

## Polyaniline/silver/cerium nitrate ternary composite: Synthesis, characterization and enhanced electrochemical properties

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**ABSTRACT:** Polyaniline/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composites were prepared by in situ polymerization in a poly (2-acrylamido-2-methylpropane sulfonic acid) aqueous solution. Fourier transform infrared spectroscopy and Ultraviolet-visible spectroscopy analyses indicated that Ce ions had a conjugated interaction with N, O of polyaniline (PANI), and poly (2-acrylamido-2-methylpropane sulfonic acid). By comparison with PANI and PANI binary composite, this ternary composite had a better thermal stability, a high conductivity (3.49 S/cm), a large capacitance, and a high electrochemical activity. Especially, the corrosion potential of this ternary composite can reach -418 mV and the inhibition efficiency can be increased by 68.08%. This ternary porous composite has promising applications in capacitor, conductive materials, anticorrosion coating, and other related fields. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42785.

**KEYWORDS:** composites; conducting polymers; electrochemistry; functionalization of polymers; synthesis and processing

Received 9 March 2015; accepted 26 July 2015

DOI: 10.1002/app.42785

### INTRODUCTION

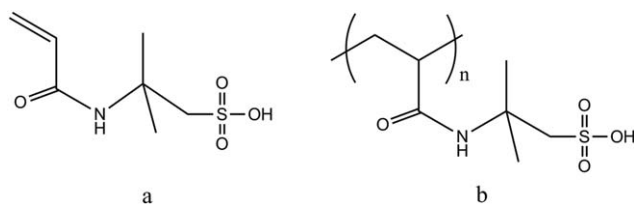
Polyaniline (PANI) is an important intrinsically conducting polymer and has been attracted considerable attention due to easy preparation, low cost, good environmental stability, and electrical conductivity.<sup>1</sup> Up to now, numerous reports show that PANI has potential applications in energy storage, electromagnetic shielding, biosensors, anticorrosion coatings, and so on.<sup>2-7</sup> However, the comprehensive properties of pure PANI hardly meet the demands of the fast-growing industry. It is still an important part of PANI materials research to get a higher conductivity, a better anticorrosion, a larger capacitance, and so on.

PANI/Ag composite is such a composite that not only retains the original, intrinsic performances of PANI but also exhibits a coadjutant effect. The incorporation of silver composite could effectively improve the electrical, optical, and dielectric properties of PANI composites.<sup>8</sup> The electrical conductivity of PANI/Ag composite can reach up to 8000 S/cm when the content of Ag is 70%.<sup>9</sup> This value is much higher than that of PANI doped by acid.<sup>10-15</sup> Besides, the good bactericidal property, sensing property, catalytic property, and so on.<sup>16-18</sup> of silver particles endow PANI composites with many applications. Consequently, a special attention has paid on PANI/Ag composites and numerous articles in literature focus on the synthesis and applications of PANI/Ag composite.

In recent years, PANI/rare earth composites also have received a considerable attention due to the distinctive optical, electrical, magnetic properties, and so on of rare earth elements. PANI/La<sup>3+</sup>, PANI/Tb<sup>3+</sup>, PANI/Eu<sup>3+</sup>, and PANI/Ce<sup>3+</sup> composites have been studied by many researchers.<sup>19,20</sup> Among these, PANI/Ce<sup>3+</sup> composite is of particular interest because Ce<sup>3+</sup> ions show the maximum corrosion protection efficiency and a very fast release ability than that of proton.<sup>21-24</sup> PANI/Ce<sup>3+</sup> composite exhibits widespread applications in anticorrosion coatings, conducting materials, capacitors, and so on and becomes an important function composite.

Poly (2-acrylamido-2-methylpropane sulfonic acid) [PAMPS, Figure 1(b)] is a kind of polymeric acid synthesized via 2-acrylamido-2-methylpropane sulfonic acid [AMPS, Figure 1(a)] monomers. It has an excellent hydrophilicity and an adsorption for metallic ions because of the sulfonic acid group in side chains and can be used as an efficient adsorbent in the wastewater treatment and ions capture.<sup>25,26</sup> In addition, it also can be used as a dopant in the synthesis of PANI with a high electrical conductivity and a water solubility.<sup>27-29</sup> Therefore, PAMPS is a good candidate to prepare PANI/rare earth composites.

