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# Preparation of colloidal solution of silica encapsulating cyanobiphenyl units-capped ZnO QD emitting in the blue region

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**We report on the synthesis, characterisation and optical study of ZnO@silica nanoparticles emitting in the blue region. This new nanomaterial is based on the encapsulation of ZnO nanoparticles (5 nm) coated by cyanobiphenyl units (Cya) into silica by sol-gel technique. The as-prepared ZnO-Cya@$SiO_2$ nanoparticles (150 nm) have a perfect spherical shape with a good monodispersity and display blue emission in water under UV excitation.**

Functional silica nanoparticles with magnetic or optical properties find numerous applications in the fields of biotechnologies[1, 2] or photonics.[3] They are usually achieved through the encapsulation of superparamagnetic nanoparticles such as ferrites[4] or metal nanoparticles[5, 6] or luminophores such as organic dyes,[7, 8] semi-conductor quantum dots,[9-13] organometallic complexes,[14, 15] metal cluster[16, 17] or doped nanocrystals.[18, 19] Concerning luminescent silica nanoparticles, the use of quantum dots (QDs) with high luminescent efficiency, especially II-VI semiconductors nanoparticles, have been the subject of continuous scientific interest for applications in optoelectronics.[20, 21] In particular, ZnO QD is a direct band gap semiconductor showing great potential applications in biological cell-labelling,[12, 13, 22, 23] UV/Vis light emitters,[24, 25] transparent electronics,[26] gas sensors and spin functional devices.[27] ZnO QDs show a broad luminescence emission that can be modulated, in theory, from the blue to the yellow region, by controlling the size of the ZnO nanoparticles.[12, 25, 28] There is an increasing interest in blue emission of QD nanoparticles for applications in blue QD-LEDs and biological fluorescence labelling.[29] However, it is difficult to obtain ZnO nanoparticles showing blue luminescence by synthetic methods.[30] The ZnO nanoparticles emission can be strongly affected by the surrounding materials attached to the surface of the ZnO nanoparticles and blue luminescence has been reported for surface-modified ZnO nanoparticles in silica,[31, 32] polymers[33-35] and liquid crystalline matrices.[36, 37] Various chemical methods have been used to prepare functional ZnO@$SiO_2$ nanoparticles and the most popular strategy is based on the sol–gel chemical synthesis in alcoholic media.[12, 13, 22, 23, 38-41] Usually, the final aqueous colloidal solution of ZnO@$SiO_2$ nanoparticles have been prepared through a two or three-step silanisation using tetraethylorthosilicate (TEOS) or functional silane or siloxane[12, 13, 23] except for the most recent works reported by Matsuyama *et al.* in which they are obtained in a one-step synthesis.[22]

We demonstrate herein the one-pot preparation of monodispersed ZnO-Cya@$SiO_2$ nanostructured particles. The ZnO QD are coated by cyanobiphenyl (CB) containing ligands, called ZnO-Cya.which are encapsulated into silica. The use of of cyanobiphenyl units to coat the surface of ZnO QD, allows their homogenous dispersion into the silica matrix leading to nanoparticles with high loading levels of ZnO. The ZnO-Cya@$SiO_2$ nanocolloids are dispersible in ethanol and water and show stable emission in the blue region. In contrast, coating the ZnO nanoparticles with long alkyl chains leads to aggregation of ZnO QD making their encapsulation into silica matrix not possible. We recently reported the thermotropic liquid crystal (LC) properties of such hybrid nanomaterial and demonstrated that it could be homogeneously dispersed in commercial LC matrix in order to modulate electrically its blue photoluminescence in a LC cell.[36] In its pure form, this material presents at high temperature a nematic phase followed on cooling by a layered phase with an interlayer spacing distance of around 10 nm. However, ZnO-Cya nanoparticles are not soluble in any solvent. Therefore, it appears that the self-assembling abilities of ZnO-Cya are mandatory to design homogeneous and highly loaded ZnO-Cya@$SiO_2$ nanoparticles.

