

Ultrahigh Active Pd Nanocatalyst Supported on Core-Sheath Conducting Polymer/Metal Oxide Composite Nanorods

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Abstract A facile and aqueous-phase method based on the electron transfer reduction process for fabricating core-sheath structured polyaniline (PANI)/SnO₂ composite nanorods supported Pd nanocatalyst has been demonstrated. The Pd nanoparticles synthesized by this strategy have a small size of smaller than 3.0 nm. The well dispersed Pd nanoparticles with small sizes supported on core-sheath PANI/SnO₂ composite nanorods exhibited an ultrahigh catalytic activity during the catalytic reduction of *p*-nitrophenol into *p*-aminophenol by NaBH₄ in aqueous solution. The kinetic apparent rate constant (k_{app}) reach to be about $26.9 \times 10^{-3} \text{ s}^{-1}$. It is believed that this method could be extended to cover many kinds of other functional composite nanomaterials where the active component is expected to bring in new features and applications.

Keywords Electron transfer reduction · Polyaniline · Tin oxide · Palladium · Catalysis

1 Introduction

Noble metal nanoparticles with controllable sizes and shapes have attracted growing attention for their unique physical and chemical properties and potential applications in catalysis, sensors, information storage, surface enhanced Raman scattering, biomedicine, and so on [1–11]. Especially, metal nanoparticles become more and more

important in catalytic applications because of their large surface area and super-high activity. However, the metal nanoparticles with small size are easily aggregated for the high surface energy, reducing their catalytic activity. To overcome this problem, metal nanoparticles are often immobilized onto some less expensive solid supports, such as metal oxides, carbon and polymers, etc. [12–20]. Moreover, the deposition of metal nanoparticles on metal oxide supports often exhibit enhanced catalytic activity and selectivity because of the synergistic effect between them [21–23]. Early reports on the fabrication of metal nanoparticles onto metal oxide support mainly involved the calcination of metal precursors on the surface or inside metal oxide nanostructures at a high temperature [24–26]. However, the metal nanoparticles produced by this method are often poorly dispersed on the support. Therefore, it is still a challenge to develop a facile method to fabricate composite nanostructures consisting highly dispersed metal nanoparticles onto the metal oxide matrix.

Among various metal/metal oxide composite nanostructures, supported Pd nanocatalysts have been found to play an important role for a number of reactions, including hydrogenation reaction, the carbon–carbon cross-coupling reaction, the oxidation of primary alcohols, the direct generation of H₂O₂ from H₂ and O₂, and so on [27–30]. Recently, Lee et al. [31] reported the preparation of Pd/SnO₂ composite nanorods by using NaBH₄ as reducing agent via a solution process, but the size of the Pd nanoparticles is large, limited their applications in the catalysis. Here, we report a simple and water-phase route for the synthesis of a polyaniline (PANI)/SnO₂/Pd tri-component hybrid nanorod consisting of sub-3 nm Pd nanocrystals supported on core-sheath PANI/SnO₂ nanorods with a out-diameter of about 100–150 nm through an electron transfer reduction process. It is well known that the oxidation

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potential of PANI is much higher than that of the palladium ions, so PANI/Pd composites could be simply synthesized by directly mixing the PANI and palladium ions via a redox reaction [32, 33]. However, the size of Pd nanoparticles supported on PANI matrix is too large via such a direct redox reduction method because the growth is fast. To prevent the Pd nanocrystals grow too fast, we have synthesized a core-sheath PANI/SnO₂ composite nanorods firstly. Then they were mixed with Na₂PdCl₂ to generate small Pd nanocrystals supported on the core-sheath PANI/SnO₂ composite nanorods by an electron transfer reduction process. Using this approach, we were able to synthesize PANI/SnO₂/Pd composite nanorods with good dispersion of Pd nanocrystals in high yields. This procedure is simple and mass-produced, because it does not require high temperature calcination or other reducing agents. It was found that the as-prepared PANI/SnO₂/Pd composite nanorods exhibit an ultrahigh activity as catalysts for the reduction of *p*-nitrophenol by sodium borohydride (NaBH₄) at ambient conditions.

