SUPPLEMENTARY INFORMATION



Figure 1S: . SEM micrograph and corresponding size dispersion of Ge nanoparticles synthesized from 47 mM of GeBr₂.



Figure 2S: XRD spectrum of Ge NCs for the case of 77 mmM of GeBr2, together with reference peaks of diamondcrystalline Ge, rutile GeO2 and GeBr2.



Figure 3S: Comparison of XRD of colloidal Ge NCs synthesized from no-treated and pre-treated (dried) GeBr₂

Dynamic Light Scattering (DLS) technique is a powerful method to determine the size of particles in solution. According to this technique, the correlation function, g(t), of the photons scattered by dispersed particles in a solution has a characteristic decay time, Γ , following to the relationship: $g_2(t) \propto \exp(-2\Gamma/t)$ [1, 2].

The decay constant 2Γ , derived from experimental data by exponential curve fit, is proportional to the diffusion coefficient (D_t) through the relationship: $\Gamma=D_tq^2$ where q is the scattering vector, given by $q=(4\pi n/\lambda)\sin(\theta/2)$. The refractive index of the liquid is n (for toluene at 660 nm n=1.49). The wavelength of the laser light is $\lambda=660$ nm, and scattering angle, θ . D_t is defined by the Stokes-Einstein equation of particles in Brownian motion, $D = kT/6\pi R \eta$, and allow to extract the hydrodynamic size from the measurement of the decay time 2Γ .

As shown in figure 4S, the decay time decreases by increasing the amount of dissolved Ge. 2Γ increases from a value of 9.1×10^3 s⁻¹ for 24 mM GeBr₂ to 2.7×10^4 s⁻¹ for 95 mM GeBr₂. By considering the case of spherical Ge particles immersed in toluene ($\eta = 9.1 \times 10^3$ Pa×s) at room temperature (T=20° C), the extracted values of hydrodynamic diameter ranges from about 69 nm for 24 mM to 22 nm for 95 mM of GeBr2. Such a trend gives support to the presence of smaller particles in more concentrated solution of Ge. The systematic discrepancy between the size estimated by DLS and XRD is due to two different reasons: 1) DLS analysis gives evaluation of the hydrodynamic size of particles, which is typically larger than real structural size; 2) partial aggregation of single particles in dimers or trimers cannot be excluded. However, the trend of particle size vs. precursor follows the same behavior found for the size values extracted by XRD analysis.



Figure 4S: Time dependence of the correlation fungtion g(t) of photons scattered by colloidal Ge particles in solution as a function of Ge precursor.



Figure 5S: Transmittance spectra of colloidal solution (dispersed 1:3 in toluene) of Ge NC with 5 and 17 nm size and comparison with transmittance of 200 nm film of PEDOT:PSS and 78 nm P3HT film (from ref. 43).

Supplementary References:

[1] M. Zimbone, P. Musumeci, P. Baeri, E. Messina, S. Boninelli, G.Compagnini, L. Calcagno, Rotational dynamics of gold nanoparticle chains in water solution, Journal of Nanoparticle Research 14 (12), 1-11

[2] H. Jans, X. Liu, L. Austin, G. Maes and Q. Huo, Dynamic light scattering as a powerful tool for gold nanoparticle bioconjugation and biomolecular binding studies, Anal Chem. 2009 Nov 15;81(22):9425-32. doi: 10.1021/ac901822w.