Defect Transition Can Enhance Band-Edge Emission in Semiconductor Nanocomposites

Defects are usually considered a big disadvantage in solid-state emitters because they reduce the quantum efficiency of bandgap emission. However, researchers at National Taiwan University have found that coating a layer of CdSe/ZnS core–shell nanoparticles can convert the defect loss into bandgap emission in ZnO nanorods. The bandgap emission of ZnO nanorods can be enhanced as much as 30 times. The possible mechanism is based on the resonance effect between defect transition and band-to-band excitation and the transfer of excited electrons between conduction band edges.

In the March 15, 2008, issue of *Optics Letters* (DOI: 10.1364/OL.33.000569, p. 569), L.-J. Tzeng, C.-L. Cheng and Y.-F. Chen reported preparing ZnO nanorods on the surface of gold-coated sapphire using a mixture of high-purity ZnO and carbon powders by a vapor–liquid–solid process. The nanorods were well aligned and had an average diameter of 50 nm and a length of about 1 μm. The researchers used a sol-gel process to synthesize CdSe/ZnS core–shell quantum dots. First, CdSe cores were made using CdO and Se precursors in stearic acid at 320°C in the presence of trioctylphosphine oxide and hexadecylamine. Then, the researchers used diethylzinc and hexamethyldisilathiane as the Zn and S precursors to form a ZnS shell on the CdSe cores. Finally, the core–shell quantum dots dissolved in methylbenzene were spin-coated onto the ZnO nanorods.

After the preparation, the researchers used a spectrometer equipped with a He-Cd (325 nm) laser source, a Spex 0.85 m double-grating monochromator, and a cooled photomultiplier tube to obtain the photoluminescence spectra of pure ZnO nanorods and CdSe/ZnS quantum dots, and the composite of ZnO nanorods coated with CdSe/ZnS quantum dots. They found that the weak bandgap emission of ZnO nanorods at 380 nm is enhanced in the composite, while the emission of CdSe/ZnS quantum dots at 570 nm is reduced. This indicates that energy is transferred from CdSe/ZnS quantum dots to the ZnO nanorods where it is converted into the bandgap emission. The researchers concluded that the defect emission at 540 nm should be in resonance with the bandgap excitation of the quantum dots to obtain the most efficient energy conversion. When they prepared samples coated with core–shell CdSe/ZnS quantum dots prepared such that the defect transition in the ZnO nanorods was in resonance with the bandgap excitation of the CdSe/ZnS quantum dots, the bandgap emission of the ZnO nanorods was enhanced by more than a factor of 30 and the bandgap emission of the CdSe/ZnS quantum dots was greatly reduced. The researchers believe that the enhancement involves a mechanism similar to fluorescence resonant energy transfer between the ZnO defect transition and the band-to-band transition in the CdSe quantum dots. This approach can become a general strategy for the design of many other nanocomposites with enhanced photoluminescence at the bandgap wavelengths.

ZHAOYONG SUN

Resonant Scheme for Interferometric Lithography Improves Spatial Resolution Beyond Diffraction Limit

M. Kiffner and J. Evers from the Max-Planck-Institut für Kernphysik, in Heidelberg, Germany, and M. Suhail Zubairy from Texas A & M University, USA, recently proposed a novel approach for generating subwavelength structures in interferometric optical lithography based on the preparation of the system in a position-dependent trapping state via phase-shifted standing wave patterns.

In the February 22 issue of *Physical Review Letters* (DOI: 10.113/PhysRevLett. 100.073602), the researchers proposed preparation of atoms in a position-dependent state by coherent population trapping. In the simplest case, two stable ground states were resonantly coupled to an excited state by laser fields with Rabi frequencies R and S. Thus, the system was optically pumped into a coherent superposition of the two ground states, decoupled from the applied light fields. The population of each ground state depended only on the ratio of the Rabi frequencies. The researchers explained that this scheme works, in principle, for arbitrarily low laser intensities in contrast to schemes based upon multiphoton absorption, which require high field intensities. The spatial modulation was obtained by applying resonant laser fields that shift the phases of the standing waves with respect to each other such that their ratio becomes position dependent. The researchers also demonstrated that this analysis can be generalized to level schemes with an $N \times$ three-level structure. The only requirement is that all Rabi frequencies R_n or all S_n $(1 \le n \le N)$ address different atomic transitions. A product of N sinusoidal waves with wave number k_0 can lead to the population in a designated level with spatial oscillations with frequency wave number Nk_0 only, cancelling all other harmonics by a suitable choice of the relative phase shifts of the standing waves.