2 Experimental

2.1 Chemicals

Aniline monomer was distilled under reduced pressure before use. All the other chemicals were of analytical grade and used as received without further purification.

2.2 Synthesis of PANI Nanorods

The preparation of PANI nanorods was according to previous report [34]. In a typical procedure, an aqueous solution of 0.3 mL aniline monomer in 10 mL of 1.0 M HCl and another aqueous solution of 0.18 g ammonium peroxydisulfate in 10 mL of 1.0 M HCl were prepared and mixed rapidly. After shaking for about 30 s, the mixture was left for 2 h. The obtained green precipitate was centrifuged and washed with deionized water and ethanol for several times. At last, it was dried in vacuum at 40 °C for one night.

2.3 Preparation of Core-Sheath PANI/SnO₂ Composite Nanorods

The core-sheath PANI/SnO₂ composite nanorods were prepared by the hydrolysis of SnCl₂ on the surface of PANI nanorods. Typically, 30 mg of PANI nanorods were dispersed in 18 mL of water containing 0.15 mL HCl at room temperature. Then 0.66 g of SnCl₂·2H₂O and 0.3 g urea were added into the above solution. The mixture was continually stirred at 60 °C for 6 h. The obtained jade-green product was centrifuged and washed with water and

ethanol for several times, then the product was dried at 40 °C under vacuum for one night.

2.4 Preparation of PANI/SnO₂/Pd Composite Nanorods

The PANI/SnO₂/Pd composite nanorods were prepared by the reduction of NaPdCl₄ via an electron transfer process. Briefly, 5 mg of the as-prepared core-sheath PANI/SnO₂ composite nanorods were dispersed into 10 mL of water. After that, 1 mL aqueous solution containing 5 mg NaPdCl₄ was added into the above reactive medium. The reaction was going on for about 5 h. The product was centrifuged and then washed with water and ethanol for several times. At last, the product was dried at 40 °C under vacuum for one night.

2.5 Reduction of *p*-Nitrophenol Catalyzed by PANI/SnO₂/Pd Composite Nanorods

Typically, the aqueous solution of *p*-nitrophenol (1.7 mL, 2.0×10^{-4} M) and NaBH₄ (1.0 mL, 1.5×10^{-2} M) were added together into a quartz cuvette. Then, 0.3 mL of an aqueous solution containing PANI/SnO₂/Pd composite nanorods (0.224 mg/mL) was injected into the cuvette to start the reaction. The intensity of the absorption peak at 400 nm in ultraviolet–visible (UV–Vis) spectroscopy was used to monitor the process of the conversion of *p*-nitrophenol to *p*-aminophenol.

2.6 Characterization

Transmission electron microscopy (TEM) experiments were performed on JEM-1200 EX (JEOL) electron microscopes with an acceleration voltage of 100 kV. High-resolution TEM (HRTEM) imaging and energy-dispersive X-ray (EDX) analysis were performed on a FEI Tecnai G2 F20 high-resolution transmission electron microscope operating at 200 kV. Fourier transform infrared (FTIR) spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR 22 Spectrometer. UV–Vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer. Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII using Al as the exciting source. The weight percent of Pd in the nanocomposites was determined by inductively coupled plasma (ICP) atomic emission spectrometric analysis (POEMS, TJA).

3 Results and Discussion

In this study, PANI nanorods were synthesized by a rapid mixing method through the oxidation polymerization between aniline monomer and the oxidant ammonium

Fig. 1 **A** TEM image of PANI nanorods synthesized via a rapid mixing polymerization method. **B** TEM image of PANI/SnO₂ composite nanorods obtained by the hydrolysis of SnCl₂. **C** TEM image of PANI/SnO₂/Pd composite nanorods obtained by electron transfer reducing Na₂PdCl₄ with PANI nanorods in a aqueous solution. **D**, **E** HRTEM images of PANI/SnO₂/Pd composite nanorods. **F** EDX analysis of PANI/SnO₂/Pd composite nanorods. **G** EDX mapping images of PANI/SnO₂/Pd composite nanorods

