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A Simple Synthesis of Pd@Au Core/Shell Nanosheets

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Abstract*—A simple method has been successfully developed to synthesize Pd@Au core/shell nanosheets for 3 h at room temperature. It indicates to be an eco-friendly and simple method for the synthesis of Pd@Au core/shell nanosheets. The thickness of Au shells covered on the Pd nanosheets' surfaces were formed at room temperature in 3 hours. The prepared Pd@Au core/shell nanosheets have been characterized by UV-vis, XRD, TEM, HRTEM, elemental-mapping EDX and EDX line profile. The prepared Pd@Au core/shell nanosheets could be a promising material for applications in the field of sensing, biosensor, image, determination of biomolecules and biomarkers, photothermal therapy, and optical catalyst, etc. in the current time and in future.*

***Keywords*—** *Pd@Au core/shell nanosheets (Pd@Au NSs); eco-friendly, simple, room temperature*.

I. INTRODUCTION

In numerous last decades, the development of nanotechnology as well as metal nanocrystals attracted profound attention from both the scientific and industrial communities because of their widespread applications in plasmonics, magnetic, catalysis, electronic, and biological medicine (i.e, drug delivery, cancer diagnosis,…) [1-12].

Therefore, nanomaterials have shown substantially distinctive properties when compared to bulk materials [13-20]. Tuning their plasmonic properties is particularly important for achieving advances in many areas such as surface-enhanced Raman scattering, energy harvesting and conversion, sensing, photovoltaic, photocatalytic and imaging [12, 21-25]. As we are well-known that plasmonic properties of metal nanocrystals are highly sensitive to their composition, size and shape [4, 26-30]. For example, Au@SiO_2 nanoparticles, Au@SiO_2 nanorods, Ag/Au/Pt nanocubes, strong near-infrared (NIR) light absorption and good biocompatibility have been used to photothermal therapy and other biomedical fields [31-33].

Palladium (Pd) is not a promising candidate to support LSPR at high intensity. Besides, its LSPR peak is commonly achieved in the ultraviolet spectral range making the LSPR properties much more difficult to be demonstrated because of the strong absorption of light at these wavelengths by glass vessels and most solvents [34-36]. Overall, it is still very difficult to synthesize Pd nanocrystals with their LSPR peaks located in NIR regions, which is very important for applications in SERS, biomedicine,… Therefore, using of the Pd (core) as the nanosheet material also allows for tuning of the optical properties of Au (shell) due to the electronic interaction between the two metals. Since, bimetallic core/shell nanostructures with the atomically thin shell have been prepared to augment the absorption of light within NIR regions for photothermal hyperthermia therapy [37, 38].

In this work, we report a simple approach to cover uniform Au layers on the Pd nanosheets' surfaces. Herein, the synthetic method used at room temperature is simple, easy to perform, uniform shell thickness, stable and sustainable. Thus, the synthesized Pd@Au core/shell nanosheets could be a promising material for applications in the field of sensing, biosensor, image, determination of biomolecules and biomarkers, photothermal therapy, and optical catalyst, etc. in the current time and in future.

II. EXPERIMENTAL SECTION

2.1 Materials

Palladium (II) acetylacetonate ($Pd(acac)_2$, 99%); polyvinylpyrrolidone (PVP; M_{wt} ~ 10.000); Tungsten hexacarbonyl ($W(CO)_6$; 97%), hydrogen tetrachloroaurate ($HAuCl_4.3H_2O$, ≥ 99.99%), Rhodamine 6G (R6G; ≥99%), citric acid, and N,N-Dimethylformamide (DMF) were purchased from Sigma-Aldrich and Merck. Cetyltrimethylammonium bromide (CTAB), amoniac solution, aceton, and ethanol were bought from Acros. All solutions were prepared with deionized water from a MilliQ system.

2.2 Methods

2.2.1. Preparation of Pd nanosheets

Palladium nanosheets (Pd NSs) were synthesized by a simple and effective approach using tungsten hexacarbonyl ($W(CO)_6$) as a reducing agent without using CO gas directly. In a typical synthesis, 60 mg of CTAB and 30 mg of PVP were dissolved in 10 mL of DMF. And then, 16 mg of $Pd(acac)_2$ and 10 mg of citric acid were also added to 10 mL of the above DMF mixture and stirred for 20 min at room temperature. The above homogeneous solution was transferred into a 50 ml glass (flask) and 100 mg of $W(CO)_6$ be quickly added into the flask as a reducing agent for the reduction of $Pd(acac)_2$. After that, the solution was continuously stirred and heated at 90^{o}C for 90 minutes, then was centrifuged (12000 rpm; 15 min) and washed with acetone/ethanol to remove excess and redisposed in ethanol/deionized water (DI H_2O). The average size of the as-prepared Pd nanosheets is approximately 20-30 nm.