ZnO-Cya@$SiO_2$ nanoparticles were prepared in a one pot process involving three major steps: i) the synthesis of ZnO QD, ii) their functionalisation with carboxylic acid derivatives, and, iii) their embedment in silica NPs. Briefly (see ESI for

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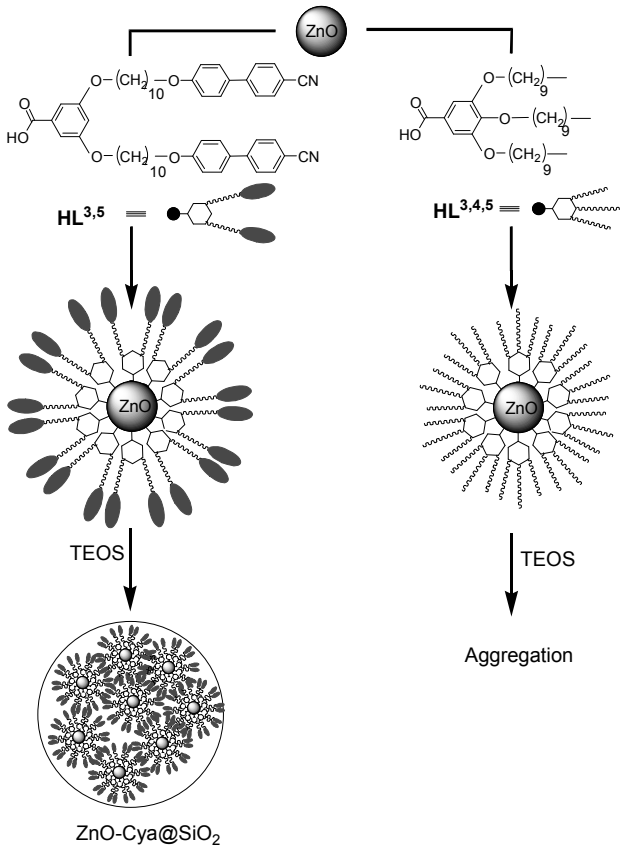
Electronic Supplementary Information (ESI) available: experimental details, XRD pattern, IR spectra, UV-Vis spectra. See DOI: 10.1039/x0xx00000x

experimental details, **scheme 1** presents the two last steps of the chemical process), ZnO QD were prepared by hydrolysing zinc acetate with tetramethyl ammonium hydroxide in DMSO. The surface of the formed ZnO nanocrystals were then modified by either 3,5-didecyloxycyanobiphenyloxy-benzoic acid ($HL^{3,5}$) or 3,4,5-trisdecyloxy benzoic acid ($HL^{3,4,5}$) directly into the solution. Indeed, these organic carboxylic acids are soluble in DMSO and able to react strongly with oxide surface leading to very stable hybrids. Finally TEOS was used to obtain a silica layer around ZnO-$HL^{3,5}$ QD and synthesise functional silica nanoparticles. After centrifugation, the as-prepared ZnO-$HL^{3,5}$@$SiO_2$ could be dried or redispersed in ethanol or water. On the contrary, the same method used on the ZnO-$HL^{3,4,5}$, containing only alkyl chains, coated QD, leads to the aggregation of the nanoparticles. This behaviour has been confirmed by TEM **(Figure 1)**. Thus, the interations of CB units imply the non-segregation of ZnO QD, allowing their good dispersion in $SiO_2$ matrix.




**Scheme 1.** Schematic representation of functionalised ZnOnc

**Figure 1** presents Transmission Electron Microscopy (TEM) pictures of ZnO-$HL^{3,5}$@$SiO_2$ and ZnO-$HL^{3,4,5}$@$SiO_2$ that were obtained by dropcasting from an ethanol solution. It is clear from these pictures that the two ZnO coated QD behave differently once the silica precursor is inserted in the reaction mixture. Although we did not investigate the lyotropic behavior of ZnO-$HL^{3,5}$ at this stage of the study, it seems straightforward that the presence of CB units around the ZnO QD improves drastically the dispersion of ZnO QD in the silica matrix. The nanoparticles ZnO-$HL^{3,5}$@$SiO_2$ present the so-called homogenous architecture and are relatively monodispersed in size with a mean diameter around 150 nm **(Figure 1a and S1)**. From Figure 1a, it is clear that a high loading level of ZnO QD (corresponding to the dark areas) into $SiO_2$ nanoparticles is achieved by this new technique of synthesis. Meanwhile, no aggregation of ZnO QD within the silica matrix is observed. One might also estimate the minimum inter ZnO QD distance within the silica (around 10 nm) that seems very close to the interlayer spacing distance previously determined by SAXS in the thermotropic layered phase[36].