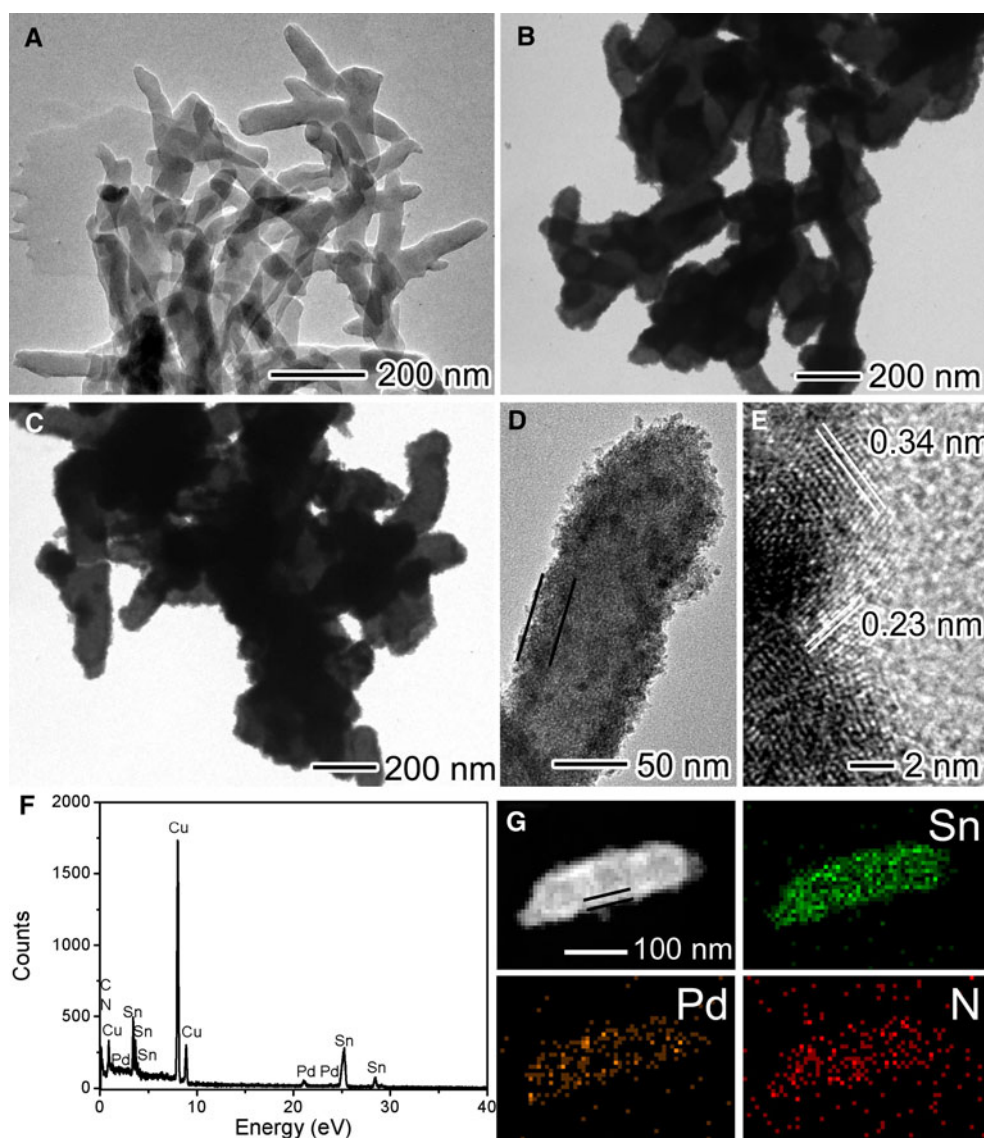
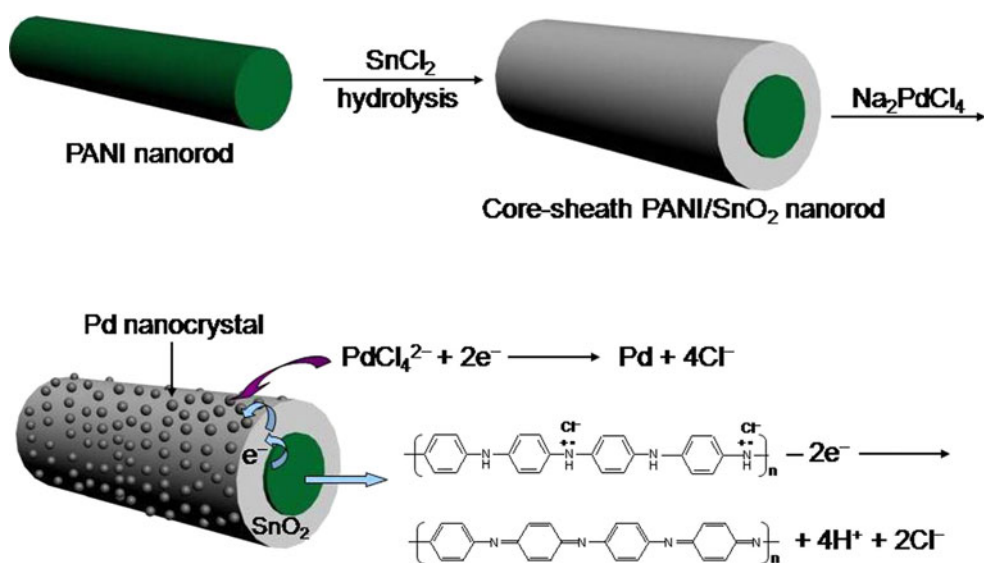


