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Fluorescence from Coated Oxide Nanoparticles

D. Vollath, I. Lamparth, D. V. Szabó

Forschungszentrum Karlsruhe, Institut fuer Materialforschung III
P.O.Box 3640, D-76021 Karlsruhe, Germany

ABSTRACT

In many cases, coated nanoparticles behave like isolated ones. Using the microwave plasma process, it is possible to produce oxide nanoparticles with ceramic or polymer coating. Coating the particles has the additional advantage that by proper selection of the coating it is possible to suspend the particles in distilled water without using any colloid stabilizer. From quantum dots made of sulfides or selenides, it is well known from literature that fluorescence depends strongly on the coating of the kernels. In the case of CdSe, the kernels are coated with CdS. Within this study, similar phenomena are found with coated oxide nanoparticles having sizes of ca. 6 nm exhibiting a very narrow particle size distribution. The coating consists of a second ceramic phase or a polymer one, each one influencing fluorescence differently. Obviously, the type of coating is a tool to modify fluorescence. This behavior is demonstrated on kernels made of Al_2O_3 , ZrO_2 , HfO_2 , ZnO etc. PMMA, PTFE, or Al_2O_3 were used as coating material. In most cases, the fluorescence spectra showed broad bands. In some cases, such as ZnO , additionally, a sharp emission line in the UV appears. It is interesting to note that coatings made of fluorine containing polymer materials did not lead to fluorescence intensities comparable with PMMA coatings. The observed spectra are equivalent whether the powder is in aqueous suspensions or dry on a quartz glass carrier. The experimental results in this study indicate that the combination of non-fluorescent oxide core with a non-fluorescent polymer coating may lead to a nanocomposite with strong fluorescence. This is a phenomenon not described in literature until now.

INTRODUCTION

Many applications of nanoparticles use fluorescence properties, e.g. in medical, biological, or pharmaceutical area. [1-7] Usually, fluorescence is a property of organic molecules or single isolated nanoparticles. Therefore, in most cases, fluorescence is determined in suspensions. Best fluorescence efficiency is obtained with semiconductor nanoparticles and semiconductor quantum dots based on sulfides, selenides, or tellurides. [8, 9] The best-described fluorescent nanoparticles are GaN [10, 11], doped ZnS [12], or doped CdSe. [13] All of these particles have the disadvantage of being as well poisonous as carcinogenic. Additionally, these particles show a very limited thermodynamic stability against oxidation. Therefore, research in the direction of fluorescent oxide nanoparticles is under way. [14-16] In most cases, fluorescence is obtained by doping with small amounts of rare earth ions. [17] In many cases, electron excitation of the fluorescent material led to the best results.

The Karlsruhe Microwave Plasma Process is capable to synthesize ceramic nanoparticles coated with a second ceramic layer [18,19] or a polymer. [20] In situ coating of each single particle is possible, because the particles leave the plasma zone, where the reaction occurs, with electric charges of equal sign. Therefore, the particles repel each other. This avoids agglomeration and makes it possible to coat the particles in a second step. The coating is performed in a

second step of a cascaded process of synthesis. The coating may consist of a ceramic or a polymer layer.

The availability of non-agglomerated coated nanoparticles is the basis for a new class of fluorescent nanoparticles based on non-toxic oxides. This study describes the fluorescence behavior of isolated respectively separated nanoparticles in suspension or as a powder. As particle cores Al_2O_3 , ZrO_2 , HfO_2 , TiO_2 , SnO_2 , WO_x , and ZnO were selected. Coating material was Al_2O_3 , PMMA, or PTFE, respectively. Electron microscopy revealed that the particle size of the different cores was in the range between 5 and 10 nm. The thickness of the coating was in the range from 0.5 to 2 nm for alumina and 2 to 5 nm for the polymer coatings.

