Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


Supplementary Information for:

# Self-assembled nanoparticle patterns on carbon nanowall surface

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We observed that thermally treated carbon nanowalls serve efficiently as a template governing the formation of the quasiperiodic patterns for nanoparticles deposited. Here we report self-assembled quasi-regular structures of diverse nanoparticles on a freestanding multilayer graphene-like material, i.e. carbon nanowalls. Metallic (Ag, Al, Co, Mo, Ni, Ta) and semiconductor (Si) nanoparticles form coaxial polygonal closed loop structures or parallel equidistant rows, which evolve upon further deposition into bead-like structures and, finally, into nanowires. The carbon nanowall surface serves efficiently as a template governing the formation of the quasiperiodic patterns. Weakly bonded nanoparticles decorate atomic steps, wrinkles and other extended defects on the carbon nanowalls as a result of anisotropic diffusion of atoms or clusters along the hexagonal *sp*$^2$-carbon network followed by their aggregation and agglomeration. The decorated carbon nanowalls are found to be a promising material for the surface enhanced Raman scattering analysis (SERS).

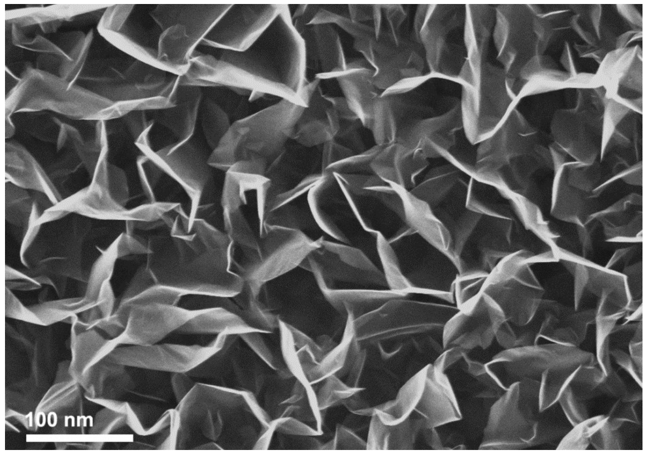


**Fig. S1**. SEM image of as-grown CNW film surface.

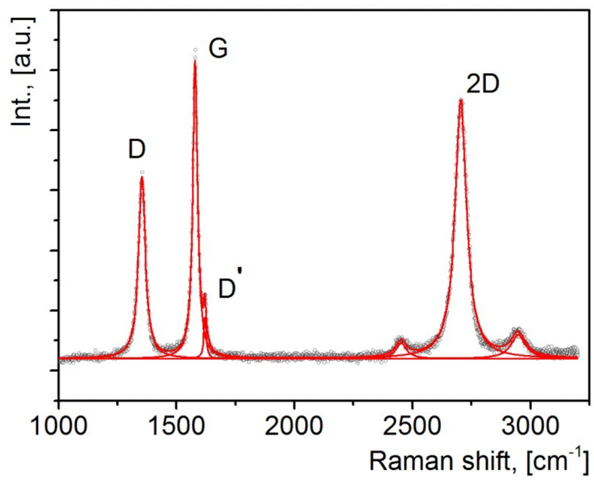


**Fig. S2**. Raman spectrum of as-grown CNW film. Red- Lorenzian deconvolution. The spectrum in a region of 1200-3200 cm$^{-1}$ includes all features typical for graphite-like materials. They are G mode, usually observed for the graphite-based materials, distinguished D and D' modes, associated with the lattice defects of different nature, and 2D mode that corresponds to the second order of the D mode.

**Self - assembling of metal nanoparticles on graphene sheets**

Almost all common models of decoration of graphene derivatives with noble metal nanoparticles deposited from a vapor phase (CVD, PVD) utilize the dominating role of graphene growth defects. In particular, graphene domain boundaries and wrinkles are usual sites of nucleation of nanoparticles and that leads to visualization of such defects as discussed in related papers [1, 2].