Fig. 2 Schematic illustration of the fabrication of PANI/SnO₂/Pd composite nanorods via an electron transfer reducing process



peroxide, as reported previously [34]. Figure 1A shows a TEM image of as-prepared PANI nanorods. It was found that they were uniform with a diameter about 50 nm and a length of several hundred nanometers. After coating with SnO_2 , the PANI nanorods are homogeneously encapsulated by a SnO_2 layer with the thickness of about 20–30 nm. The formation of SnO_2 layer on the surface of PANI nanorods could be attributed to the hydrolysis of SnCl_4 to form SnO_2 nanocrystals and spontaneously formed on the surface of PANI nanorods. From Fig. 1B, it was found that the SnO_2 layer on the surface of PANI nanorods was compact and form a core-sheath structure. These core-sheath PANI/ SnO_2 composite nanorods were then used as supports for the preparation of PANI/ SnO_2 /Pd composite nanostructures. Pd nanocrystals were directly grown on the surface of PANI/ SnO_2 nanorods upon the reduction of PdCl_4^{2-} by the electrons generated from PANI in an aqueous solution. Figure 1C shows a typical image of the PANI/ SnO_2 /Pd composite nanorods, revealing that the morphology of the product does not change after the formation of Pd nanocrystals on their surface, and there are not isolated Pd nanocrystals in the product. To further prove the formation of the PANI/ SnO_2 /Pd composite nanorods, HRTEM images were shown in Fig. 1D and E, which clearly exhibits the formation of most of Pd nanocrystals with sizes of 1–3 nm on the surface of core-sheath PANI/ SnO_2 composite nanorods. The lattice spacing of 0.34 and 0.23 nm corresponds to those {110} facets of SnO_2 and {111} facets of Pd, respectively. From HRTEM image, it was also found the formation of the metal–metal oxide interface because no large capping agents formed on the surface of Pd nanocrystals by using our method. The strong metal–metal oxide interaction would increase the activation energy for some catalytic reactions [35]. The overall weight percentage of Pd in the PANI/ SnO_2 /Pd composite nanorods was 7.9 %, which was determined by ICP atomic spectrum measurements. As shown in Fig. 1F, the energy-dispersive X-ray spectroscopy (EDS) also confirms that the element of Pd, Sn, C, N exists in the PANI/ SnO_2 /Pd composite nanorods, and no other obvious element is observed except Cu. The signal of Cu in the EDS spectrum originates from the carbon-coated copper grid. All results demonstrate the feasibility of our approach for the preparation of PANI/ SnO_2 /Pd composite nanorods.