The researchers proposed two ways for the implementation of this scheme: the use of suitable level structures in atomic gases and directly exposing a photoresist on a surface using suitable coherence times between spin states similar to that in doped solids. "Either way," the researchers said, "the applicability of our scheme already at low-field intensities considerably facilitates the realization, in particular in extended systems."

JOAN J. CARVAJAL

Ants Inspire Algorithm for the Design of Conducting Polymer Alloys

Recently, researchers at the Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, Sao Paulo, Brazil, adapted an ant algorithm to design conducting polymer alloys. Ants establish optimal paths by depositing pheromone as they travel. The insects tend to follow trails having high pheromone concentrations, a positive-feedback mechanism termed autocatalytic. In this research, a trail is created when a virtual ant walks from one point to another on the potential surface, depositing virtual pheromone in an amount proportional to the solution at the end point. Evaporation removes pheromone from trails that are not traveled by other ants. In a given cycle, 20 ants are distributed randomly on the potential surface and are allowed to take a given number of steps. In this approach, the best trails are marked with more pheromone, because they are more traveled in the same time. The simulation ends when no improvement on the best solution is obtained in a given cycle.

As reported in the March issue of *Chemical Physics Letters* (p. 290), B.V.C. Martins, D.S. Galvão and co-workers considered as a test case a well-studied system of conducting polymers: polyaniline, which can have three different monomeric units. Conductivity is determined by the relative concentrations of the three forms in the polymer chain. The researchers solved the problem as a proof of concept by systematic search: determining the optimal relative concentrations of the three polyaniline forms in a polymer chain with a total of 100 monomers. Polymer bandgaps were calculated using a Hückel Hamiltonian (tight-binding model). The electron delocalization was estimated by the inverse participation number, calculat-

https://doi.org/10.1557/mrs2008.96 Published online by Cambridge University Press

Laser-Beam Method Yields 3D Synthesis of Copper Nanoparticles Inside a Polymer Substrate

Researchers from The Institute of Scientific and Industrial Research at Osaka University, Japan, recently reported the first 3D writing of copper nanoparticles inside a polymer matrix. M. Sakamoto, T. Majima and co-workers used a two-color laser-beam technique often employed in 3D dense wiring of microelectronic components and photonic devices such as photonic crystal waveguides.

In a recent issue of *Chemistry of Materials* (DOI: 10.1021/cm702170h), the group demonstrated that simultaneous irradiation with low-power UV and relatively high-power visible laser beams could be a successful combination for the production of copper nanoclusters without ablation of the polymer substrate.

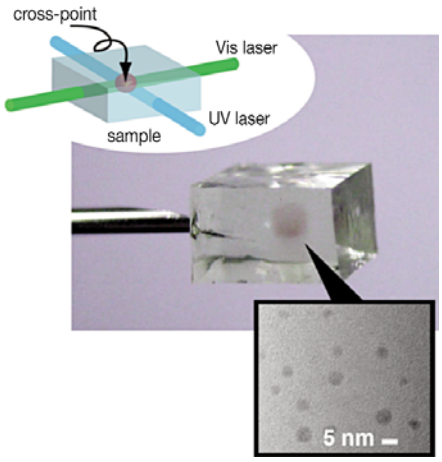

Figure 1. Optical image of a 3D array of copper nanoparticles in a polymeric substrate. The top inset shows a schematic of the synthesis process, while the bottom inset is a high-resolution transmission electron microscope image of the nanoparticles. Reproduced with permission from M. Sakamoto, T. Tachikawa, M. Fujitsuka, and T. Majima, *Chem. Mater*. **20**, 6 (2008) 2060. © 2008 by the American Chemical Society.