In the case of carbon nanowalls grown by sliding and colliding of graphene layers [3], grain boundaries, wrinkles and stepped rims of the nanowalls are readily decorated with nanoparticles almost independently on their chemical origin. Thus wrinkles, boundaries and steps made of elementary graphene layers reveal instantly the role of primary nucleation sites for nanoparticles.

The following images demonstrate large variety of nanoparticle patterns formed by different materials.

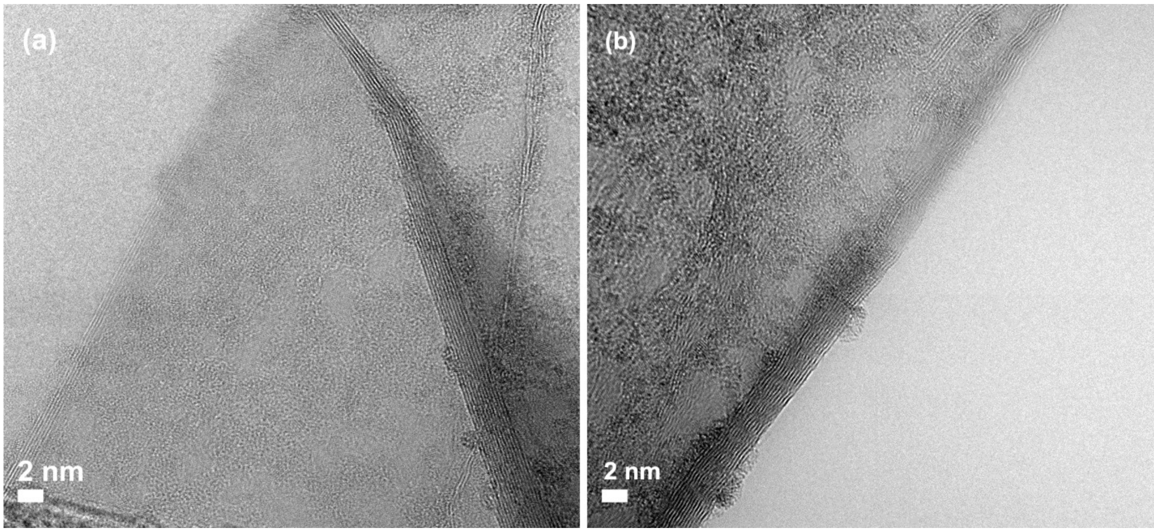