The mechanism of the formation of Pd nanocrystals on the surface of core-sheath PANI/ SnO_2 composite nanorods could be explained in two ways. The first explanation is that PdCl_4^{2-} will diffuse into the interface between SnO_2 layer and PANI matrix where it could be reduced by PANI nanorods to form Pd nanocrystals. In this case, Pd nanoparticles would be formed homogeneously at the interface between SnO_2 layer and PANI nanorods or inside PANI nanorods, and not formed on the outside of the surface of

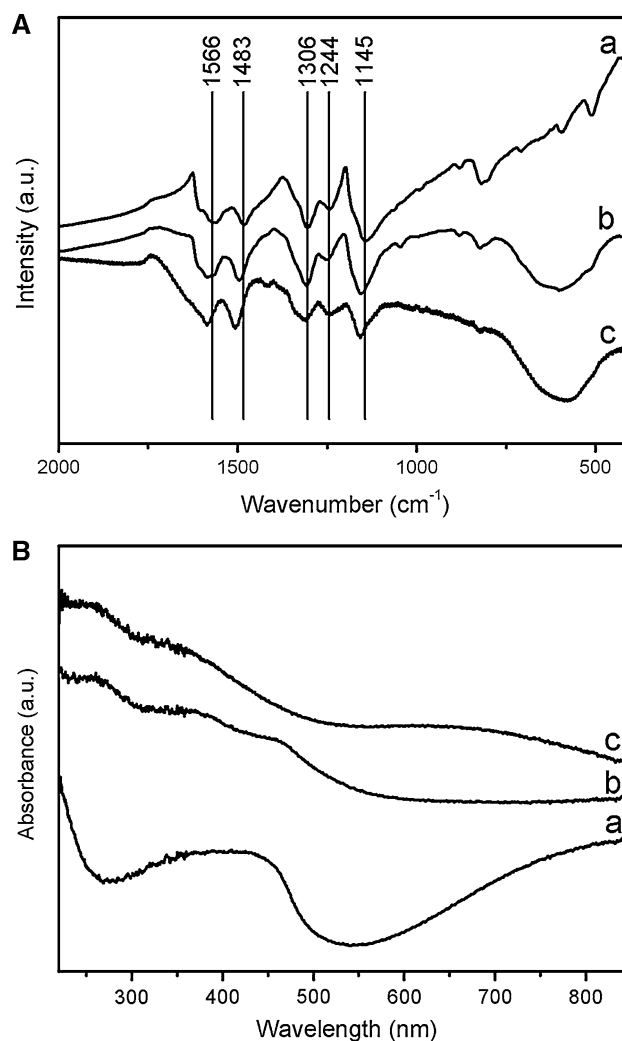


Fig. 3 A FTIR spectra of (a) PANI nanorods, (b) core-sheath PANI/ SnO_2 composite nanorods and (c) PANI/ SnO_2 /Pd composite nanorods; B UV-Vis absorption spectra (a) PANI nanorods, (b) the as-prepared core-sheath PANI/ SnO_2 composite nanorods and (c) PANI/ SnO_2 /Pd composite nanorods

