Al in agreement with fascinating morphological variation. The emergence of surface plasmon peaks at 375 nm and 474 nm, respectively, is ascribed to truncated and smooth surface of nanospheres in contrast to the absence of surface plasmon for bulk Rh(0) in the visible range. Interestingly, once the nucleating sites are formed further growth of the nanostructures with time is controlled by kinetics instead of thermodynamics of site-specific adatom incorporation at (311) versus (111) faces.

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[21] See supplementary material at http://dx.doi.org/10.1063/1.3447927 for transmission electron microscopy and electron dispersive spectra along with detailed results.