**Fig. S3**. TEM images of Mo (a) and Si (b) nanoparticles anchored on graphene layer edges.

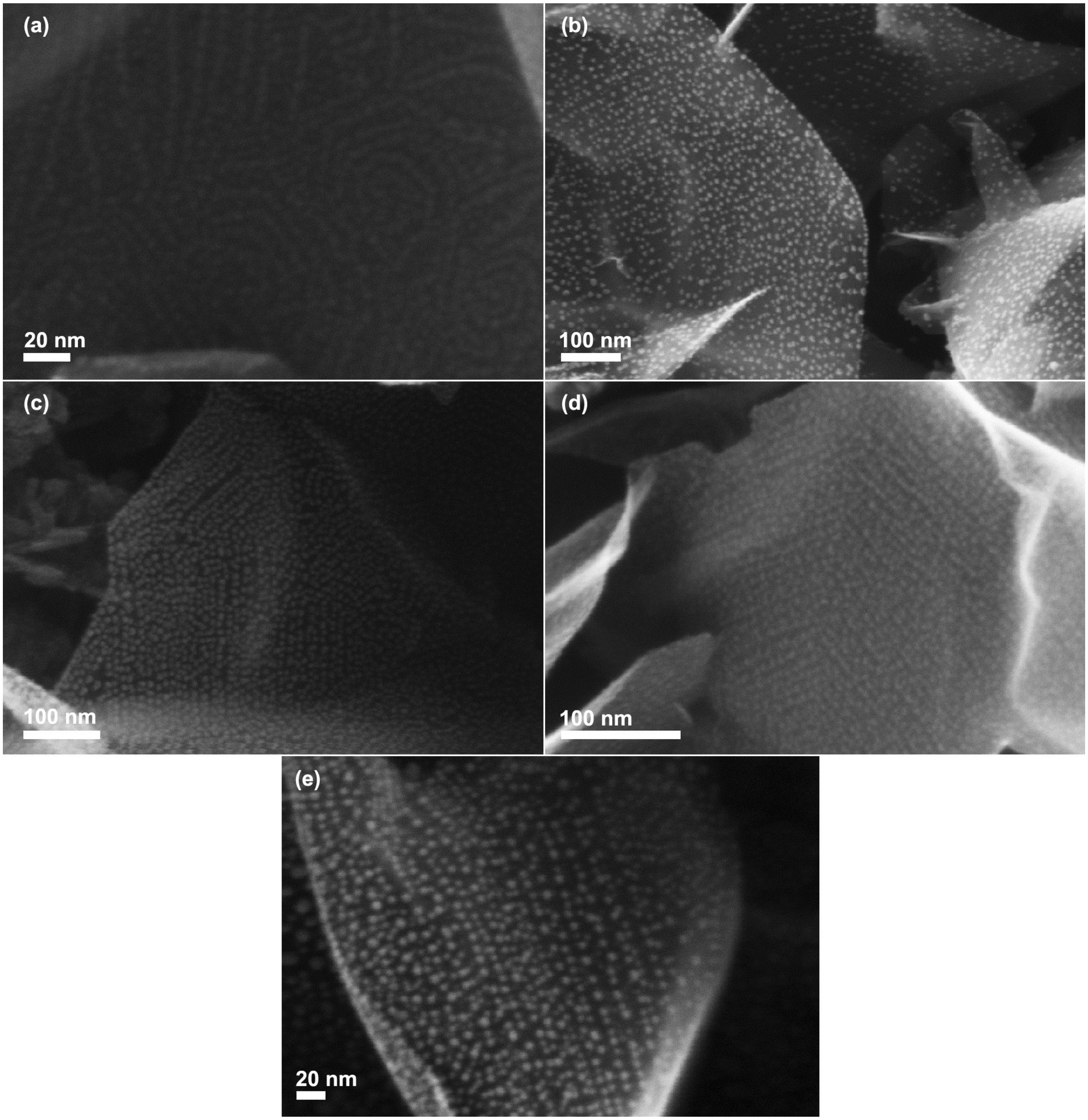


**Fig. S4**. SEM images of self-assembled Si (a), Ni (b), Co (c), Ta (d) and Ag (e) nanoparticle patterns of the CNW surface. Images demonstrate similar behavior of different materials on CNW surface.

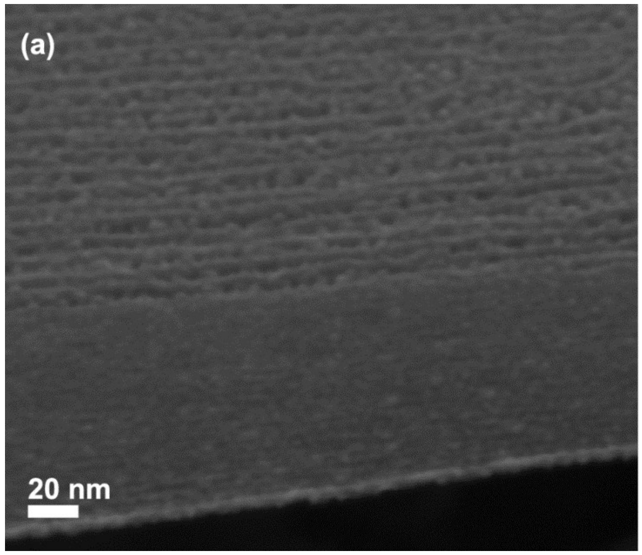


**Fig. S5**. SEM image of decorated CNW edges with Si clusters. An obvious effect of cluster nucleation onto the graphene sheet defects near the rim. At the same time, nanoparticles deposited onto nanowalls undergo self - assembling forming quasiperiodic structures.

