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ORIGINAL

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2  
3 NANOPARTICLE PHOSPHORS MANUFACTURED USING THE BICONTINUOUS CUBIC  
4 PHASE PROCESS  
5

6 **Background of the Invention**

7 **1. Field of the Invention**

8 The present invention relates to generally to phosphors and more specifically to the  
9 production of nanoparticulate phosphors.  
10

11 **2. Description of the Background Art**

12 There is a resurgence in phosphor research due to the recent interest in developing emissive  
13 flat panel displays, e.g. full-color low-voltage field emitter displays (FEDs), large area plasma  
14 displays (PDs), and electroluminescent displays (ELDs). For example, to make low-voltage FEDs,  
15 decreasing the required electron energy by two orders of magnitude from the 30KV range of CRTs  
16 while maintaining significant light output is quite challenging. In low-voltage FEDs, the incident  
17 electron mean free path in the phosphor is extremely short, and some researchers feel that the photon  
18 generation process should occur reasonably close to the electron-hole pair creation point to avoid  
19 non-radiative recombination at nearby defects. Furthermore, there is the belief that present day  
20 micron size phosphors are surrounded by a dead layer of defective material whose thickness is  
21 comparable to or greater than the mean free path of low energy electrons used in low voltage FEDs.

1 The defects in this surface layer, which are produced, for example, by ball milling and other harsh  
2 surface (and bulk) defect producing processes, are believed to be non-radiative recombination  
3 centers. These result in low optical output when these phosphors are bombarded by low energy  
4 electrons.

5 Research interest in the general field of nanoscale materials has been growing fast. New  
6 methods of developing nanoparticles are being developed, and their novel physical properties are  
7 being studied. For example, in Yang et al., U.S.S.N 08/841,957, filed April 7, 1997, the entirety  
8 of which is incorporated herein by reference, nanocrystalline semiconductor particles are produced  
9 within the mesoporous cavities of a bicontinuous cubic phase. The cavities contain at least one of  
10 the reactants required to form the semiconductor compound. Any other required reactants are  
11 diffused into the mesoporous cavities.

12  
13 **Summary of the Invention**

14  
15 Accordingly, it is an object of the present invention to provide phosphors having a high light  
16 output level.

17 It is another object of the present invention to provide nanocrystalline phosphors that have  
18 no or few bulk defects.

19  
20 These and additional objects of the invention are accomplished by forming doped  
21 nanocrystalline semiconductor particles within the mesoporous cavities of a bicontinuous cubic

1 phase. The cavities contain at least one of the reactants required to form the semiconductor  
2 compound. Any other required reactants are diffused into the mesoporous cavities. Doped  
3 nanocrystals are produced by diffusing dopant or activation ions into the mesoporous cavities along  
4 with the other reactants or by including dopant or activation ions within the mesoporous cavities of  
5 the BCP under conditions such that the nanoparticles are doped with an average of one or less dopant  
6 ions per particle. For the purposes of the present specification and claims, the words "dopant" and  
7 "activator" are used interchangeably to describe the ion that, when placed within the interior of a  
8 nanocrystalline particle, provides the particles with phosphorescence.

9  
10 **Brief Description of the Drawings**

11  
12 A more complete appreciation of the invention will be readily obtained by reference to the  
13 following Description of the Preferred Embodiments and the accompanying drawings in which like  
14 numerals in different figures represent the same structures or elements, wherein:

15 Fig. 1 is a schematic representation of the synthetic approach used in the method of the  
16 present invention.

17 Fig. 2 is a comparison of the excitation and emission spectra of a nanocrystalline sample with  
18 a bulk reference.

19 Fig. 3 show the dependance of quantum yield on the manganese salt concentration. A freshly  
20 made Rhodamine-B solution was used as a calibration standard.



1 phosphors appear to indicate that the intrinsic luminescence efficiency of doped phosphors can be  
2 drastically improved by reducing the particle size to nanometer dimensions.

3 The invention allows for a very narrow size distribution and physical particle isolation, and  
4 allows one to obtain well isolated activator ions which emit the visible light. That is, the present  
5 invention provides nanoparticles having an average of just one activator ion per nanoparticle  
6 phosphor grain. Self-assembled three dimensional structures which are comprised of mesoporous  
7 cavities are used for this purpose.

