Fluorescent silver nanoclusters as potential tool for bio-applications

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Optical properties of metal nanomaterials greatly depend on the dimensional scale. If their overall size is reduced below two nm, metal particles are named nanoclusters (NCs), and present a different physical behaviour with respect to the bigger ones. The small size produces discrete energy levels within the density of states (DOS), and the photo-excited electrons give rise not only to specific absorption bands, but also to a bright fluorescence. The fluorescence emission of these NCs are widely used in many different applications in science and engineering, such as chemical sensors, fluorescent probes for bio-imaging and in environmental issues[1,2]. In the present study, we synthesized silver nanoclusters (AgNCs) in water solution through chemical pathway using silver nitrate as source of Ag ions, Lipoic Acid (LA) as capping agent and sodium borohydride ($NaBH_4$) as reducing compound. In a typical synthesis, the LA powder is solubilized in water, changing the pH value until 12 by NaOH 1M and then a water solution of AgNO₃ is mixed with the capping agent. Subsequently, the NaBH₄ solution is added dropwise to reduce not only silver ions, but also the LA into dihydrolipoic acid (DHLA), allowing bonds between AgNCs surface and sulphur atoms of the ligand. After 2 hours under vigorous stirring, the pH value was adjusted to 7 by HCl 1M. Before use for biological applications, we purified the solution by centrifugation and dialysis to eliminate unreacted compounds. The AgNCs system was characterized using absorption and fluorescence spectroscopy. Figure 1 shows optical features of lipoic acid in water (dotted curve) and the final AgNCs-LA solution (solid curve). Figure 2 represents the normalized photoluminescence (PL) of the system excited at 340 nm. The band maximum is centred at 660 nm. Changing excitation wavelength from 340 nm to 540 nm, no changes in the energy and shape of the fluorescence was found. This feature indicates a high degree of monodispersion in size of the AgNCs[3]. The AgNCs-LA can be excited with visible light, and the excitation process is even more efficient with wavelengths in the range 490-510 nm. Preliminary investigation of biocompatibility on human cells shown that AgNCs-LA could be used as fluorescent probes for cells morphology. These results are promising and show the high potential of fluorescent AgNCs as a good alternative to the standard fluorescent probes such as organic dyes or quantum dots.

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Figure 1. UV-Vis spectra of lipoic acid solved in water (dotted line) and Ag-NCs (solid curve). The inset shows AgNCs solution under white light.

Figure 2. Normalized photoemission of AgNCs capped with lipoic acid, inset shows a photograph of the NCs solution under UV light.