

## Preparation of Gold-Nickel Phosphide Core-Shell Nanoparticles Via a Facile Solution Method

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**Abstract.** Core-shell nanomaterials have been one of the most attracting research targets in the field of nanoscience and technology due to the multiple functionalities contributed from different components. In this paper, we report a facile solution synthetic method for the preparation of gold-nickel phosphide core-shell nanoparticles that have a near-spherical morphology and a size of ~20 nm. Transmission electron microscopy along with energy dispersive X-ray spectroscopy analyses reveals a core-shell structure consisting of gold core and nickel phosphide shell. The optical absorption data show that the surface plasmon resonance band of gold in the visible range is greatly decreased by coating nickel phosphide shell. The result of magnetic measurement reveals that the as-prepared core-shell nanoparticles basically exhibit paramagnetic characteristics. The obtained gold-nickel phosphide core-shell nanoparticles can be applied in application fields such as catalysis.

### Introduction

Core-shell nanomaterials have attracted much attention due to their potential applications in wide fields such as catalysis, drug delivery, anion detection, DNA separation, and magnetic resonance imaging (MRI) enhancement and inkjet printing. Due to the synergistic effect caused by different components and the specific structure, core-shell nanomaterials may possess enhanced or even novel properties that are not owned by each component [1-3]. Nowadays, a lot of methods have been developed for the synthesis of core-shell nanomaterials. For example, Huang et al. used the successive reduction process to fabricate Au@Pd core-shell nanocrystals with different shapes which exhibited an excellent electrocatalytic activity [4]. Li's group employed a one one-pot protocol for the synthesis of gold-based hybrid magnetic nanostructures [5].

Transition metal phosphide nano-materials are important materials for their interesting properties such as ferromagnetism, semiconductivity, catalytic activity, magnetocaloric behavior, and magnetoresistance [6,7]. Among them, nickel phosphides have been widely used in industrial fields such as catalysis. In recent years explorations on the synthesis and novel properties of nanoscale nickel phosphides have been conducted in many investigations [8-10]. Gold is not only a plasmonic metal that can be used in fields such as sensing and biomedical application, but also an excellent catalyst. The combination of nickel phosphide and gold into a core-shell structure may bring many advantages for practical applications. However, the reports on the preparation of core-shell nanoparticles containing both nickel phosphide and gold are very rare.

In this paper, we report a facile solution synthetic method for the preparation of gold-nickel phosphide core-shell nanoparticles. The formed core-shell structure has been confirmed by transmission electron microscopy (TEM). In addition, the optical and magnetic properties of the as-prepared core-shell nanoparticles have also been investigated. The synthetic method revealed in this study offers a useful route for the synthesis of core-shell structured nanostructure containing both transition metal phosphides and noble metals.

## Experimental details

The synthetic procedures for gold-nickel phosphide core-shell nanoparticles are as follows: 0.02 g of  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  was pre-dissolved in the mixture of 2 mL of dibenzyl ether (DE) and 0.5 mL of toluene. Then the solution containing  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  along with 0.5 mmol of nickel(acetylacetonate)<sub>2</sub> ( $\text{Ni}(\text{acac})_2$ ) and 6 mL of oleylamine (OAm) were introduced into a three-necked flask and kept under a flow of high-purity argon gas at 120 °C for 10 min before 2 mmol of trioctylphosphine (TOP) was injected. After stirring for another 5 min, the resulting solution was heated up to 210 °C and aged at this temperature for 80 min. Then another 2 mmol of TOP was injected in and the resulting solution was heated up to 285 °C and aged at this temperature for another 60 min. After cooling to room temperature, the products were separated by centrifugation, washed with the mixture of hexane and ethanol and dried under ambient conditions. TEM images, energy dispersive X-ray spectroscopy (EDS) data, and electron diffraction patterns were obtained using a JEM-2100 transmission electron microscope under an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded using a Panalytical X'pert PRO X-ray diffractometer with  $\text{Cu K}\alpha$  radiation. UV-vis spectra were taken using a Shimadzu UV-2550 ultraviolet visible spectrophotometer. Magnetic hysteresis loops were obtained on a physical properties measurement system (PPMS-9) in the temperature of 5 to 300 K.