2.2.2 Synthesis of Pd@Au core/shell nanosheets

A typical synthesis of Pd@Au core/shell nanosheets, 100 μL of amoniac solution (25%) was dropwise into the above synthesized mixture of Pd nanosheets solution (10 mL)

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and stirred for 30 minutes at room temperature. Next, 500 µL of the gold salt ($HAuCl_4.3H_2O$) solution (1 mM) was also added dropwise into the above mixture solution and stirred with various reaction times (respective of 1 h, 3 h, 5 h, and 6 h) and then get undisturbed in 6 h at room temperature. Later, all the above were centrifuged, washed several times with acetone and redisposed into the DI H_2O to obtain the Pd@Au core/shell nanosheets with an Au layers of about 3-4 nm thickness which were covered uniformly on the Pd nanosheet's surfaces.

2.2.3 *Characterization techniques*

The absorbance spectra of Pd@Au core/shell nanosheet solutions were examined by UV–vis spectrophotometry (UV-675; Shimadzu). The phase structure of Pd@Au core/shell nanosheet was determined by a X-ray diffractometer (Rigaku Dmax-B, Japan) with Cu K_α source operated at 40 kV and 100 mA. A scan rate of 0.05 deg^{-1} was used for 2θ between 10^o and 70^o. The shape and particle size, elemental-mapping analysis by EDX and EDX line profile of Pd@Au core/shell nanosheets were examined by transmission electron microscope (TEM) with a Philips Tecnai F20 G2 FEI-TEM microscope (accelerating voltage 200 kV).

III. Results and Discussion

3.1 Characterization of the Pd@Au Core/Shell Nanosheets

As shown in Figure 1, the UV-vis spectra of Pd@Au core/shell nanosheets (Pd@Au NSs) exhibited with the maximum absorption peak in the range from 849 nm to 1061 nm, respectively. At this point, the highest absorbance of Pd@Au NSs sample is at 941 nm and indexed into the NIR region – see in Figure 1(b). Moreover, the Figure 3 indicates that the Pd@Au NSs have been successfully synthesized by covering uniformly an Au layer of 4 nm thickness on the Pd nanosheet's surfaces (average diameter ~20-30 nm).

When the applied reaction time increasing, it leads the maximum absorbance also increasing and after gradually decreasing (from 941 nm to 1061 nm, and 1061 nm to 896 nm); whereas, the intensity of absorption peaks is gradually decreased– see in Figure 1(b-d). Therefore, the optimal sample with reactione time of 3 h at room temperature will be chosen to investigate other factors in the next steps for the synthesis of Pd@Au core/shell nanosheets.

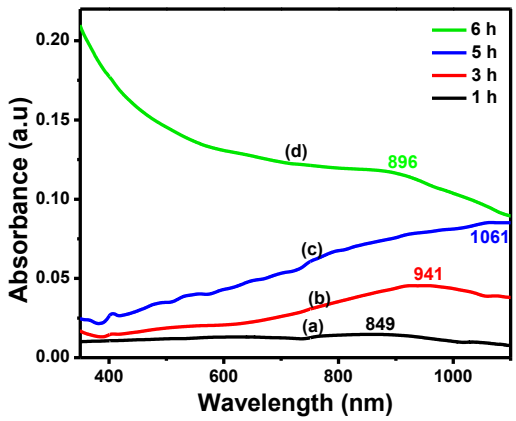

Fig. 1. UV-vis spectra of Pd@Au core/shell nanosheets with different reaction times of: (a) 1 h, (b) 3 h, (c) 5 h, and (d) 6 h, respectively.