EXPERIMENTAL

As mentioned above, the oxide nanoparticles were synthesized using the Karlsruhe Microwave Plasma Process. Except for zinc, chlorides or carbonyls were used as precursor compounds. For zinc, di-ethyl zinc was applied. PMMA coating was made using the monomer as precursor; PTFE like coating was obtained using C_{20}F_4 . Figure 1a and 1b depict typical electron micrographs of the material. Figure 1a shows crystallized HfO_2 coated with amorphous Al_2O_3 . Polymer coated material is shown in figure 1b. To obtain good contrast for printing, PMMA coated Fe_2O_3 was selected as example.

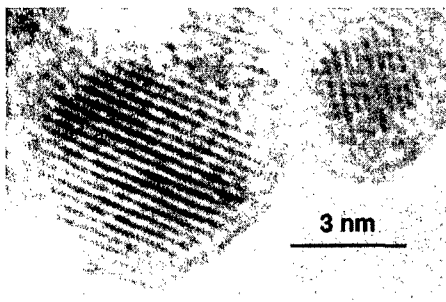


Figure 1a: Hafnia nanoparticles coated with alumina. The lattice fringes are belonging to HfO_2 ; the Al_2O_3 coating is amorphous.

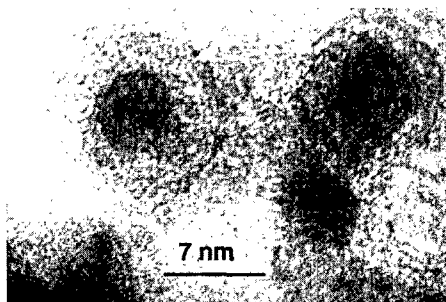


Figure 1b: Polymer (PMMA) coated ceramic nanoparticles. To obtain good visibility of the two phases, in this example, Fe_2O_3 was selected as kernel material

The fluorescence spectra were measured with a system using a Czerny-Turner monochromator. For illumination a HeCd (325 nm) or a xenon lamp were applied. The fluorescence signal was detected using a photomultiplier tube.

Figure 2 displays the fluorescence spectrum of pure alumina nanoparticles in comparison to the spectra of PMMA or PTFE coated alumina nanoparticles. Besides the fluorescence emission bands, the graph shows the exciting wavelength in first (325 nm) and second (650 nm) order. From this figure, it is obvious that PMMA coating enhances fluorescence and - most important - narrows the emission band.

Figure 2 leads to the assumption that the coating is an essential element of the fluorescent particle design. It is obvious that PMMA coating results in a maximum gain of the fluorescence. The effect of PTFE coating is significantly smaller, whereas the fluorescence of pure alumina is

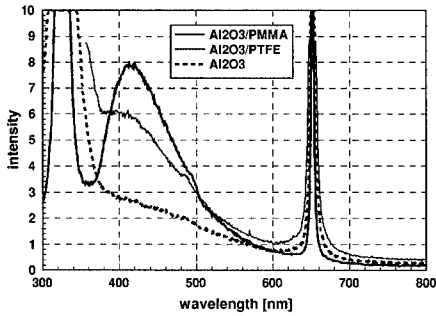


Figure 2: Fluorescence spectra of bare and polymer coated alumina nanoparticles

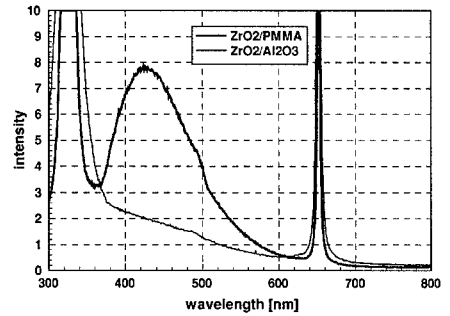


Figure 3: Comparison of the fluorescence spectra of alumina and PMMA coated zirconia nanoparticles.

nearly negligible. The figure 3 depicting the fluorescence behavior of zirconia with alumina or PMMA coating supports this assumption. Both figures clearly show the amplification of fluorescence by coating. Obviously, polymer coatings are more effective than coating with Al_2O_3 . Comparing the spectrum of alumina coated ZrO_2 with the one of bare Al_2O_3 particles, one may assume that the small fluorescence observed in this case stems from the alumina. In this context, the question arises whether it is possible to stimulate fluorescence with any oxide kernel that is coated with PMMA.

