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.

The researchers first prepared 3-mm thick films containing polyvinyl alcohol as a future hydrogenation source, Cu²⁺ 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 (BP⁎) and polyvinyl alcohol radicals. Both radicals can reduce Cu²⁺ 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 Cu²⁺ would oxidize back to Cu²⁺. The simultaneous irradiation with a visible laser further excites BPH⁰ 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 BPH⁰ 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).

**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.

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Titanium Dioxide Nanoparticle 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 TiO₂ nanorods 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 co-workers from Tsinghua University and N. Wang from the University of Electronic Science and Technology of China prepared TiO₂ nanorods 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 nanorods 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, TiO₂ nanorods were obtained. The researchers removed these nanorods 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 TiO₂ colloid by the doctor-blading method. Then they immersed the arrays in an ethanol solution of N719 dye (Bu₄N)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 I₂, 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 that the efficiency of the cell (η) is about 6.58% with a short circuit current density Jₛₑ of 15.2 mA/cm². They also fabricated dye-sensitized solar cells with commercial TiO₂ powder as a photoanode to compare the photovoltaic performance. The result was that η and Jₛₑ of the TiO₂ powder were around 5.64% and 13.5 mA/cm², respectively. These figures were lower than that of the nanorod 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 TiO₂ 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 nanorods 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-
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 $\text{H}_2\text{Ti}_5\text{O}_{11}\cdot\text{H}_2\text{O}$. 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.”

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