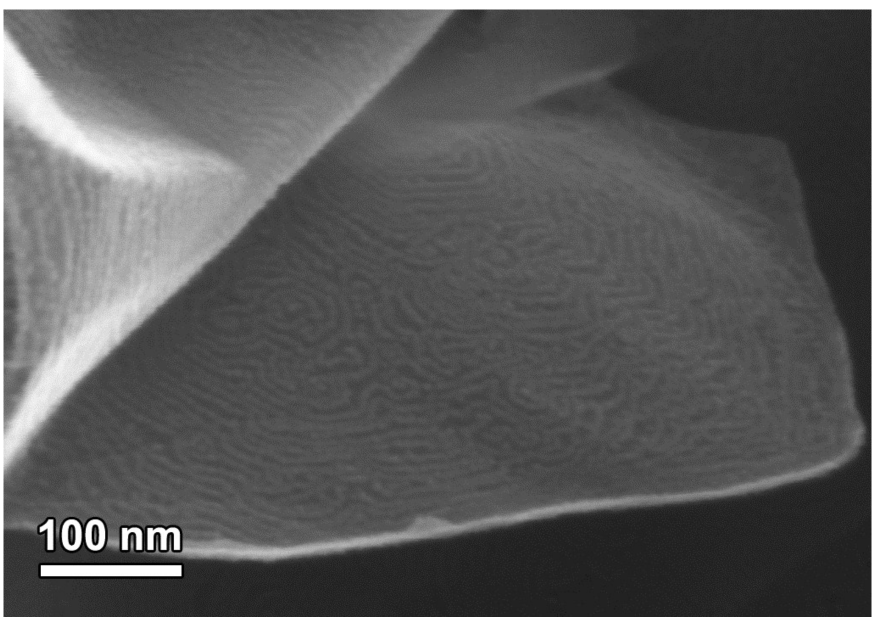


**Fig. S6.** Mo particle arrangement on complex wrinkle patterns.

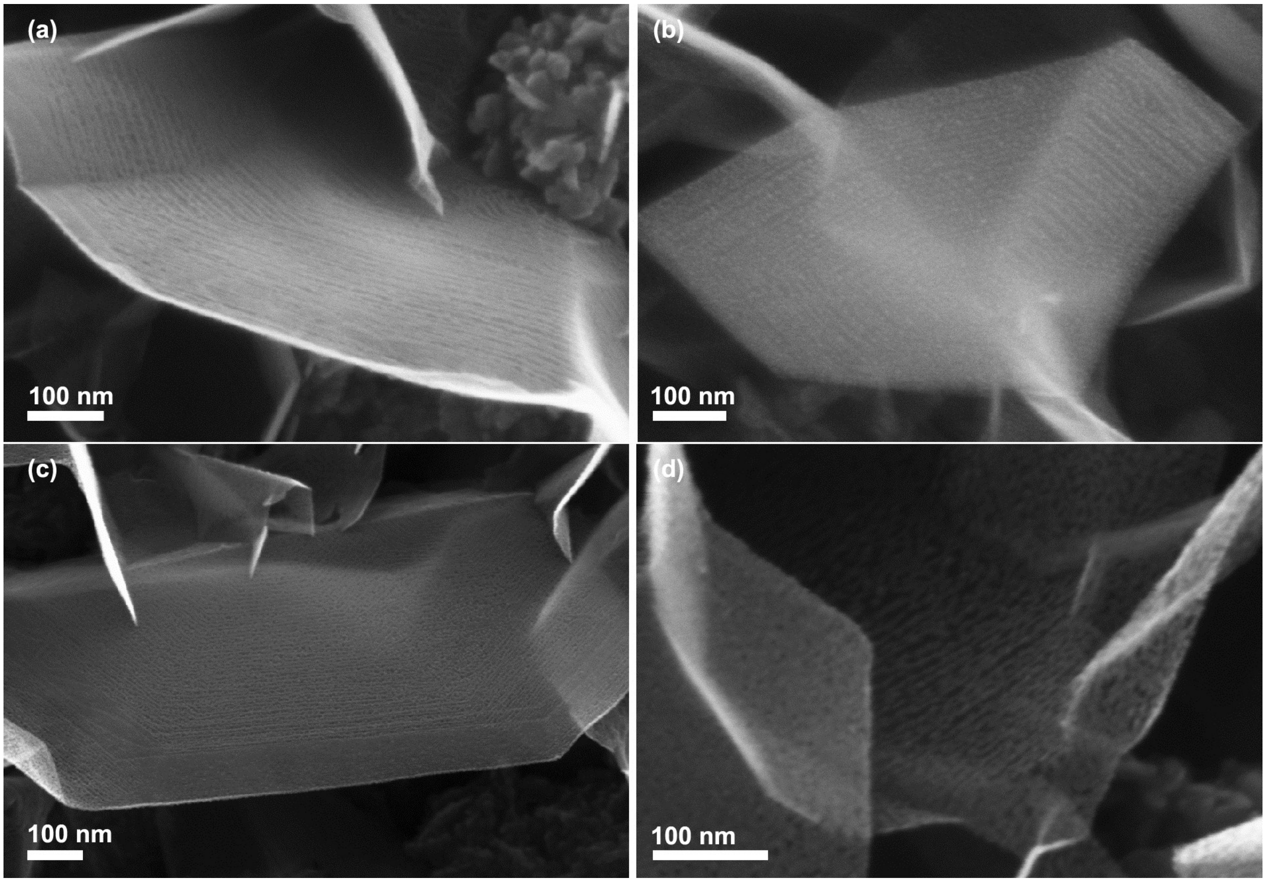


**Fig. S7**. SEM images of Mo (a), Co (b), Si (c) and Al (d) nanowires of the CNW surface.

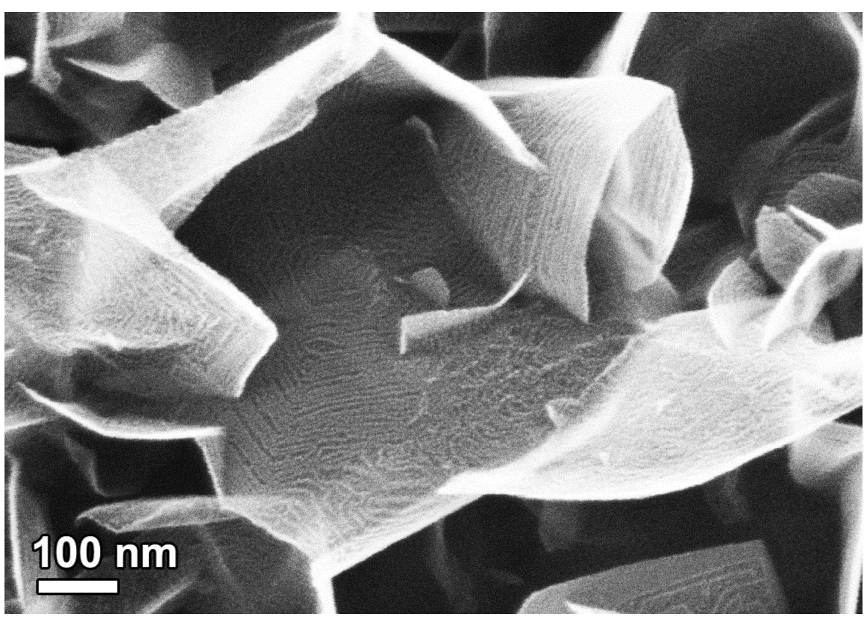


**Fig. S8**. SEM image of huge bending of the CNWs decorated with Mo clusters.

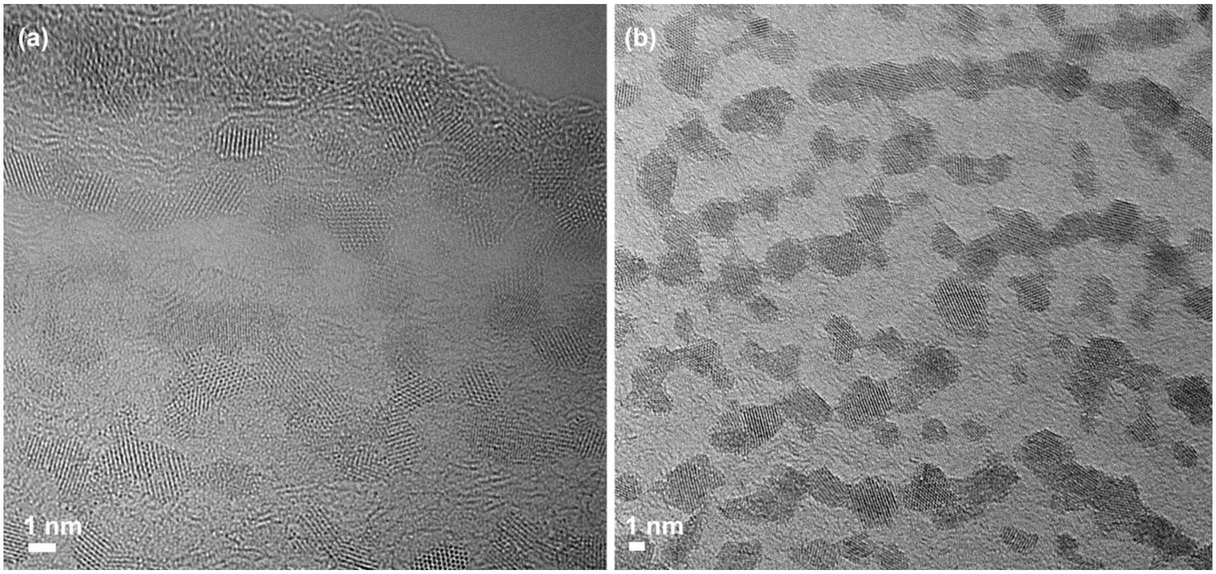


**Fig. S9**. TEM images of Mo nanoparticles on a CNW surface. Some X - like arrangements of nanoparticles with angles of 60 - 120 grad are observed with no visible defects of graphene layers nearby. Almost all the nanoparticles demonstrate random orientation of their lattice with respect to each other and, in turn, to the underlying graphene structure. This would evidence for relatively weak interaction between carbon and the nanoparticles.

