

Abstract

Two types of 3-dimensional (3D) Ag nanosponge aggregates were prepared and tested as samples for surface-enhanced Raman scattering (SERS) and as active surfaces for surface-enhanced luminescence. 3D Ag nanosponge aggregates were assembled from 2D fused fractal aggregates ($D = 1.87 \pm 0.02$) prepared by modification of Ag nanoparticle (NP) hydrosol resulting from the reduction of AgNO_3 by $\text{NH}_2\text{OH}\cdot\text{HCl}$. For SERS measurements, 3D Ag nanosponge aggregates with incorporated $[\text{Ru}(\text{bpy})_3]^{2+}$ cations and chloride anions were prepared and overlaid by a thin layer of aqueous phase. For SEL measurements, the 3D Ag nanosponge aggregates were assembled from fused fractal aggregates of chloride-modified Ag NPs. After preparation the active surface was overlaid by a 1×10^{-5} M aqueous solution of $[\text{Ru}(\text{bpy})_3]^{2+}$.

The SERRS (1×10^{-15} M) and SER(R)S (1×10^{-14} M) limits of detection of $[\text{Ru}(\text{bpy})_3]^{2+}$ determined at 445 and 532 nm excitations, respectively, correspond to the single molecule level of the complex detection. Its achievement is attributed to a large electromagnetic mechanism enhancement experienced by $[\text{Ru}(\text{bpy})_3]^{2+}$ incorporated in “hot spots”, an efficient localization of “hot spots” in the 3D aggregate to the focus of the laser beam in micro-Raman spectral measurements and to a molecular resonance contribution to the overall enhancement. Another benefit for SERS spectral measurements from the 3D Ag nanosponge aggregate is protection of the analyte (i.e. $[\text{Ru}(\text{bpy})_3]^{2+}$) against thermal decomposition by the thin aqueous phase overlayer.

Phosphorescence measurements from 3D Ag nanosponge aggregate overlaid by 1×10^{-5} M aqueous solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ have shown enhancement of fluorescence intensity by factor of 70. The phosphorescence lifetime imaging microscopy (PLIM) measurement yielded three different lifetimes. The 367 ns lifetime belongs to free $[\text{Ru}(\text{bpy})_3]^{2+}$, while the other two lifetimes – 75 and 17 ns are attributed to $[\text{Ru}(\text{bpy})_3]^{2+}$ cations localized in the vicinity of the aggregate or in the aggregate pores.

2D arrays of co-assembled hydrophobic Au NPs and SQDs were prepared from their organosols in toluene at water surface in various weight ratios. The 1:1, 1:2 and 2:1 ratios were found to be optimal for semiregular 2D co-assembling of Au NPs and SQDs. In these assemblies, localization of SQDs between Au NPs led to enhancement of the SQDs fluorescence by the factor of 7 – 8.

Keywords: plasmonic nanoparticles, SERS, SERRS, surface-modified luminescence, semiconductor quantum dots, Ru (II) tris(2,2'-bipyridine)