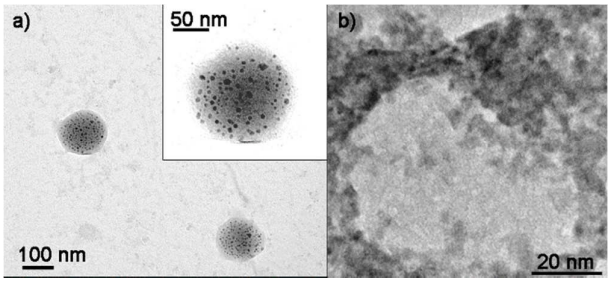



**Figure 1.**TEM images of a) ZnO-$HL^{3,5}$@$SiO_2$ and b) ZnO-$HL^{3,4,5}$@$SiO_2$.

To confirm that the nanocrystals observed in Figure 1a are effectively ZnO QD, we first performed XRD analyses. A typical XRD pattern of the composite sample is shown in **Figure S2**. The pattern fits well with zinc oxide (nanocrystals with a diameter of 5 nm) observed in our previous works.[4, 36] An additional broad diffraction peak located at around $2\theta = 21^{o}$ is attributed to the amorphous silica.[42] Therefore, we can assess that ZnO QD of 5 nm in diameter are homogeneously encapsulated in $SiO_2$ shells.

Infrared spectroscopy was further used and confirmed the presence of the organic carboxylate around the ZnO QD within the silica particles **(ESI Figure S3)**. First, the intense band corresponding to the stretching vibration of C=O groups (1700-1725 $cm^{-1}$) in a free carboxylic acid are not detected, showing that only carboxylate functions are present in the NP. Second, the positions of the carboxylate antisymmetric stretching and symmetric stretching modes give valuable informations about the nature of the coordination of the carboxylate group. Indeed, the carboxylate antisymmetric stretching and symmetric stretching bands appear at 1576 and 1413 $cm^{-1}$, respectively. The difference in frequencies (~163 $cm^{-1}$) is characteristic of a monodentate coordination of the carboxylate group and is in very good accordance with our previous reported results, thus confirming that the carboxylate group are bonded to the ZnO QD surface.[36]

UV-Vis absorption spectra were recorded for ZnO QD in DMSO and ZnO-$HL^{3,5}$@$SiO_2$ nanoparticles in water and DMSO (**Figure 2, ESI Figure S4**). The first one showed an absorption band at

$\lambda_{1/2}$ ~ 362 nm ($\lambda_{1/2}$ represents the wavelength where the absorption is half of that at the absorption shoulder) that corresponds to the bandgap energy of ZnO QD with size around 5 nm according to Meulenkamp's experiental formula $1240/\lambda_{1/2} = a + b/D^2 - c/D$ (D represents the average size of ZnO QD and a, b and c are parameters when D is ranging between 2.5 to 6.5 nm).[43] Regarding the composite, a clear absorption at the same energy is observed along with a strong $HL^{3,5}$ absorption in the UV region. These results indicate that ZnO-Cya QD are present in the $SiO_2$ shells with nearly the same size as that of starting ZnO QD.