8 Any combination of surfactant and liquid hydrophilic phase, at any ratio that produces a  
9 bicontinuous cubic phase, may be employed. As stated earlier, the formation of bicontinuous phases  
10 has been well characterized in the prior art. Thus, the specifics of forming the bicontinuous phase  
11 will not be discussed here.

12 Bicontinuous cubic phases include mesoporous cavities that are interconnected by channels.  
13 The cells and the channels interconnecting the cells are filled with the liquid hydrophobic phase. In  
14 the present application, the liquid hydrophilic phase is typically exemplified by an aqueous phase.  
15 Another liquid hydrophilic phase such as ethanol or methanol, however, may be used in place of an  
16 aqueous phase according to the present invention. Thus, unless otherwise stated, teaching in the  
17 present application relating to the use of an aqueous phase are applicable to the use of any liquid  
18 hydrophilic phase used in place of an aqueous phase.

19 The size of the mesoporous cavities in a bicontinuous cubic phase is controlled, in an art-  
20 known and recognized manner, by selection and concentrations of the aqueous (or non-aqueous)  
21 phase and surfactant. Typically, mesoporous cavities (aka "pores") in a bicontinuous cubic phase

1 have a diameter of about 2 nm to about 30 nm, and more often about 2.5 to about 10 nm. Of course,  
2 the only upper limit on the size of the mesoporous cavities useful in the method of the present  
3 invention is that they must be sufficiently small to restrict the diameter of semiconductor particles  
4 grown therein to about 30 nm or less. Therefore, bicontinuous cubic phases having mesoporous  
5 cavities as large as about 30 nm are useful according to the present invention.

6 Surfactants used to form the BCP structure have at least one long chain ( $C_8$  or above)  
7 hydrophobic (typically alkyl) chain and at least one polar head group. These surfactants may be  
8 glycerated or non-glycerated, and may be nonionic, amphoteric, anionic, or cationic. These  
9 surfactants may also be lipids. Some typical surfactants useful in forming bicontinuous cubic phases  
10 include sodium diethyl hexylsulphosuccinate (AOT), potassium octanoate, decyltrimethylammonium  
11 chloride, dodecyltrimethylammonium chloride and mono-1-olein hexadecyllysophosphatidylcholine.

12 The reactants used to form the semiconductor particles should be soluble in the phase (i.e.,  
13 hydrophobic chain of the surfactant, the aqueous phase of a non-inverted bicontinuous cubic phase,  
14 or the non-aqueous phase of an inverted bicontinuous cubic phase) which fills the pores of the  
15 bicontinuous cubic phase, and should react, in solution, to form semiconductor particles that are  
16 insoluble in the pores of the bicontinuous cubic phase.

17 To form semiconductor particles according to the method of the present invention, at least  
18 one of the reactants required to form the semiconductor compound, but less than all of the required  
19 reactants, are usually included in the surfactant or aqueous phase used to make the bicontinuous  
20 cubic phase, so that the latter formed bicontinuous cubic phase includes that at least one reactant in  
21 solution within its pores. The remaining required reactants are then diffused into the pores of the

1 bicontinuous cubic phase. Once these remaining materials diffuse into the pores, they react with the  
2 at least one reactant to form the desired semiconductor particles.

3 Alternatively, the at least one required reactant, but less than all the required reactants, are  
4 initially diffused into the pores of a preformed bicontinuous cubic phase. After this initial diffusion  
5 has completed, the remaining reactants are diffused into the pores, where they react with the  
6 reactant(s) previously diffused into the pores, thus forming semiconductor particles. Most  
7 semiconductor compounds are binary compositions, for example II-IV and IV-VI semiconductors.  
8 Typically, binary semiconductor compositions are readily formed by reacting two reactants. In  
9 these cases, one of the reactants is within the pores before the other reactant is diffused into the  
10 pores. Some binary semiconductor nanocrystals that can be made according to the present invention  
11 include doped semiconductors such as PbS, CdS, PbSe, CaS, SrS, and ZnS.

