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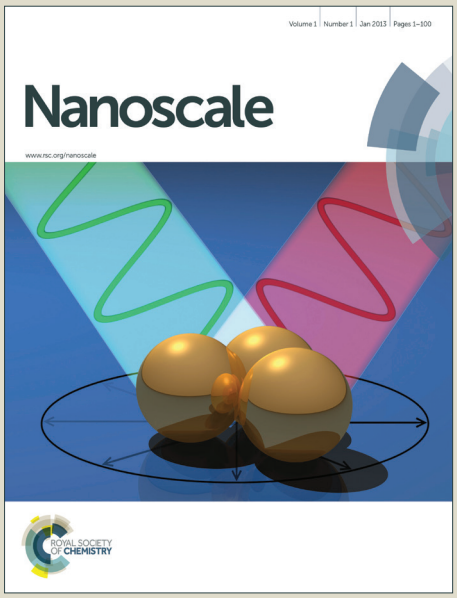

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Universal chitosan-assisted synthesis of Ag-included heterostructured nanocrystals for label-free in situ SERS monitoring

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A universal chitosan-assisted method was developed to synthesize various Ag-included heterostructured nanocrystals, in which chelation probably plays a vital role. The as-prepared Ag/Pd heterostructured nanocrystals show outstanding properties when being used as bifunctional nanocomposites in label-free in situ SERS monitoring of Pd-catalytic reaction.

Surface-enhanced Raman scattering (SERS) possesses inherent advantages in label-free in situ monitoring the catalytic reaction process, which can help to understand the reaction mechanism and optimize the catalyst formula.[1-5] It is well known that some noble metal structures, such as Ag and Au nanocrystals, are required for magnifying the molecule information in the SERS process.[5-9] Moreover, SERS is a short-range effect, and the catalytic reaction is a process taking place at the surface of the catalyst. Hence, assembling nanocrystals with SERS activity and catalyst together is significant for realizing an accurate and highly effective monitoring.

Recently, various protocols in fabricating the bifunctional units, which combine both catalytic and SERS activity, have been developed for label-free in situ monitoring.[3,5,7,8,10-16] A general strategy to fabricate the units is to coat a SERS-active core with a catalytically active surface, including assembling small Au nanoparticles (NPs) on the core or coating the core with a shell of Pt or Pd.[4,5,10,11,17] However, it is difficult to achieve a balance between high catalytic efficiency and SERS enhancement in this method, as the plasmon of the core will be significantly decreased with the increase of shell thickness.[4,12,17]

In addition, other methods, such as depositing isolated Au NPs and Pt NPs simultaneously onto the glass substrate to study Pt-catalyzed reaction, provide a different route.[1] But the non-chemically bound metal nanoparticles are unpractical as a system under real catalytic conditions.[3] It is known that Au core is the most employed materials in the fabrication of bifunctional units, including Au nanorods and nanowires.[3-8,10,11,18-20] In fact, Ag has a stronger localized surface plasmon resonance (LSPR) and can provide a higher enhancement factor than Au even though the latter is more chemically inert, which is an advantage in assembling bifunctional structures.[17,21-23]

Heterogeneous metal nanocrystals (HMNCs) are a common entity formed by integrating some metal nanocrystals of different compositions, which are jointed through permanent bonding interfaces.[24-29] Particularly, the oligomer-type HMNCs, which are different from the core-shell type ones, expose multiple material surfaces, which can avoid the dilemma in keeping the balance between catalytic and SERS activity.

Pd and Pt are the most important catalysts in many applications, including the conversion of chemical to electrical energy and a series of vital organic chemical reactions.[30-31] Therefore, it is highly desirable to synthesize oligomer-type HMNCs containing Ag and Pd (Pt) and use them as the substrate for the lable-free in situ SERS monitoring.

Herein, we demonstrate a facile synthesis of Ag/Pd oligomer-type heterostructured nanotubes (OHNTs), in which some Ag NPs are jointed to a one-dimensional (1D) Pd nanotubes (NTs) through permanent bonding interfaces. Chitosan plays a vital role in the successful preparation of Ag/Pd OHNTs; Without chitosan, Ag could not heterogeneously nucleate and grow on the NTs uniformly. The method was then successfully used to grow Ag NPs on bimetallic NTs, such as PdPt alloy NTs or quasi-1D Au/PtAu heterojunction NTs. Finally, Ag/Pd OHNTs were used to monitor the reaction process of p-nitrothiophenol (p-NTP) to p-aminothiophenol (p-ATP) in label-free in situ by SERS in aqueous solution.

The Te nanowires (NWs) were synthesized at first. Then the Pd NTs were synthesized by using Te NWs as the template and chitosan as the stabilizing agent in aqueous solution at room temperature. The TEM images of the as-prepared Te NWs and Pd NTs are shown in Fig. S1 and 1A, respectively. It is shown that Pd NTs have the same size with Te NWs template (about 30 nm in diameter and 420 nm in length), and it can be observed that the centers of the 1D Pd nanostructures are obviously brighter than the edges, suggesting that they are hollow nanotubes. The XRD pattern of the Pd NTs (Fig. S2) shows a characteristic diffraction peak which can be assigned to

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