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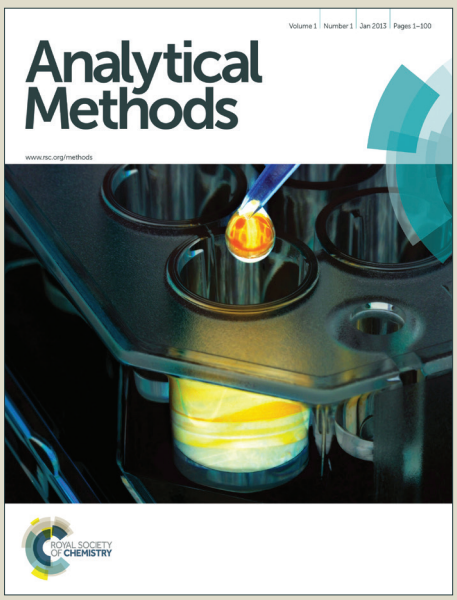

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Comment on "Simple fluorescence-based detection of Cr(III) and Cr(VI) using unmodified gold nanoparticles" by M. Elavarasi, S. A. Alex, N. Chandrasekaran and A. Mukherjee, *Anal. Methods*, 2014, 6, 9554

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Recently,[1] Mukherjee et al. presented a fluorescence-based method for the determination of both Cr(III) and Cr(VI) in aqueous samples using 31.2 nm sized citrate coated gold nanoparticles (AuNPs) that were synthesized based on Frens or Turkevich method.[2] They claimed that the complexation of AuNPs by Cr(III) leads to the quenching of the fluorescence intensity of AuNPs, which is directly proportional to the concentration of Cr(III).

Gold nanoparticles exhibit a high order of magnitude extinction coefficients (~ 3×10^{11} mol L^{-1} cm^{-1}) when the incident photon frequency is in resonance with the collective excitation of the conduction electrons. This phenomena is known as surface plasmon resonance (SPR) and depends on the size, shape, and inter-particle spacing of gold nanoparticle as well as its own dielectric properties and those of its local environment.[3,4] When the size of AuNPs is reduced to around 2 nm or less, the continuous band structure of AuNPs breaks into discrete energy states,[5] similar to the energy levels of molecules. These molecular quantum clusters of AuNPs do not show plasmonic properties anymore, but exhibit strong luminescence emission.[5]Since the particle size of the AuNPs synthesized in is around 31 nm, it seems that the major problem of the work done by Mukherjee et al.[1] is: "*The Rayleigh scattering peak of Au NPs that appeared around 580 nm was introduced as the fluorescence peak of Au NPs"*, which is a clear mistake. In addition, the authors could also confirm the presence of this Rayleigh scattering peak by reporting different excitation wavelengths in their work (which was not reported). As Mukherjee and coworkers believed, multiply charged aggregants such as Cr (III) ions can act as cross-linking agents that bind nanoparticles into dense aggregates. [6] So, by increasing Cr(III) concentration, unstable aggregated AuNPs will precipitate, leading to a decrease in the intensity of their corresponding Rayleigh scattering peak.

References

1) M. Elavarasi, S. A. Alex, N. Chandrasekaran and A. Mukherjee, *Anal. Methods*, 2014, **6**, 9554–9560.
2) G. Frens, *Nature*, 1973, **241**, 20–22.
3) N. T. Kim Thanh and Z. Rosenzweig, *Anal. Chem*., 2002, **74**, 1624–1628.
4) D. Vilela, M. Cristina Gonzalez and A. Escarpa, *Anal. Chim. Acta*, 2012, **751**, 24–43.
5) J. Zheng, P. R. Nicovich and R. M. Dickson, *Annu. Rev. Phys. Chem.*, 2007, **58**, 409–431.
6) A. N. Shipway, M. Lahav, R. Gabai and I.Willner, *Langmuir*, 2000, **16**, 8789–8795.