12 In another alternative, all the reactants may be placed within either the aqueous phase or the  
13 surfactant, and the temperature of the aqueous phase and/or surfactant maintained below the reaction  
14 temperature until after mixing the aqueous phase (or non-aqueous phase) and surfactant to form the  
15 bicontinuous cubic phase.

16 The choice of which reactant(s) is provided in the bicontinuous cubic phase either during  
17 formation of the phase or during initial diffusion depends upon the diffusion characteristics of the  
18 reactants, and may vary depending upon the selection of the surfactant. Preferably, the reactants that  
19 diffuses slowest through bicontinuous cubic phase are the reactants initially present inside the pores.  
20 Otherwise, a substantial loss in yield may occur during diffusion of the final reactants into the  
21 bicontinuous cubic phase, since the initial reactants will be diffused out of the pores as the final

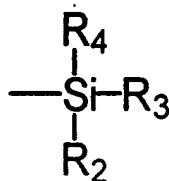


1 reactants are diffusing in. Persons skilled in the art can predict the diffusion characteristics of many  
2 compounds for a variety of surfactants. Thus, the selection of appropriate combinations of solvents,  
3 reactants, and surfactants to form semiconductor nanoparticles of a specified composition should not  
4 be difficult. The reactants used to form the nanocrystalline semiconductor particles according to the  
5 present invention are generally either negatively or positively charged ions that react with at least one  
6 oppositely charged ionic reactant to form the desired semiconductor compound. Dopant/activator  
7 ions may also be provided in the matrix in the same manner as the reactants, i.e., either by diffusion  
8 or by inclusion in the solvents and/or surfactants mixed to form the bicontinuous cubic phase.

9 To form phosphors, the dopant ion should be an activator ion that possesses a high level  
10 empty state and a lower level empty state, both of which are within the bandgap of the host  
11 semiconductor material. Upon excitation, which may occur from exposure to kinetic (e.g., collision  
12 with a high energy subatomic particle) thermal, chemical, electrical, or electromagnetic energy (e.g.,  
13 visible, u.v., or ionizing radiation) depending upon the combination of host and dopant, the excited  
14 electrons populate the upper level of the host material. A radiative transition from such a localized  
15 higher energy level to a lower empty level in the same activator ion is characterized by the emission  
16 of visible light. The dopants are typically transition metals or rare earth metals that act as the  
17 luminescent centers or phosphorescent centers. A number of different activator ions in different host  
18 materials have been measured. For example, Mn-doped ZnS is known to emit in the 580 nm range,  
19 whereas copper (or terbium) and silver doping will result in green and blue emission respectively.

20 Once the reactants have formed the doped semiconductor compound, the bicontinuous cubic  
21 phase is dissolved in solvent that in which the doped semiconductor compound is insoluble. The

1 doped semiconductor nanoparticles may then subjected to a final wash in a solution including a  
2 passivating compound that serves as an antiagglomeration agent. The passivating compound is a  
3 long chain hydrocarbon Y-R-SH, where R is a hydrocarbon carbon chain of at least two, and  
4 typically three or more, carbons and Y is a hydrophobic or hydrophilic end group, depending upon  
5 the dispersing solvent (i.e., hydrophobic for non-aqueous dispersants, and hydrophilic for aqueous  
6 dispersants). Typical Y groups include alkyl groups, -COOH, -OH, -SH and



7  
8  
9 where R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> may be the same or different and are ethyl or methyl. These antiagglomeration  
10 agents attach to the surface of the nanoparticles and protect them from agglomeration and reaction  
11 with the environment, for example, air. Semiconductor compounds passivated with compounds  
12 having Y = -SH have the potential to organize into new and interesting structures.

13 Of course, the reactants and materials used should be as free as possible of potential  
14 impurities that might significantly reduce the usefulness of the semiconductor nanocrystals produced  
15 according to the present invention as nanocrystalline semiconductor phosphors. The stoichiometric  
16 composition of the nanoparticle with respect to the dopant ion can also be controlled very accurately  
17 via the relative concentration of the precursor ions, as shown the accompanying examples.