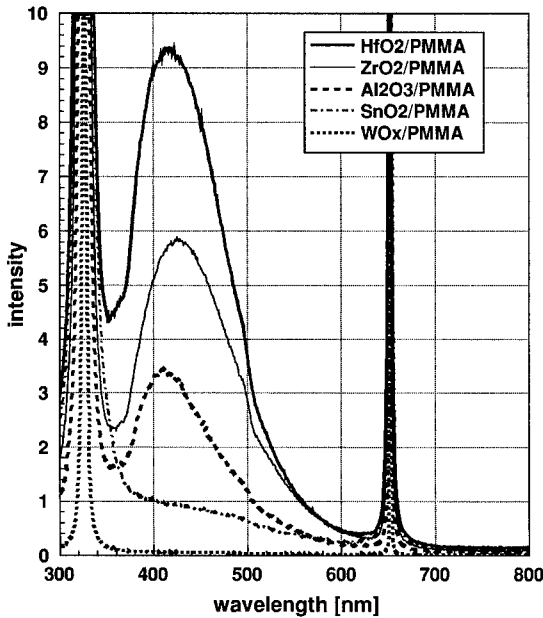


Figure 4: Fluorescence spectra of different oxide nanoparticles coated with PMMA.

Figure 4 summarizes of fluorescence spectra of different oxide kernels coated with PMMA. This figure demonstrates that polymer coating obviously enhances fluorescence, provided the kernel itself promotes fluorescence. The graph depicts drastically that the fluorescence intensity varies strongly with the oxide core. In the selected example, HfO_2 coated with PMMA has the highest fluorescence intensity, whereas WO_x is not fluorescing at all. This product is amorphous and has a deep blue color. Most probably it is one of the mixed $\text{W}^{4+} / \text{W}^{6+}$ oxides. On the other hand, it is interesting to note that the intensity maximum of the emission is not significantly dependent on the composition of the kernel. The small shift visible for the different oxide particles may be an artifact due to wavelength dependent self-absorption in the oxide cores. The similarity of the emission bands depicted for different oxide kernels with PMMA coating proposes an interpretation of these lines as Raman scattering or a related phenomenon. To clarify this point, the experiments were repeated with wavelengths of 250 and 350 nm. One of these results, depicted in figure 5, obtained with PMMA coated ZrO_2 shows clearly that the position of this emission band is independent of the exciting wavelength.

The fluorescence behavior of ZnO coated with PMMA is different (Figure 6). This nanocomposite exhibits the broad emission band with a maximum around 567 nm and additionally, a relatively sharp line emission with a maximum around 379 nm and 20 nm FWHM. Especially in aqueous suspensions, the intensity ratio of these two emission lines depends strongly on the concentration of the particles in the suspension. This is due to self-absorption phenomena.

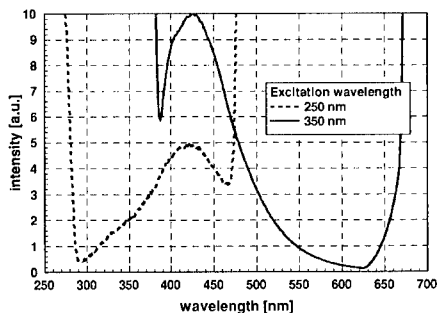


Figure 5: Fluorescence spectra of PMMA coated ZrO_2 dispersed in water as a function of the excitation wavelength. The intensity of the emission at 250 nm was multiplied by a factor of 20 to make the fluorescence visible for comparison.