## Results and discussion

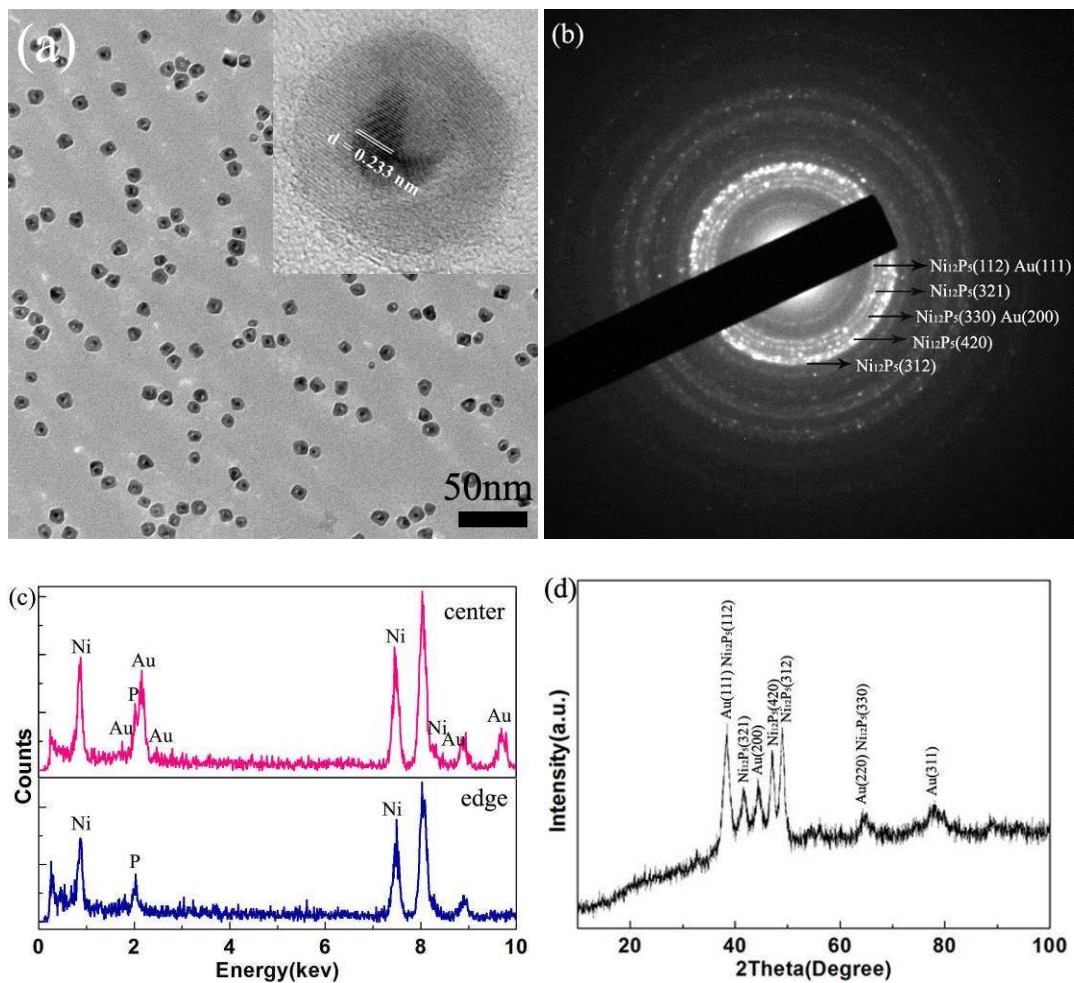


Fig. 1 (a) Low-magnification TEM image of gold-nickel phosphide core-shell nanoparticles. The inset in (a) is the HRTEM image. (b) SAED pattern from multiple nanoparticles. (c) EDS spectra recorded from the center (above) and edge (below) of a single particle. The Cu peak (not labeled) is due to the TEM grid. (d) Typical XRD pattern.