18 Typical dopants/activators used in the present invention include Mn; Cu; Ag; Eu; Cu,Cl;  
19 Cu,Tb; Tb; Ag,Cl; Cl; Cu,Al; Ce; Er; Er,Cl; Zn. Where the dopant/activator is a mixture, such as

1 Cu,Cl, some nanoparticles are doped with Cu, while other nanoparticles are doped with Cl. Typical  
2 hosts include ZnS, ZnO, CaS, SrS,  $Zn_xCd_{1-x}S$ ,  $Y_2O_3$ ,  $Y_2O_2S$ ,  $Zn_2SiO_4$ ,  $Y_3Al_5O_{12}$ ,  $Y_3(AlGa)_5O_{12}$ ,  
3  $Y_2SiO_5$ , LaOCl, InBO<sub>3</sub>, Gd<sub>2</sub>O<sub>2</sub>S, ZnGa<sub>2</sub>O<sub>4</sub>, yttrium niobate, TAG and YAGAG.

4 Some examples of host-activator/dopant pairs according to the method of the present  
5 invention include: ZnS:Mn; ZnS:Cu,Mn; ZnS:Cu; ZnS:Ag; ZnS:Cu,Cl; ZnS:Eu; ZnS:Cu,Tb;  
6 ZnS:Tb; ZnS:Ag,Cl; ZnS:Cu,Al;  $Zn_xCd_{1-x}S$ :Mn;  $Zn_xCd_{1-x}S$ :Ag,Cl;  $Zn_xMg_{1-x}S$ :Mn; SrS:Mn; SrS:Ce;  
7 CaS:Mn; CaS:Er,Cl; CaS:Tb; and ZnO:Zn. Other possible phosphors that may be made according  
8 to the present invention include: ZnS:Cu.Mn; ZnS:Cu; ZnS:Ag; ZnS:Cu,Cl; ZnS:Eu; ZnS:Cu,Tb;  
9 ZnS:Tb; ZnS:Ag,Cl; ZnS:Cu,Al;  $Zn_xCd_{1-x}S$ :Mn;  $Zn_xCd_{1-x}S$ :Ag,Cl;  $Zn_xMg_{1-x}S$ :Mn; SrS:Mn; SrS:Ce;  
10 CaS:Mn; CaS:Er,Cl; CaS:Tb.

11  
12 Having described the invention, the following examples are given to illustrate specific  
13 applications of the invention including the best mode now known to perform the invention. These  
14 specific examples are not intended to limit the scope of the invention described in this application.

## 15 16 EXAMPLES

### 17 **Example 1 - Synthesis of ZnS:Mn nanoparticles**

18 Nanoparticles of zinc sulfide doped with manganese (ZnS:Mn) were prepared at room  
19 temperature in the BCP of a surfactant/water system. The nanoparticles were purified, isolated, and  
20 surface passivated (See Fig. 1) to prevent agglomeration. They were found to be highly stable under

1 a 200keV electron beam of a transmission electron microscope (TEM). The TEM micrographs  
2 showed the particles to have a size in the 2-3 nm range and were monodispersed. The average  
3 particle size ( $2.5 \pm 0.5$  nm) determined from x-ray diffraction studies agreed well with the TEM  
4 measurements. From high resolution TEM studies, it was determined that the nanoparticles were  
5 monocrystalline with a zinc-blende cubic lattice.

### 6 7 **Example 2 - Photoluminescence studies**

8 Excitation and emission spectra, measured using a fluorimeter, were compared with that of  
9 a 'bulk' sample, as shown in Fig. 2. The excitation peak from the nanoparticle phosphor, centered  
10 at about 300 nm (4.1 eV), was found to be narrower (25 nm or  $\sim 0.32$ eV) and blue shifted compared  
11 to the bulk micron size particle phosphor, due to the quantum confinement. On the other hand, the  
12 emission peak showed a slight red shift with decreasing particle size. This red shifting of the  
13 emission peak might be due to a distortion of the nanoparticle lattice, the creation of a slight  
14 compression or relaxation of the lattice, and/or a change in the unit cell volume. Interestingly,  
15 absorption measurements (not shown) indicate that the  $Mn^{2+}$  absorption peaks appear relatively  
16 unaffected by the nanocrystalline environment.