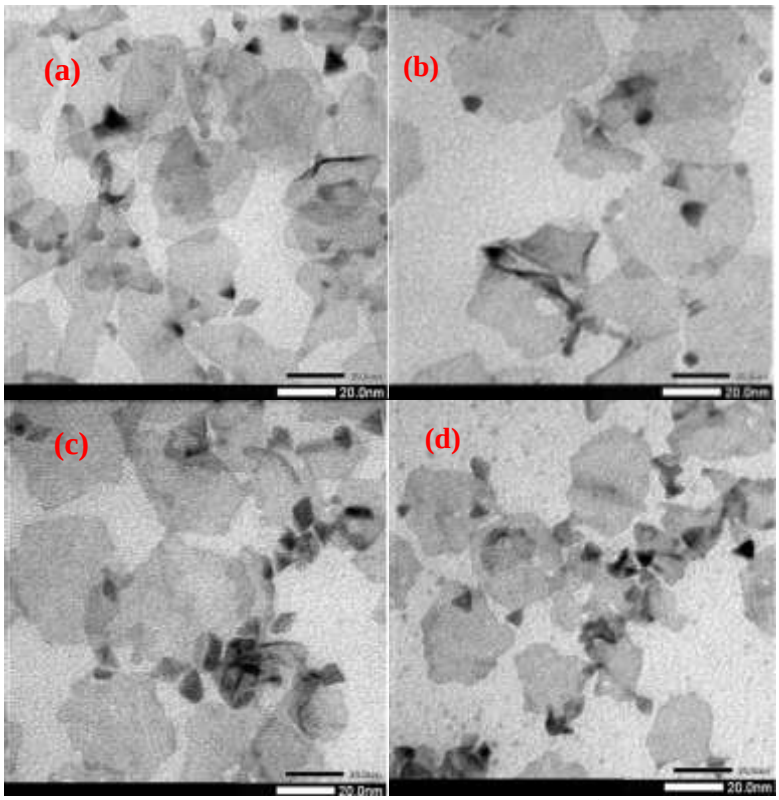

Fig. 2. TEM images of Pd@Au core/shell nanosheets (Pd@Au NSs) with various reaction times of: (a) 1 h, (b) 3 h, (c) 5 h, and (d) 6 h, respectively.

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As shown in Figure 2, the representative TEM images of Pd@Au core/shell nanosheets (Pd@Au NSs) samples and the core/shell nanosheets still adopt a hexagonal plate-like shape and had an average diameter of ~25-30 nm, similar to that of Pd nanosheet seeds. However, the average thickness of the layer Au covered on the Pd nanosheets' surface is about 4 nm, leading to the Pd@Au nanosheets average diameter be larger than that of Pd nanosheets – see in Figures (2b) and (3). Furthermore, when increasing the reaction time leads to form porous nanostructures on the Pd/Au nanosheets' surface – see in Figure 2(d). It demonstrated that the Pd/Au nanosheets have been respectively obtained with nanostructure of the alloy, non-structural of the core/shell. Thus, the optimal sample with reactione time of 3 h at room temperature will be chosen to investigate other factors in the next steps for the synthesis of Pd@Au core/shell nanosheets.

The study of elemental distribution of Au on Pd nanosheets' surface was also performed by energy dispersive X-ray (EDX) spectroscopy. Moreover, the elemental mapping analysis (Figure 3(a, b) and the EDX line profile (Figure 3(c)) show that both Au and Pd atoms were homogeneously distributed throughout the as-synthesized Pd@Au core/shell nanosheets. It indicated that Au was successfully covered on the Pd nanosheets.