The typical TEM image of the as-synthesized gold-nickel phosphide core-shell nanoparticles is presented in Fig. 1a. Clearly, these particles adopt a core-shell structure. The inset in Fig. 1a is the high-resolution transmission electron microscopy (HRTEM) image of a single gold-nickel phosphide core-shell nanoparticle. Lattice fringes are clearly evident in the image, indicating crystalline characteristics. In the core region, the measured lattice spacing of 0.233 nm corresponds well to the (111) reflection of face centered cubic (fcc) Au. Fig. 1b is the selected area electron diffraction (SAED) pattern recorded from multiple nanoparticles and the diffraction rings can be indexed to fcc Au and tetragonal  $\text{Ni}_{12}\text{P}_5$ . In order to confirm the core-shell structure, the chemical compositions in center and edge are analyzed by EDS. The results (see Fig. 1c) show that the compositions at the edge are basically Ni and P while Au only appears in the center. Fig. 1d is the typical XRD pattern of the as-prepared core-shell nanoparticles. The prominent peaks basically match well with fcc Au and tetragonal  $\text{Ni}_{12}\text{P}_5$ , consisting with the SAED data. The above results demonstrate that a core-shell structure consisting of gold core and nickel phosphide shell is obviously formed.

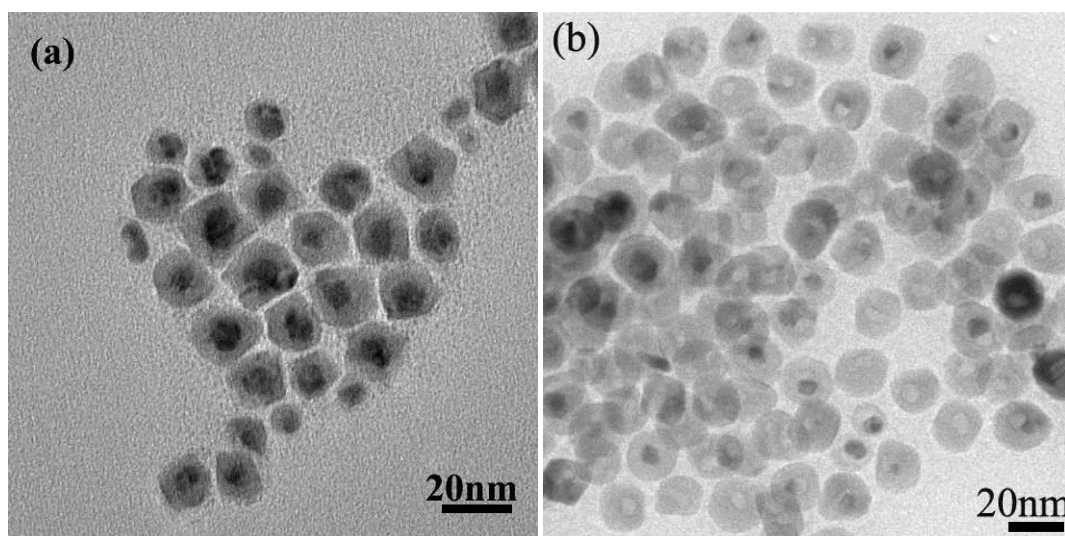


Fig. 2 TEM images of gold-nickel phosphide core-shell nanoparticles synthesized at (a) 280 °C and (b) 300 °C.

We also synthesized gold-nickel phosphide core-shell nanoparticles at different temperatures for comparison. Fig. 2a is the TEM image of the nanoparticles synthesized at 280 °C. Obviously the particles adopt an angular surface and parts of the shells are square. The particles synthesized at 300 °C (Fig. 2b) form a hollow nanostructure. This is mainly caused by the different diffusion rates between Ni and P in the phosphorizing process, which known as Kirkendall Effect [10]. The possible formation process is as follows: Ni experienced the heterogeneous nucleation and growth at Au surface and then the surface Ni became phosphide. The outward diffusion rate of Ni was faster than the decomposition of TOP. Thus excessive Ni diffused outside and a hollow nanostructure was thus formed. As shown in the results, to obtain well specified core-shell structure, the reaction temperature should be carefully controlled.

