

Nanonecklace Structure of Carbon Nanotubes for Ultrahigh Loading Metal Nanoparticles

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Abstract

We report a simple protocol for the fabrication of nanonecklace structure of multiwall carbon nanotubes (MWCNTs) for loading metal nanoparticles (NPs) in ultrahigh density. MWCNTs have been initially coated with anionic polyelectrolyte (PE), polystyrene sodium sulfonate (PSS) by a noncovalent interaction (MWCNT/PSS). The nanonecklace structures were fabricated by stepwise assembly of both the positively charged poly(allylamine) hydrochloride (PAH) and negatively charged poly(acrylic acid) (PAA) in a nonstoichiometric ratio on the MWCNT/PSS as a template. (Fig. 1a) The zeta potential values and XPS data confirmed the stepwise coating of PEs on MWCNT substrate.

It was observed that the PSS did not wrap the MWCNTs in a continuous way but form discontinuous bumps on the surface of the MWCNTs (Fig. 1b). Therefore, when the MWCNT/PSS was employed as a template for additional coating with cationic PAH through electrostatic interaction, some interaction points on the bumps of the MWCNT/PSS can be easily exposed for the next coating. Fig. 1c clearly shows the grown bumps onto the MWCNT/PSS/PAH surface. The MWCNT/PSS/PAH was further coated with anionic PAA, and the necklace structure of MWCNT/PSS/PAH/PAA was obtained (Fig. 1d-f). When the PSS was coated onto the MWCNTs, the thickness of PSS at the bumps was about 8 nm which was 4 times, compared to normal thickness of PSS (approx. 2 nm). This means that the PSS was coated on the MWCNTs as the entangled form and it led to the formation of bump structures on the MWCNTs. We believe that based on the MWCNT/PSS template, the formation of necklace structures was completed by using a nonstoichiometric ratio of PEs (MWCNT/PSS/PAH to PAA). In earlier, we reported a synthesis of self-assembled spherical polyelectrolyte complexes (PECs) in aqueous solution by controlled mixing of PAH and PAA in a nonstoichiometric ratio.[1] The driving force for the formation of spherical PECs is mainly based on the electrostatic interactions between carboxylic and amino groups in a nonstoichiometric ratio. In similar way, nonstoichiometric ratio of PAH to PAA has been applied for the coating of MWCNT/PSS.

The necklace structure of the CNT/PSS/PAH/PAA has been employed as a support for loading bi- or tetrametallic NPs such as Au/Ag, Pt/Ag, Au/Pt, Ag/Pd or Au/Pt/Ag/Pd NPs.[1-4] For this purpose, metal precursor-loaded PAH (PAH-Au or Pt ions) and PAA (PAA-Ag or Pd ions) were used to assemble on MWCNT/PSS template instead of bare PAH and PAA, respectively. Control loading of metal precursors ensured that 45-50% and 30-43% of charged groups in the PAH ($-\text{NH}_3^+$) and the PAA ($-\text{COO}^-$) were available for further interactions with opposite charge groups in subsequent steps as we reported earlier, respectively.[4] Therefore, metal precursor-embedded PAH and PAA also enable to construct necklace structure on MWCNT/PSS. After coreduction of multi-metallic precursor-embedded MWCNT/PSS/PAH/PAA by NaBH_4 , we obtained the corresponding metal NP-decorated nanonecklace structures.(Fig. 2)

The nanonecklace structures with highly loaded multi-metallic NPs were demonstrated to be used as catalytic materials for conversion of 4-nitrophenol to 4-aminophenol as well as a convenient SERS substrate for biological tags and molecular detection. We expect that the methodology presented here can be extended to other systems opening up the way of novel applications through synthesis of unique nanostructures.

References

- [1] Md. Sahinul Islam, Won San Choi, Ha-Jin Lee, Young Boo Lee, Il Cheol Jeon, J. Mater. Chem. **22** (2012) 8215.
- [2] Md. Arifur Rahim, Bora Nam, Won San Choi, Ha-Jin Lee, Il Cheol Jeon, J. Mater. Chem. **21** (2011) 11831.
- [3] Md. Arifur Rahim, Md. Sahinul Islam, Tae Sung Bae, Won San Choi, Young Yong Noh, Ha-Jin Lee, Langmuir, **28** (2012) 8486.
- [4] Md. Sahinul Islam, Won San Choi, Young Boo Lee, Ha-Jin Lee, J. Mater. Chem. A, **1** (2013) 3565.

Figures

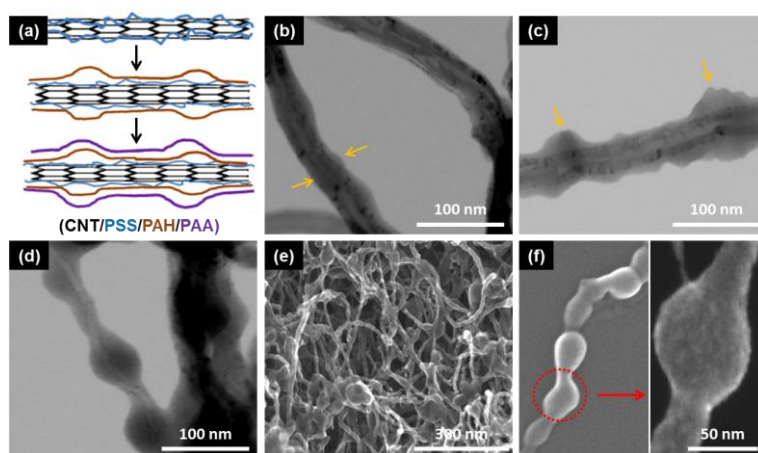


Figure 1. (a) A schematic representation for the necklace-shaped MWCNTs fabricated by chronological mixing of anionic and cationic PEs in nonstoichiometric ratio. Representative TEM images of (b) MWCNT/PSS, (c) MWCNT/PSS/PAH, and (d) MWCNT/PSS/PAH/PAA. Arrows indicate discontinuous bumps consisting of PEs on MWCNT surface. (e and f) URH-FESEM images of MWCNT/PSS/PAH/PAA.

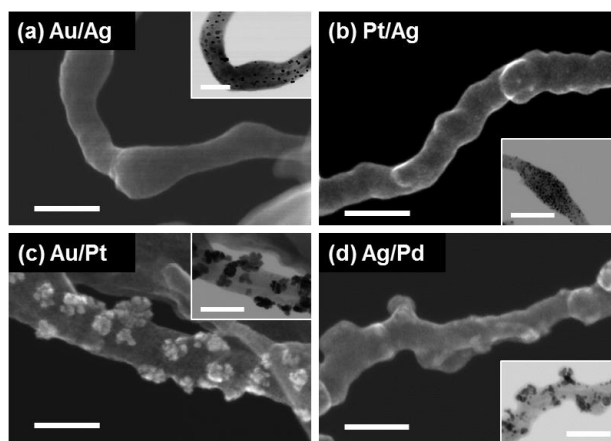


Figure 2. UHR-FESEM micrographs for bi-metallic NP-embedded p-CNT/PSS/PAH/PAA. Insets are the corresponding STEM images. All scale bars represent 50 nm.