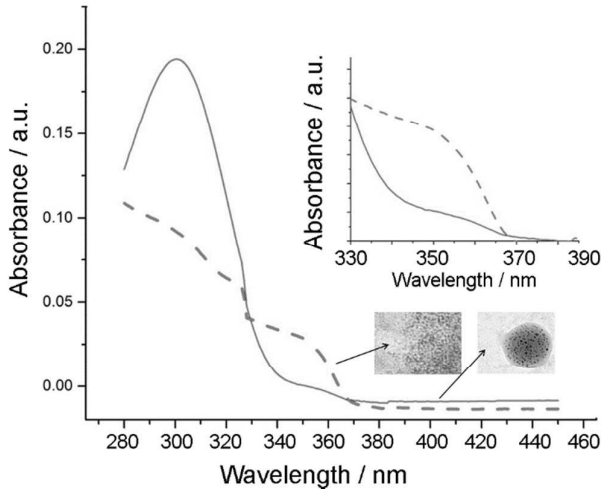



**Figure 2.** UV-Vis spectra of ZnO-DMSO (dashed line) and ZnO-Cya@$SiO_2$ (plain line).

**Figure 3** shows the room temperature photoluminescence spectra of the ZnO-$HL^{3,5}$@$SiO_2$. A visible emission centered at 395 nm can be clearly observed. ZnO QD are known to usually present two emission bands: one relatively weak and very narrow below 365 nm corresponding to the radiative recombination of excitons and an intense and broad one centered in the visible region between 400 and 600 nm that is known as trap emission. Generally, the green-yellow emission of ZnO QD is more intense than the blue one.[24, 44, 45] The mechanism for ZnO visible emission remains an unclear and controversial issue in the literature. It has been agreed that the green-yellow emission is due to electrons or holes trapped on ZnO surface oxygen vacancies,[39, 41] but it is rather difficult to determine the energetic position of the trapped carriers. Hence, the mechanism of the visible luminescence of ZnO could be either a recombination of a delocalised electron with a deeply trapped hole[46] or a recombination of a delocalised hole with a deeply trapped electron.[47] The green-yellow emission for ZnO nanoparticles is the only one that is concerned with the mechanisms, while the origin of the blue emission is rarely investigated. The shift in the emission spectrum to shorter wavelengths was proposed to be due to special surface states or to the quantum confinement of electrons and holes. Kahn et al.[48] have linked this blue fluorescence to a transition of an electron from a level close to the conduction band to a superficial trapped hole in the ZnO surface vacancy that owns an energetic position a little higher than the ZnO valence band.

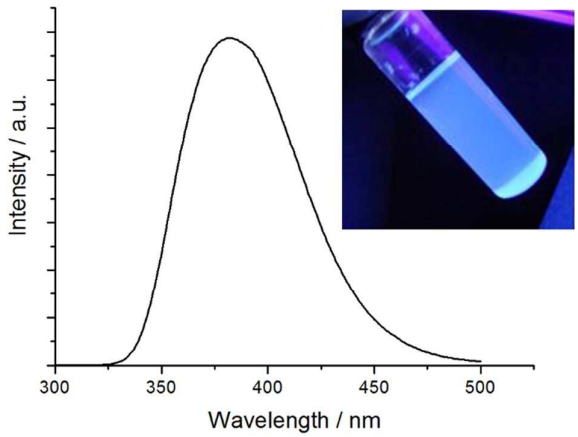



**Figure 3.** Room temperature PL emission spectra of ZnO-Cya@$SiO_2$ under 300nm excitation, inset: ZnO-Cya@SiO2 suspension in water under UV irradiation at 365 nm.

As investigated by Spanhel *et al.*, the emission wavelength can be tuned from 500 nm for freshly prepared ZnO nanoparticles of 3 nm to 560 nm after 5 days of aging and size of 5.5 nm. Thus to obtain blue emission, particles size smaller than 3 nm are necessary.[41] Nevertheless, Abdullah *et al.* have shown that blue luminescence can be achieved by encapsulating freshly prepared ZnO nanoparticles (particle size of 3 nm) into silica.[28] We can assume that in our ZnO-$HL^{3,5}$@$SiO_2$ composite nanoparticles, the photogenerated electrons transfer from the excited state of the CB units to the conduction band of ZnO nanoparticles, and then combine with the superficial trapped holes in ZnO surface vacancies. An equivalent blue photoluminescence was also observed by H.-M.Xiong et al. with methacrylic acid functionalised ZnO QD (MA@ZnO) coated by a thin layer of polymethylmethacrylate (PMMA) polymer.[49] In our previous studies we also observed this blue photoluminescence with ZnO-$HL^{3,5}$ in the LC phase. Therefore, it shows that the grafting of CB terminated carboxylate onto the ZnO surface is strong enough to keep the blue luminescence properties of the native ZnO-$HL^{3,5}$ within the silica nanoparticles.

The control of the luminescence property of nanomaterial is mandatory for many applications as for instance in photonic and biomedical areas. By exploiting important colloidal phenomena, the goal of this work was to synthesize luminescent and stable nanocolloids and nanomaterials. A simple one-pot synthesis process has been developed for the preparation of blue luminescent nanocolloids in organic or aqueous media. By using a $HL^{3,5}$ containing CB units to modify the surface of ZnO QD, it was possible to obtain monodispersed homogenous silica nanoparticles with a high loading levels of ZnO QD. For instance, these blue emission nanocolloids could have great interest for biological fluorescence, anti-counterfeiting labelling, or full-color display.

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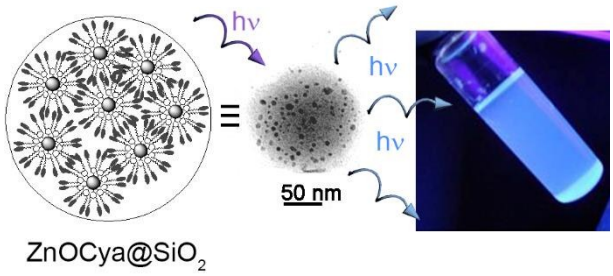


ZnOCya@$SiO_2$