The researchers first prepared 3-mm thick films containing polyvinyl alcohol as a future hydrogenation source, Cu^{2+} from copper(II) acetate, and benzophenone (BP), starting from a formic acid solution. Upon irradiation with a UV laser, BP was excited to a triplet state, BP(T1), which easily abstracts hydrogen from polyvinyl alcohol to form the ketyl (BPH•) and polyvinyl alcohol radicals. Both radicals can reduce Cu^{2+} ions to Cu^{+}, as demonstrated in separate measurements by laser flash photolysis. This one-photon process is, however, inefficient in further reducing the Cu^{+} ions. These ions have a highly negative reducing potential, and the Cu^{+} would oxidize back to Cu^{2+}. The simultaneous irradiation with a visible laser further excites BPH• to BPH•(D1), which has some efficiency in reducing Cu^{+} ions. This efficiency is further amplified after the formation of the first neutral copper clusters because two helping phenomena occur: The copper ions absorbed by the clusters have a significantly higher reducing potential, accessible now to the BPH• and PVA radicals, and the film better absorbs the visible laser radiation, generating thermal effects that accelerate the reduction process of the ions. The result, after about one hour of irradiation, is the formation of a 3D array of copper nanoparticles at the intersection of the two laser beams, visible with the naked eye as a red coloring in the film (Figure 1).

EUGEN PANAITESCU

ed from the coefficients of the highest occupied molecular orbitals. Because good conductors have bandgaps lower than 25 meV (the thermal energy at room temperature) and also have inverse participation numbers close to zero, the researchers defined a potential surface function as the negative log of the product of bandgap and inverse participation number. Symmetry reduces the number of possible configurations to a grid of 5151 points with high peaks corresponding to metallic signatures. The 10 best polymer compositions, which are all metallic states, were located in 100 search runs. The researchers demonstrated that the ant algorithm can outperform genetic algorithms for this kind of problem. "[We] see the present methodology as more than an optimization technique; we consider it an effective tool to design new materials, such as metals, semiconductors, or oxides. The information gained from the simulations can help chemists synthesize new structures with the desired properties."

STEVEN TROHALAKI

TiO_2 Nanoarray Photoanode Improves Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSCs) have attracted many researchers in the field of photovoltaics because of their low cost. Nanostructured materials have been found to increase the performance of the cells. Researchers from Tsinghua University and the University of Electronic Science and Technology of China have demonstrated improvement in the photovoltaic performance of dye-sensitized solar cells through the use of TiO_2 nanoarrays as a photoanode.

In the February issue of the *Journal of the American Ceramic Society* (DOI: 10.1111/j.1551-2916.2007.02132.x), H. Lin and coworkers from Tsinghua University and N. Wang from the University of Electronic Science and Technology of China prepared TiO_2 nanoarrays by immersing pure titanium substrates into 10 M NaOH aqueous solution and heating them at different temperatures (140°C–200°C) for different amounts of time (2–6 hours). Then they immersed the nanoarrays in 0.1 M HCl aqueous solution for 12 hours and washed them in deionized water. After postannealing in air at 300°C–550°C for two hours, TiO_2 nanoarrays were obtained. The researchers removed these nanoarrays from the Ti plates and pasted them onto the indium tin oxide (ITO) glass that had first been coated with a 1-μm thick layer of a TiO_2 colloid by the doctor-blading method. Then they immersed the arrays in an ethanol solution of N719 dye $(Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$ for 15 hours to prepare the photoanode. The electrolyte used contains a mixture of 0.3 M LiI, 0.03 M I_2, and 0.5 M tertiarybutylphosphine (TBP) in an acetonitrile solution. By using a platinum film on a conducting glass as a counter electrode, they measured the photovoltaic performance under air mass (AM) 1.5 solar conditions. They found the efficiency of the cell (η) to be about 6.58% with a short circuit current density J_{SC} of 15.2 mA/cm^2. They also fabricated dye-sensitized solar cells with commercial TiO_2 powder as a photoanode to compare the photovoltaic performance. The result was that η and J_{SC} were around 5.64% and 13.5 mA/cm^2, respectively. These figures were lower than that of the nanoarray photoanode. The researchers claimed that this was due to the fast electron transfer in the one-dimensional structure of the nanowire. However, in the case of TiO_2 nanoparticles, electron transfer is hampered by the defects in the boundaries of the nanoparticles.

The researchers also used scanning electron microscopy to study the form of the nanoarrays as a function of reaction temperature and time. They found that, for short reaction times, primarily short and flat nanobelts formed at the lowest reaction temperatures, whereas the nanobelts evolved into multilayer nanowire struc-

https://doi.org/10.1557/mrs2008.96 Published online by Cambridge University Press