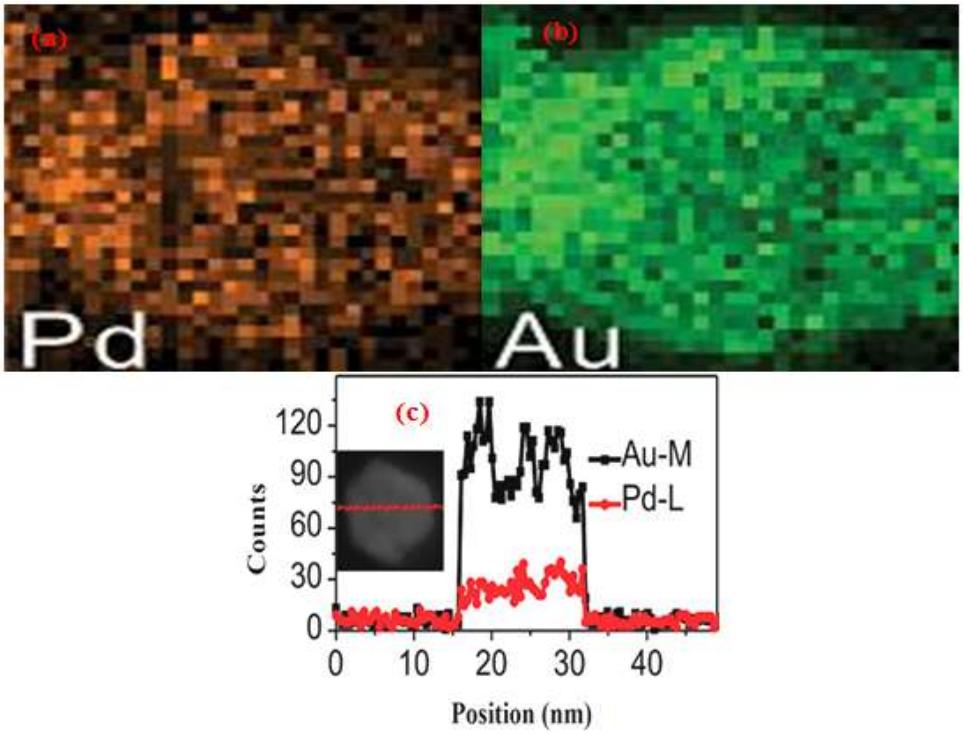

Fig. 3. Elemental mapping analysis (STEM-EDX) (a) and (b); and (c) EDX line profiles of Pd@Au core/shell nanosheets (Pd@Au NSs) (respective left inset Figure HAADF-STEM) with reaction time for 3 h at room temperature.

The composition of the synthesized core/shell nanosheets was examined by X-ray diffraction (XRD) (Figure 4) and the elemental mapping analysis was tested by using scanning transmission electron microscopy–energy-dispersive X-ray spectrometry (STEM–EDX) (Figure 3(a,b). As shown in Figure 4, the XRD peaks of the synthesized Pd@Au core/shell nanosheets, pure Au and Pd nanocrystals could be indexed as a face-centered cubic (fcc) structure. The characteristic peaks of Au achieved at 38.1°, 44.3°, 64.7°; and of Pd at 40.9°, 46.9°, and 68° correspond to crystal facets of {111}, {200}, and {220} of gold (Au) and palladium (Pd) as compared and interpreted to standard data respective of pure fcc Au (JCPDS No. 04-0784) and pure fcc Pd (JCPDS No. 05-0681), which proposed the successful synthesis of Pd@Au core/shell nanosheets.

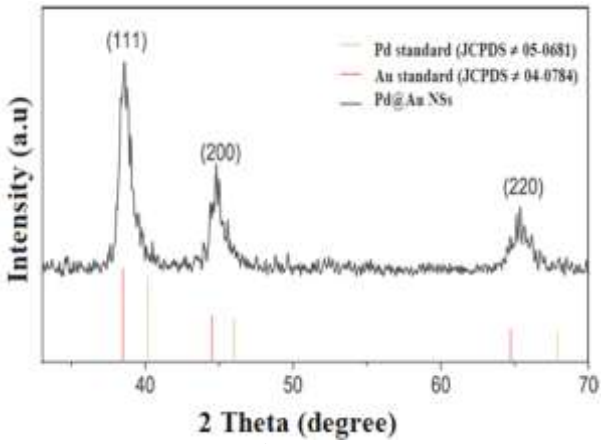

Fig. 4. XRD patterns of Pd@Au core/shell nanosheets.

IV. CONCLUSIONS

In summary, a simple synthetic method of Pd@Au core/shell nanosheets (Pd@Au NSs) at room temperature was

successfully developed. The formation of high quality Pd@Au core/shell nanosheets with the Au layer of ~3-4 nm thickness covered uniformly on the Pd nanosheets' surface was generated for 3 h at room temperature. The prepared Pd@Au core/shell nanosheets could be used as a SERS substract, which may be significant enhanced on the SERS signal due to their good stability and a number of "hot spots" built by Pd@Au core/shell nanosheets. Therefore, it could be significantly interesting in the field of plasmon-enhanced catalysis. For the future work, the catalytic activity of this material and application in biosensor for the quantitative detection of biomarkers will be investigated.

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