

Supplementary Information for

Refillable Carbon Nanotube Cartridge for 3D Nanomanufacturing

Raman Bekarevich [†], Masami Toyoda[‡], Shuichi Baba[‡], Toshihiko Nakata[‡], Kaori Hirahara[†]

[†] Osaka University, Department of Mechanical Engineering, 2-1, Yamadaoka, Suita-shi, Osaka-fu, 565-0871, Japan

[‡] Hitachi, Ltd., Research & Development Group, 292, Yoshida-cho, Totsuka-ku, Yokohama-shi, Kanagawa-ken, 244-0817, Japan

bekarevich@ne.mech.eng.osaka-u.ac.jp, hirahara@mech.eng.osaka-u.ac.jp

S1. Loading of the first nanoparticle inside the carbon nanotube (CNT).

Loading of the first gold nanoparticle (Au-NP) can be realized in several different ways. Conditionally it is possible to separate the loadings into three groups: mechanical loading, loading due to mass-transport effects and combination of these types of loading.

Mechanical Loading can be realized when an Au-NP with diameter less than inner diameter of the host CNT is perfectly positioned with the open end (Movie S1). In this case, Au-NP can be simply inserted into the interior of CNT. A nanoparticle can be detached from the supportive CNT and immobilized inside the host CNT after applying of the voltage necessary to reduce contact area of Au–DWCNT interface. The loaded nanoparticle plays a role of the seed for further gold crystal growth.

Due to the Mass Transport Effects:

- a. An Au-NP locates far from the open end of host CNT or the size Au-NP is much larger than diameter of the host CNT. In this situation, strong current induces Joule heating of the system up to the very high temperatures. This leads to sublimation of the nanoparticles decorating the supportive CNT. (Movie S2) Sub-nanosized gold particles uniformly distribute on the inner and outer surface of the host CNT. This case is almost unsuitable for nucleation of the encapsulated gold crystal.
- b. In the case when an Au-NP located in front of the open end of host CNT and has appropriate size (less or equal to the diameter of host CNT) there are two ways of gold loading:
 - *Forced loading*. In this case loading occurs at relatively high values of the voltage and the current which can reach several tens of μA and create the strong temperature gradient forcing whole nanoparticle into the interior of host CNT (Movie S3). If positioning of an Au-NP and the open end of host CNT is not performed well, the forced loading transforms to the sublimation of gold nanoparticles.
 - *Mild loading*. In this case values of the current are rather small in comparison to the previous situation. Loading of gold inside the host CNT looks like a flow of gold atoms from an Au-NP inside the CNT (Movie S4). Mild loading looks more preferable, however in the most cases the forced loading was observed.

Combination: typical combination is “Mechanical” and “Forced” loadings (Movie S5).