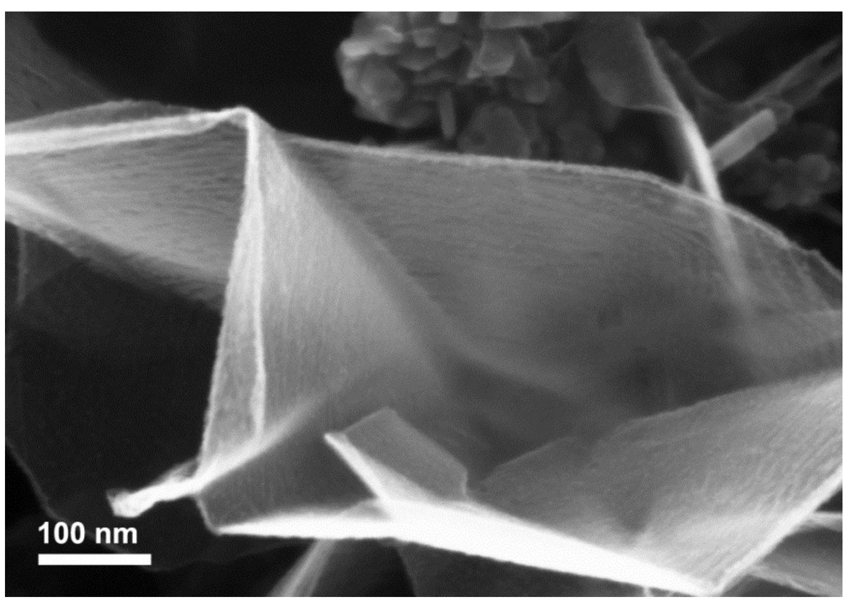


**Fig. S10.** SEM image of linear nanostructures composed of Si particles deposed on the CNW film at room temperature. The CNW film was preliminary annealed in high vacuum at 300˚ C during 30 minutes.