It is well established that the optical absorption spectra of noble metal nanoparticles consist of strong peaks that originate from plasmon excitations. Therefore, we measured the UV-vis absorption spectra of the as-prepared core-shell nanoparticles and the result is shown in Fig. 3a. The UV-vis absorption spectrum of Au nanoparticles is also included for comparison. Obviously, the absorption band of Au accords well with the paper reported previously that Au nanoparticles with sizes ranging from 5 to 20 nm give rise to the surface plasmon resonance (SPR) band at about 520 nm. After coating nickel phosphide shells, the absorption band of Au remains to be discerned but with greatly decreased intensity. This phenomenon not only confirms the successful synthesis of core-shell nanostructure but also indicates that the nickel phosphide shells are not too thick to overwhelm the SPR response of Au nanoparticles. At the same time, the SPR band also show a red-shifted and broadened feature, which

is also due to the coating of shell material with a relative high index of refraction. Fig. 3b shows the hysteresis loops obtained at 5 K. The magnetization increases roughly linearly with the applied field. The result indicates that the core-shell nanoparticles are basically paramagnetic in nature. The measured coercivity ( $\sim 44$  Oe) is not fully equal to zero, which may be caused by the presence of some magnetic impurity such as Ni.

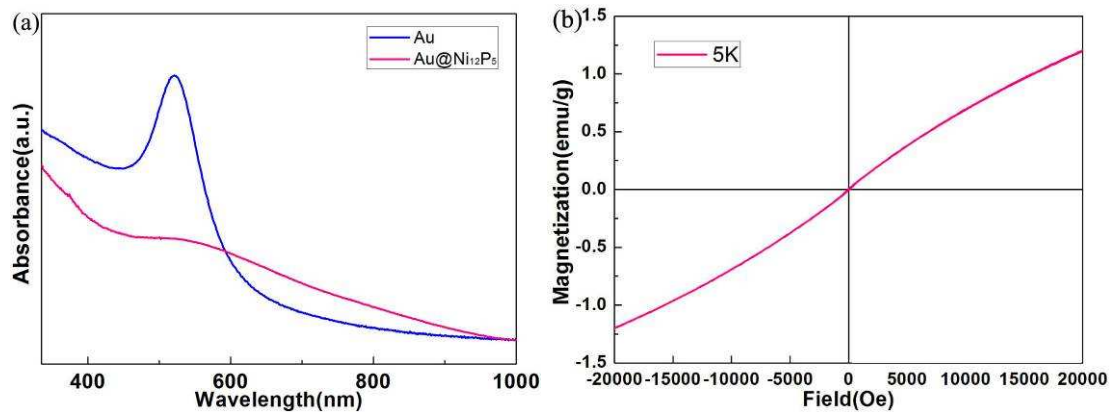


Fig. 3 (a) UV-vis absorption spectra of gold and gold-nickel phosphide core-shell nanoparticles. (b) Magnetic hysteresis loop of gold-nickel phosphide core-shell nanoparticles obtained at 5 K.

## Conclusion

We have successfully prepared gold-nickel phosphide core-shell nanoparticles using a facile nonaqueous solution method. TEM and EDS analytic results show the nanoparticles adopt a core-shell nanostructure consisting of gold core and nickel phosphide shell and have a typical size of about 20 nm. SAED and XRD results indicate that these nanoparticles are crystalline and the identified crystalline phases are fcc Au and tetragonal  $\text{Ni}_{12}\text{P}_5$ . Different reaction temperatures can influence the morphology of the core-shell nanoparticles. The intensity of the SPR band of Au in the visible range is greatly decreased by coating nickel phosphide shell. Magnetic measurement reveals that these nanoparticles show paramagnetic characteristics.

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