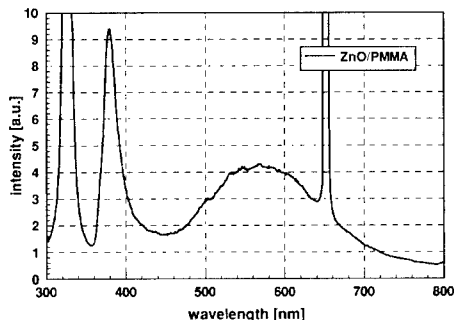


Figure 6: Fluorescence spectrum of ZnO/PMMA nanocomposites

DISCUSSION

Figures 2 and 3 clearly show that the fluorescence phenomena described in this paper are strongly dependent on the coating of the nanoparticles. Despite the different coatings on the oxide kernels, PMMA, or PTFE, in figure 2, the position of the fluorescence maximum is quite similar and in any case stronger than the fluorescence of the pure ceramic kernels. This may lead to the assumption that the fluorescence phenomena described in these figures are ones re-

lated to the interaction between ceramic kernel and polymer coating. This assumption is strongly supported by the results depicted in figure 4. In this figure, one realizes an astonishing similar fluorescence emission for the oxides HfO_2 , ZrO_2 , and Al_2O_3 . This is insofar strange as the electronic structure and the crystallization of these three compounds is very different. As nanoparticle, hafnia crystallizes monoclinic, zirconia cubic and alumina remains amorphous. Looking at the fluorescence spectra obtained with PMMA coated kernels of SnO_2 and WO_3 , one realizes that not every combination of an oxide core with PMMA leads to a light emitting system. This, in combination with the fluorescence results obtained at different wave length, as it is depicted in figure 5 using ZrO_2/PMMA as an example, makes clear that the emission peak around 420 nm cannot be attributed to Raman scattering or a related phenomenon. The phenomena lose even more systematic adding the results obtained with ZnO/PMMA composites. In this case, a strong fluorescence peak at 379 nm is observed. This peak may be attributed to the ZnO ceramic core, as it was also found by A. Mitra and R. K. Thareja in pressed and sintered pure ZnO powder with grain size significantly larger than 20 nm. [21] These authors report, for the material in use, the maximum of the emission around 395 nm. This is compatible with the blue shift of the emission of quantum dots, as the material used in this study had a grain size in the range of 5 – 10 nm. On the other hand, L. Guo et al. show that the intensity of this peak depends strongly on the amount of PVP in a ZnO/PVP mixture. It is of special importance that this peak was not found in the case of pure ZnO . [16] The broad peak, in this study observed with a maximum at 567 nm, was observed in other studies too. Depending on the environment, the maximum is at 500 nm [15], 520 nm [16] or 605 nm [22]. The reason for the difference between the composite ZnO/PMMA and the other oxide core/ PMMA composites is not clear. IR spectra of the coated particles reveal that the polymer molecules at the surface undergo partial loss of ester groups under formation of carboxylate bonds to the particle surface. [23] Even when the amount of carboxylates formed is different, this may not explain the difference in the spectra between the ZnO/PMMA and the other equivalent nanocomposites.

The experimental results concerning the effect of a ceramic coating is not clear. It can not be excluded that the fluorescence found in composites with alumina coating is just the fluorescence of the alumina.

CONCLUSIONS

Nanocomposite particles consisting of an oxide ceramic core and a ceramic or polymer coating may exhibit fluorescence. Coated particles of this type can be synthesized using the Karlsruhe Microwave Plasma Process. The experimental results indicate that the fluorescence phenomena observed are directly related to the interface between kernel and coating. The important point is that polymer coatings are promoting fluorescence more strongly than ceramic coatings. The fluorescence observed can not be attributed to Raman scattering related phenomena.

It is important to mention that the oxide/ PMMA nanoparticles are neither toxic nor carcinogenic.

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