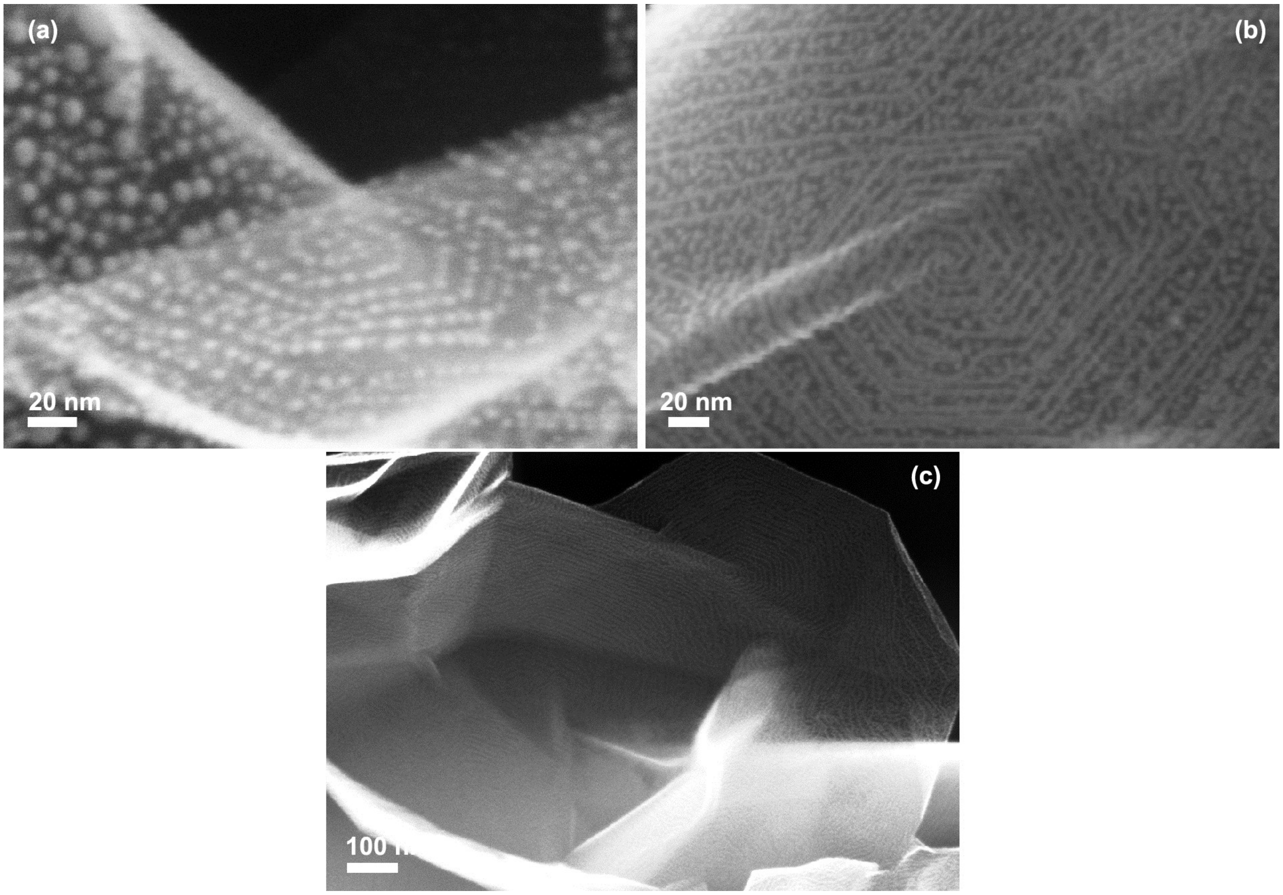


**Fig. S11**. SEM images of Ag (a), Si (b) and Mo (c) helixes formed on the CNW surface.

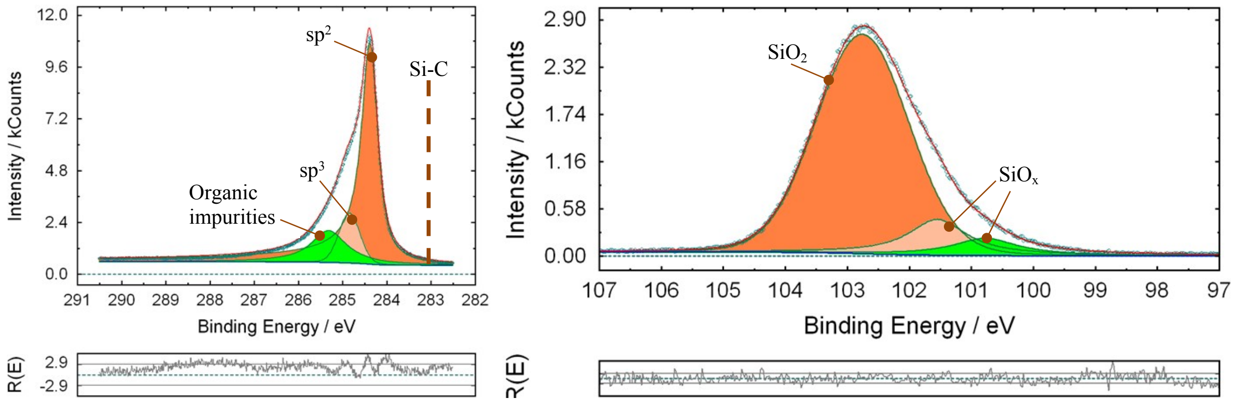


**Fig. S12.** C1s (a) and Si2p (b) photoemission spectra of the CNWs decorated with Si nanoparticles deposited at 250-300˚C.

Fig.S12 shows results of XPS study of the CNWs decorated with Si nanoparticles. Analysis of C1s and Si2p lines reveals no any carbide formation. Significant $SiO_x$ signal is a result of silicon oxidation during transfer of the sample from magnetron deposition reactor to synchrotron facility.

**References.**

1. K. Kim, H-B-R. Lee, R.W. Johnson, J.T. Tanskanen, N. Liu M-G. Kim, Ch. Pang, Ch. Ahn, S.F. Bent and Zh. Bao, *Nat. Commun.*, 2014, **5**,4781.

2. S.U. Yu, B. Park, Ye. Cho, S. Hyun, J.K. Kim and K.S. Kim, *ACS Nano*, 2014, **8**, 8662–8668.

3. K.V. Mironovich, D.M. Itkis, S.A. Semenenko, S.A. Dagesyan, L.V. Yashina, E.Yu. Kataev, Yu.A. Mankelevich, N.V. Suetin and V.A. Krivchenko, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25621-7.