Division of Synthetic Chemistry -Advanced Inorganic Synthesis-

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Scope of Research

We are focusing on the precise synthesis of inorganic nanoparticles by controlling the primary (size, shape, composition, etc.) and secondary (spatial arrangement) structures to tune their properties, such as electron confinement, carrier oscillation, spin, and catalysis. These high quality inorganic nanoparticles are applied to both high-performance nanodevices (single electron transistor, plasmon waveguide, nanocomposite magnet) and photo-energy conversion materials (overall water splitting, solar cell).

KEYWORDS

Inorganic Nanoparticles Single Electronics Plasmonics Nanocomposite Magnet Photocatalysts



Selected Publications

Sakamoto, M.; Tanaka, D.; Tsunoyama, H.; Tsukuda, T.; Minagawa, Y.; Majima, Y.; Teranishi, T., Platonic Hexahedron Composed of Six Organic Faces with an Inscribed Au Cluster, *J. Am. Chem. Soc.*, **134**, 816-819 (2012).

Furube, A.; Yoshinaga, T.; Kanehara, M.; Teranishi, T., Electric Field Enhancement in NIR Two-Photon Absorption by Indium Tin Oxide Nanoparticle Film, *Angew. Chem. Int. Ed.*, **51**, 2640-2642 (2012).

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Kanehara, M.; Arakawa, H.; Honda, T.; Saruyama, M.; Teranishi, T., Large-Scale Synthesis of High-Quality Metal Sulfide Semiconductor Quantum Dots with Tunable Surface-Plasmon Resonance Frequencies, *Chem. Eur. J.*, **18**, 9230-9238(2012).

Ikeda, T.; Xiong, A.; Yoshinaga, T.; Maeda, K.; Domen, K.; Teranishi, T., Polyol Synthesis of Size-controlled Rh Nanoparticles and Their Application to Photocatalytic Overall Water Splitting under Visible Light, *J. Phys. Chem. C* (in press).

Platonic Hexahedron Composed of Six Organic Faces with an Inscribed Au Cluster

The structures of nanomaterials determine their individual properties and the suprastructures they can form. Introducing anisotropic shapes and/or interaction sites to isotropic nanoparticles has been proposed to extend the functionality and possible suprastructure motifs. Because of symmetric anisotropy, Platonic solids with regular polygon faces are one of the most promising nanoscale structures. Introduction of Platonic solid anisotropy to isotropic nanomaterials would expand the functionality and range of possible suprastructure motifs. We demonstrate a novel strategy to obtain nano-Platonic solids through the face coordination of square porphyrins on an inscribed Au sphere with adequate size. The face coordination of the multidentate macrocyclic porphyrin thioester derivatives: tetrakis-5a,10a, 15α ,20 α -(2-acetylthiomethylphenyl) porphyrin (SC₁P), and tetrakis- 5α , 10α , 15α , 20α -(2-acetylthioethylphenyl) porphyrin (SC₂P) (Figure 1a), with four acetylthio groups facing the same direction, on the Au cluster encased the Au cluster in a Platonic hexahedron with six porphyrin faces (Figure 1). These hexahedra are regarded as novel "artificial atoms" with anisotropically interactive faces. We believe that this approach using spherical nanoparticles is a novel self-assembly technique, because the formation of Platonic solid is automatically determined by the relationship between the diameter of the inscribed sphere and shapes/sizes of the polygonal faces.

Electric-Field Enhancement in an Indium-Tin Oxide (ITO) Nanoparticle Film

Nanoparticles (NPs) of noble metals such as gold and silver are well-known to have strong plasmon bands in the visible region and show unique optical characteristics because of an enhanced near-field electric field at the NP surface. We have recently reported that indium-tin oxide (ITO) NPs have a unique plasmon property in the nearinfrared (NIR) range and the peak wavelength can be easily tuned by controlling the amount of Sn doping. Here, we have applied transient absorption spectroscopy to a dye-coated ITO NP film, where dye absorption is present at half the wavelength of the plasmon resonance so that two-photon-induced transient absorption can be expected. Since a two-photon process occurs only in a strong electric field, we can selectively observe the near field generated by ITO NPs.

The enhancement of the electric properties of a dye molecule (IR26) by indium–tin oxide nanoparticles (ITO NPs, Figure 2) has been shown by measuring the nearinfrared two-photon-excited transient absorption spectra. It was found that the dye molecules were excited much more efficiently in the presence of an ITO NP layer by a factor of 30 compared to the control sample without ITO NPs. The results show that NPs of transparent conductive metal oxides can possibly be applied in plasmonic sensors and solar cells, because in general NIR light interacts weakly with chemical substances in the wavelength window ranging from the UV/Vis electronic transition region and the IR vibrational region.



Figure 1. (a) Strategy for assembling the platonic solid from porphyrins and a Au cluster. Chemical structures of SC_nP are also shown. (b) Schematic illustration of the coordination fashion of SC_1P on the Au cluster. Hydrogen atoms are omitted for clarity. (c) Schematic illustration of the Platonic hexahedron constructed with six porphyrin faces and an inscribed Au sphere. Only the tetraphenylporphyrin moieties are shown for clarity.



Figure 2. SEM image of IR26-coated ITO NP layer on a glass substrate.