Functionalization of carbon graphite surfaces with two-dimensional arrays of biomolecular ligand-protected gold nanoparticles

Hiroshi Yao,1,* Motoi Kurokami,1 and Keisaku Kimura1

1 Graduate School of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Akogun, Hyogo 678-1297, Japan
*e-mail: yao@sci.u-hyogo.ac.jp

Well-ordered arrays or superlattices of gold nanoparticles as the chemically prepared building blocks have been receiving increasingly attention as a potential future alternative to conventional micro-fabrication techniques. Moreover, the nanoparticle arrays on carbon surfaces have also been a focus of increasing interest; for example, it is reported that single- or multi-walled carbon nanotube surfaces have been functionalized by different methods to allow the covalent attachment of gold nanoparticles [1]. However, covalent attachment is not desirable because the nanotubes’ electronic properties can be altered. Our recent studies on the synthesis of gold nanoparticle superlattices as well as a careful choice of protective ligand molecules allow us to face a challenge to fabricate well-organized gold nanoparticle arrays on carbon substrates. We here present a successful immobilization of two-dimensional (2D) arrays of biomolecular ligand-protected gold nanoparticles onto HOPG by simple immersion of the graphite substrate in “aqueous” acidic solution containing the particles. The surface of the gold nanoparticles was protected by N-acetylglutathione (NAG; note that glutathione is a tripeptide consisting of γ-L-glutamyl-L-cysteinyl-glycine). The mean core diameter of the gold nanoparticles immobilized on HOPG was about 6 nm, whereas that of the as-prepared sample was about 1 nm (see the sample XRD profile). A combined study with scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) revealed that small gold nanoparticles with their diameter of 1–2 nm never adsorbed onto the HOPG surface. Simple quantum chemical calculations suggest marginal importance of the protective ligand-graphite interaction, yielding that the gold core-graphite van der Waals attractive interaction plays a major role toward the spontaneous 2D assembly of the nanoparticles. We believe this approach provides a convenient method for attaching other nanostructures, biological molecules, or ligands to carbon materials.

Fig. 1. (a) Powder X-ray diffraction profile of the as-prepared NAG-protected gold nanoparticle sample. (b) SEM images of the 2D self-assembly of the gold nanoparticle on HOPG. The left- and right-handed images are those taken in low and high magnifications, respectively.