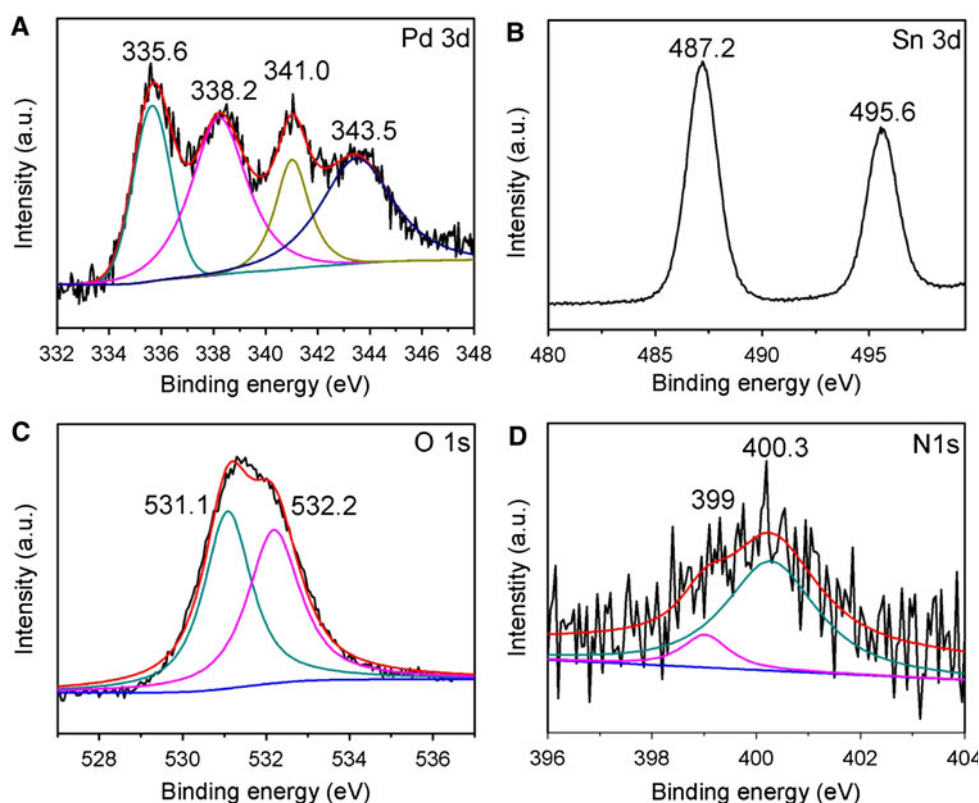
SnO_2 layers. However, Fig. 1G strongly contradicts this hypothesis, which the EDX elemental-mapping analysis revealed that Pd atoms were homogeneously distributed throughout the surface of core-sheath PANI/ SnO_2 composite nanorods. Therefore, we think that Pd nanocrystals should be in situ reduced on the surface of PANI/ SnO_2 composite nanorods by an electron transfer reduction process, which is similar with the previous report [36]. When PdCl_4^{2-} was mixed with PANI/ SnO_2 composite nanorods, PANI will be oxidized to generate electrons, which will be transferred through the semiconductor SnO_2 layer to its surface, where the PdCl_4^{2-} are reduced by the released electrons to form Pd nanocrystals (Fig. 2). Compared to the method by the directly mixing PANI nanorods and NaPdCl_4^{2-} , this process provides the preparation of Pd nanoparticles with a small size [32, 33].

The chemical composition of the as-prepared PANI/SnO₂/Pd composite nanorods was supported by the FTIR and UV–Vis absorption spectroscopies. Figure 3A shows typical FTIR spectra of PANI nanorods, the as-synthesized PANI/SnO₂ and PANI/SnO₂/Pd composite nanorods, respectively. For PANI nanorods, the peaks at 1,566 and 1,483 cm⁻¹ are ascribed to the characteristic C=C stretching of the quinonoid and benzenoid rings, respectively. The peaks at 1,306 and 1,244 cm⁻¹ are corresponding to C–N and C=N stretching vibrations. The peak at 1,145 cm⁻¹ is related to the in-plane bending of C–H. Compared to PANI nanorods, a new broad peak at about 600 cm⁻¹ has appeared in PANI/SnO₂ and PANI/SnO₂/Pd composite nanorods, which are assigned to the Sn–O–Sn vibration, indicating the formation of SnO₂ layer [37]. In addition, the ratio of the relative intensity of the peaks corresponding to C=N and C–N stretching vibrations increases significantly after the formation of Pd nanocrystals, showing that PANI was partially oxidized via an electron transfer process. The oxidation state of PANI after the electron transfer reduction process was also proved by the UV–Vis spectra. For PANI nanorods, the absorption peaks at 320–360 nm could be attributed to the π – π^* electron transition, and the absorption bands at 400–420 and \sim 800 nm could be ascribed to doping level and formation of polaron, respectively [38]. After coating with SnO₂ and Pd nanocrystals, a new broad peak at 570–670 nm appeared, indicating the formation of

emeraldine and pernigraniline base of PANI, which also proved the oxidation of PANI [39].

