PREPARATION OF ORGANIC-INORGANIC HYBRIDS BY THIOL-ENE REACTION AND THEIR APPLICATIONS

Kimihiro Matsukawa

Kyoto Institute of Technology, Materials Innovation Lab,
Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

Organic-inorganic hybrids are molecularly dispersed nano-composites of organic and inorganic components, which are noted as most attractive materials with the specific characteristics. These materials are expected to have new functions for the versatile advanced applications in many fields. The typical organic-inorganic hybrids can be prepared by a sol-gel reaction of metal alkoxides in organic polymers or with some polymerizations. We have already studied the preparation of organic-silica hybrids using the photo-curable polysilsesquioxanes prepared from the organic substituted trialkoxysilane.[1, 2] The radical and cationic polymerizations are carried out by using the polysilsesquioxane containing acrylic and epoxy groups, correspondingly. And also the polysilsesquioxane with thiol groups would be reacted by Thiol-Ene reaction, which is a radical addition reaction of thiol groups to C=C bond of olefin compounds.

We investigated that Thiol-Ene reaction with thiol-containing polysilsesquioxane and multifunctional allyl compounds produced new type of organic-inorganic hybrid materials, as shown in Fig.1. Thiol-containing polysilsesquioxanes were prepared from the hydrolysis and condensation of mercapto-propyltrimethoxysilane. When triallylisocianate (TAIC) as multifunctional allyl compounds was reacted with the silsesquioxanes under UV irradiation, these obtained hybrid materials had some specific properties such as high transparency, high refractive index, and thick film formation, in addition to low shrinkage after photo-curing. Furthermore, these hybrid materials with multi-thiol compounds showed the self-healing properties of scratched surface.

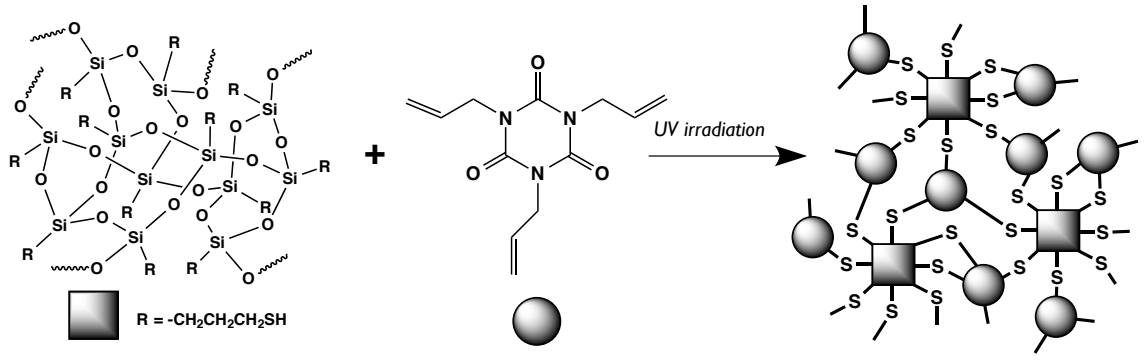

Fig. 1 Preparation of organic-inorganic hybrid with thiol-containing silsesquioxane and TAIC.

As unirradiated part of these hybrids was dissolved easily by using 2.38% aqueous tetramethylammonium hydroxide (TMAH) solution, the behaviour can be used as a negative resist. The unreacted thiol group in polysilsesquioxane can capture Pd catalyst for an electroless plating, so it could be effectively used as a catalyst layer for the electroless Cu plating. Therefore, the fine pattern of electroless Cu plating was formed, which is expected to apply to the fabrication of transparent circuit.

On the other hand, organic-inorganic hybrids can be prepared by dispersing nanomaterials, which is nanoparticles, nanosheets, etc., in polymers. For example, organic-inorganic hybrid materials containing zirconia nanoparticles are most interested in the application for high refractive index coating. As the fine dispersion of zirconia nanoparticles is necessary to prepare the transparent hybrid coating, the surface modification was investigated by using dicarboxylic acid anhydride. Especially,

5-norbornene-2,3-dicarboxylic acid anhydride (NDCAA) exhibited a good surface dispersibility to form the ester bonding with Zr-OH. The internal olefin of norbornene skeleton is a useful component for Thiol-Ene reaction with multi-thiol compounds. The stoichiometric mixture for C=C of NDCAA and TAIC and S-H groups of pentaerythritol tetrakis (3-mercaptopropionate) (PEMP) formed multiple crosslinking structure via Thiol-Ene reaction as shown in Fig. 2. Thus obtained photo-cured materials demonstrated high transparency and flexibility despite the hybrids containing zirconia nanoparticles. The refractive index of hybrid coating could be controlled by the content of zirconia nanoparticles. In the case of 80wt% content of zirconia nanoparticles, it was found that the refractive index quite high (>1.7). On the other, the flexible self-standing films could be prepared from the photo-cured hybrid of 50wt% content of zirconia nanoparticles. Furthermore, the recent results related some applications of hybrid materials with zirconia nanoparticles would be introduced.

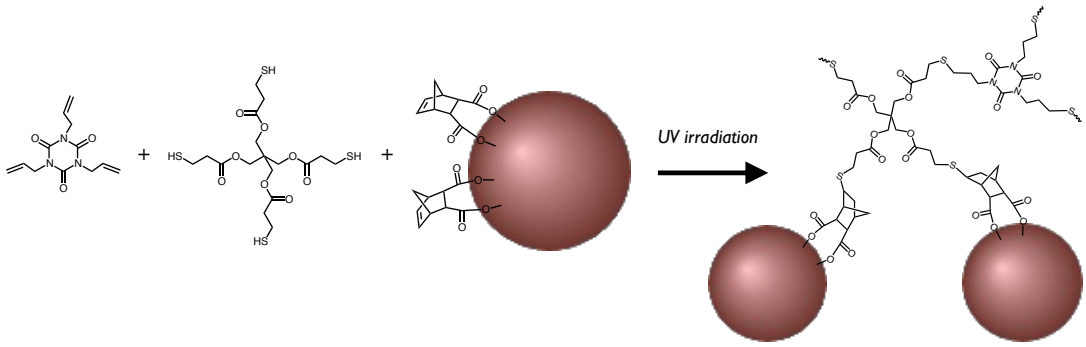

Fig. 2 Preparation of photo-cured hybrids from TAIC, PEMP, and NDCAA modified zirconia nanoparticles.

References

1. K.Matsukawa, Y.Matsuura, A.Nakamura, N.Nishioka, T.Motokawa, and H.Murase, *J. Photopolym. Sci. Tech.*, **19**, 89 (2006) .

2. K.Matsukawa, Y.Matsuura, A.Nakamura, N.Nishioka, H.Murase, and S.Kawasaki, *J. Photopolym. Sci. Tech.*, **20**, 307(2007) .