### 17 18 **Example 3 - Effect of Manganese concentration on quantum yield**

19 Using the BCP process, a number of ZnS:Mn nanoparticle samples were prepared by varying  
20 the Mn/Zn molar ratio in the initial salt solution. The quantum yield, measured as a function of Mn  
21 concentration in the initial solution, Fig. 3, shows that the photoluminescent efficiency is maximum

1 at about 0.7 mole%. EPR studies (discussed below) indicate that at this maximum efficiency, the  
2 effective doping level is about one manganese atom per nanoparticle.

3  
4 **Example 4 - Electroparamagnetic resonance studies**

5 Electron paramagnetic resonance (EPR) studies were performed on the ZnS:Mn  
6 samples discussed above in Examples 1 through 3. EPR spectra for three representative samples are  
7 shown in Fig. 4. The spectra for manganese concentrations at and below 0.5% manganese doping,  
8 e.g. the middle curve, show the six-line hyperfine structure of isolated  $Mn^{2+}$  ions. The hyperfine  
9 spectrum is due to interactions of the unpaired and isolated Mn electrons with the nuclear spin of the  
10 Mn nucleus. Mn has a nuclear spin,  $I$ , of 5/2, resulting in a six-line hyperfine spectrum.

11 At high Mn concentrations (see the spectrum with 2% Mn), the smearing of the hyperfine  
12 lines and the presence of the broad underlying structure indicates that the interactions between  
13 neighboring  $Mn^{2+}$  ions is significant (Y. Ishihara, *J. Phys. Soc. Jpn.*, **21**, 1473 (1966); J. Kreissl,  
14 *Phys. Stat. Sol. A*, **97**, 191(1986)). And this Mn-Mn interaction decreases the photo efficiency as  
15 shown in Fig. 3.

16 The presence of a broad underlying structure in the middle spectrum of Fig. 4, though not as  
17 significant as for the 2% sample, is indicative of the existence of exchange coupled  $Mn^{2+}$  ions in  
18 this sample also. In other words, even at 0.5% Mn (based on the total number of Zn ions) loading  
19 many of the Mn atoms are not isolated from each other and as such are not participating as efficient  
20 visible light emitters. These results suggest that these exchange coupled Mn pairs might be located

1 outside the nanoparticles, perhaps on the surface of the nanoparticles, and their existence might even  
2 be a channel for non-radiative recombination. In fact, this data, coupled with the fact that the  
3 photoluminescence is maximum at this Mn concentration suggests that in each ZnS nanoparticle  
4 there is, on the average, one or less than one isolated Mn ion.

5  
6 In summary of the results obtained in the Examples, the recently developed room temperature  
7 bicontinuous cubic phase (BCP) process was modified to synthesize uniformly small ZnS:Mn  
8 nanoparticles. The size of these nanoparticles was about  $2.5 \pm 0.5$  nm. Optical absorption and  
9 photoluminescence measurements confirmed an increased band-gap as a result of the quantum-size  
10 effect. Quantum yield measurements on ZnS nanoparticles as a function of Mn doping concentration  
11 coupled with EPR measurements suggest that only those nanoparticles doped with one isolated Mn  
12 atom contribute to the photoluminescence.

13 Another unique advantage of the nanoparticles according to the present invention is that they  
14 are not only photoluminescent, but they can also be cathodoluminescent and electroluminescent.  
15 The ability of nanoparticles according to the present invention to have these various forms of  
16 luminescence allows one particle to be used for several distinct applications. This versatility  
17 simplifies the design and production of luminescent displays and provides for improved economy  
18 of scale.

19  
20 Obviously, many modifications and variations of the present invention are possible in light

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Inventor's Name: Yang et al.

**PATENT APPLICATION**

- 1 of the above teachings. It is therefore to be understood that,
- 2 the invention may be practiced otherwise than as specifically described.

Docket No.: N.C. 78,815  
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PATENT APPLICATION

ABSTRACT

Nanocrystalline phosphors are formed within a bicontinuous cubic phase.