The oxidation state of Pd nanocrystals in the PANI/SnO₂/Pd composite nanorods is determined by XPS as shown in Fig. 4. The XPS spectrum of the as-synthesized PANI/SnO₂/Pd composite nanorods exhibits characteristic signals for Pd3d_{5/2} and Pd3d_{3/2} and the elements of Sn, O, C, N were also observed, which is consistent with the EDX analysis. The Pd3d peaks could be deconvoluted into two components, which are corresponding to the two oxidation states of Pd in the PANI/SnO₂/Pd composite nanorods. The peaks at 335.6 eV (Pd3d_{5/2}) and 341.0 eV (Pd3d_{3/2}) are assigned to Pd(0), and the other peaks at 338.2 eV (Pd3d_{5/2}) and 343.5 eV (Pd3d_{3/2}) are related to the oxidized palladium(II) centers [40]. Previous studies also showed that oxidized palladium were consistent with Pd nanocrystals when the size of Pd nanocrystals are small (2.5 nm or less) [41]. As shown in Fig. 4B, Sn3d_{5/2} and Sn3d_{3/2} doublet with the binding energies of 495.6 and 487.2 eV are observed, respectively, indicating that SnO₂ is coated on the surface of PANI nanorods. The N1s spectrum could be deconvoluted into two components, with binding energy at 400.3 and 399 eV. The former peak is attributed to neutral nitrogen moieties in PANI [42]. The signal of 399 eV is usually ascribed to uncharged deprotonated imine (=N–) atoms [42], which is also consistent with the process of the oxidation of PANI by PdCl₄²⁻.

Fig. 4 XPS spectra of the as-synthesized PANI/SnO₂/Pd composite nanorods, **A** Pd3d, **B** Sn3d, **C** O1s, **D** N1s



It is well known that Pd is an excellent catalyst for hydrogenation reactions. In this study, we evaluated the catalytic activity of the PANI/SnO₂/Pd composite nanorods by using a well-known catalytic reaction involving the reduction of *p*-nitrophenol into *p*-aminophenol with an excess amount of NaBH₄ in aqueous solution as a model system. The *p*-nitrophenol solution exhibited an absorption peak at $\lambda_{\text{max}} = 400$ nm in the presence of NaBH₄, corresponding to its ions in alkaline conditions. The intensity of this peak as a function of time could be used to monitoring the kinetic process of the reduction process. After the PANI/SnO₂/Pd composite nanorods was added into the reaction system, the characteristic absorption peak of *p*-nitrophenolate ion at 400 nm decreased gradually and disappeared within 100 s, while a new peak at 298 nm which ascribed to the *p*-aminophenol emerged. Correspondingly, the yellow color of the *p*-nitrophenolate ions diminished after 100 s, indicating that *p*-nitrophenol had been completely converted to *p*-aminophenol. In this experiment, NaBH₄ was in excess in the reaction system, so the reduction process could be regarded as pseudo-first-order with respect to the concentration of *p*-nitrophenolate. Since the absorbance of *p*-nitrophenolate is proportional to its concentration in the system, the ratios of *p*-nitrophenolate concentrations at time *t* (*C_t*) to its initial value at time 0 (*C₀*) can be strander for the relative intensity of the respective absorbance *A_t*/*A₀*. As shown in Fig. 5, a linear relationship between ln(*C_t*/*C₀*) and reaction time for the reduction of *p*-nitrophenol catalyzed by PANI/SnO₂/Pd composite nanorods was obtained. It was observed that the reaction could be complete within 100 s in the presence of excess NaBH₄. However, the reaction would be complete in 300 s for the reduction of *p*-nitrophenol by using SnO₂/Pd nanocatalyst, indicating the catalytic activity of PANI/SnO₂/Pd nanocatalyst was much better. The SnO₂/Pd nanocatalyst was prepared by reducing Pd nanoparticles on the surface of electrospun SnO₂ nanofibers by NaBH₄. The kinetic apparent rate constant (*k_{app}*) for the reduction of *p*-nitrophenol by using the PANI/SnO₂/Pd nanocatalyst was calculated to be about $26.9 \times 10^{-3} \text{ s}^{-1}$, which was also much higher than most of the other substrate supported noble metal nanocatalysts [15, 43–47]. The Pd nanocrystals with small sizes were well dispersed on the surface of core-sheath PANI/SnO₂ composite nanorods, affording effective contact between the catalysts and the reactants in the reaction. Therefore, the PANI/SnO₂/Pd composite nanorods exhibited an ultrahigh catalytic efficiency towards the reduction of *p*-nitrophenol.

