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.

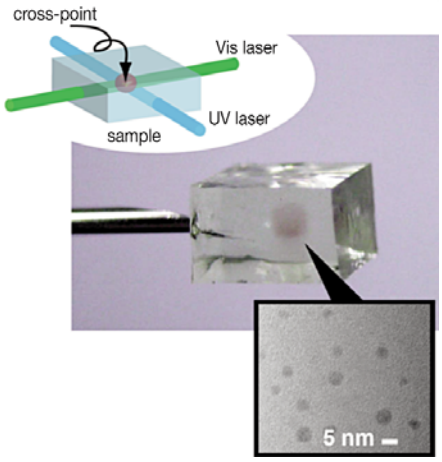

Figure 1. Optical image of a 3D array of copper nanoparticles in a polymeric substrate. The top inset shows a schematic of the synthesis process, while the bottom inset is a high-resolution transmission electron microscope image of the nanoparticles. Reproduced with permission from M. Sakamoto, T. Tachikawa, 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 ($BPH^{\bullet}$) 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 $BPH^{\bullet}$ to $BPH^{\bullet}$(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 $BPH^{\bullet}$ 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-

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tures at higher temperatures. However, if the reaction temperature was maintained constant and low, the short and flat nanobelts formed first and then evolved into the multilayer nanowire arrays. The nanowires were 70–90 nm in diameter and several microns long, and were composed of $H_2Ti_5O_{11}·H_2O$. The researchers believe that dislocations in the nanobelts cause strain in the cross-direction, which increases as the nanobelt grows. When the strain reaches a critical point, the nanobelt is converted into the multilayer structure from which the nanowires are formed.

The researchers indicated that their results show "the great potential of one-dimensional nanoarrays to be applied in DSCs to improve their photovoltaic performance."

M. GOWTHAM

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