4 Conclusions

In conclusion, for the first time, core-sheath structured PANI/SnO₂ composite nanorods were used to stabilize

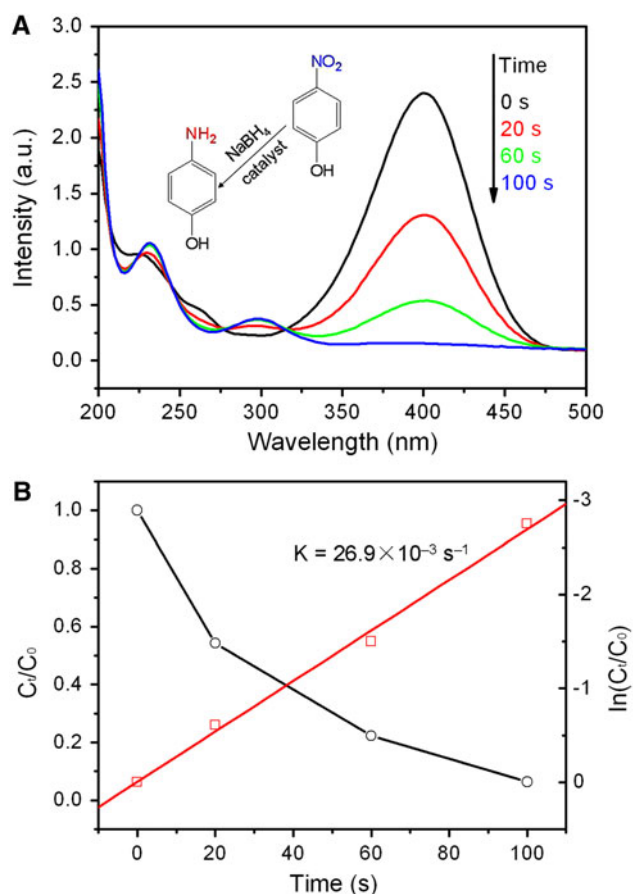


Fig. 5 **A** UV-Vis absorption spectra for the catalytic reduction of *p*-nitrophenol by NaBH₄ over PANI/SnO₂/Pd composite nanorods. **B** The circles and squares stand for the *C_t*/*C₀* and ln(*C_t*/*C₀*) versus reaction time for the reduction of *p*-nitrophenol by NaBH₄ over PANI/SnO₂/Pd composite nanorods, respectively. *C₀* stands for the intensity of the absorption at 400 nm initially and *C_t* was the absorption peak at time *t*

Pd nanocatalysts by a facile, aqueous-phase in situ electron transfer reduction method. The well dispersed Pd nanocrystals with small sizes supported on core-sheath PANI/SnO₂ composite nanorods exhibited an ultrahigh catalytic activity during the catalytic reduction of *p*-nitrophenol into *p*-aminophenol by NaBH₄ in aqueous solution. The obtained PANI/SnO₂/Pd composite nanorods in this work may be found use in many other applications such as electrocatalysis, sensors, energy conversion, and so on. In addition, this approach is expected to be extendible to prepare other kinds of composite systems.

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