Regarding the low cost and rich resources, the distinctive optical, electrical, magnetic properties, and so on of Ce ions, we



**Figure 1.** Chemical structures of (a) AMPS and (b) PAMPS.

innovatively put forward to replace some silver particles in PANI composites by using a certain amount of Ce ions. In the synthesis of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite, we used a polymer acid (PAMPS), which not only captured silver ions and Ce ions but also doped PANI. To the best of our knowledge, it is the first report to synthesize PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite. This ternary composite prepared by this method is expected to have a high conductivity, a good thermal stability, and a good electrochemical activity.

## EXPERIMENTAL

### Materials

PAMPS was prepared via the polymerization of AMPS (Purity, 99.23% and supplied by Shouguang Yuyuan Green Technology Co. in China). The number-average molecular weight and the weight-average molecular weight of PAMPS were 2006 and 2015 kg mol<sup>-1</sup>, respectively. The polydispersity index was 1.0045. Aniline was distilled prior to be used. Other reagents (silver nitrate, sodium hypophosphite, cerium nitrate, ammonium persulfate, acetone) were analytical grade and commercially available from local chemical shops.

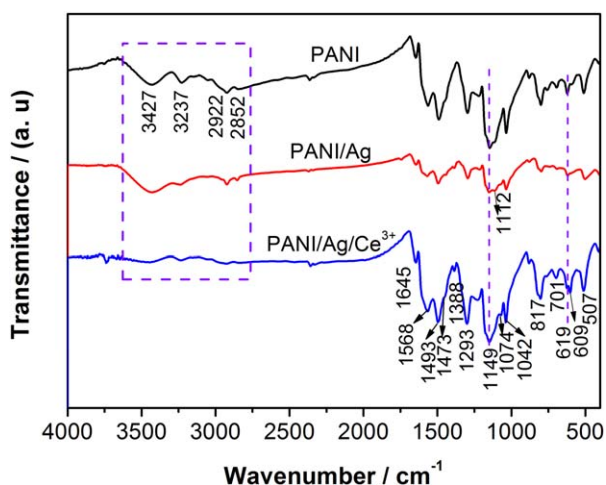
### Synthesis

PAMPS (1.0 g) was added to a 250 mL beaker containing 99.0 g deionized water. A 10 mL solution containing 0.44 g sodium hypophosphite (reducing agent) was added to this beaker. Then, this mixture was kept stirring for 15 min at 40°C. A 15 mL solution containing 1.4 g silver nitrate was added drop by drop to the

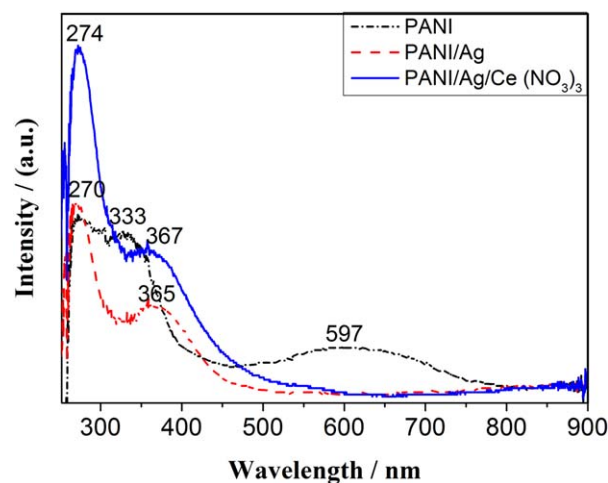
PAMPS aqueous solution that contains sodium hypophosphite. The reduction reaction was sustained for 90 min at 40°C. Aniline (2.5 g) and cerium nitrate (3.6 g) were added to this mixture when the reduction reaction completes. The mixture solution was kept stirring for 15 min at 0–5°C. Then, a 20 mL aqueous solution containing 6.1 g ammonium persulfate (oxidant) was dropped to the mixture solution. This reaction was sustained for 12 h at 0–5°C. The final mixture was treated by acetone before being centrifuged and washed several times by using deionized water. The products were dried in an oven at 60°C for 24 h. A series of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> composites were prepared by changing the amount of Ce (NO<sub>3</sub>)<sub>3</sub>. PANI, PANI/Ag, and PANI/Ce (NO<sub>3</sub>)<sub>3</sub> were also prepared likely the synthesis of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> composites. Only difference was that some reagents and synthesis processes were not necessary.

### Characterization

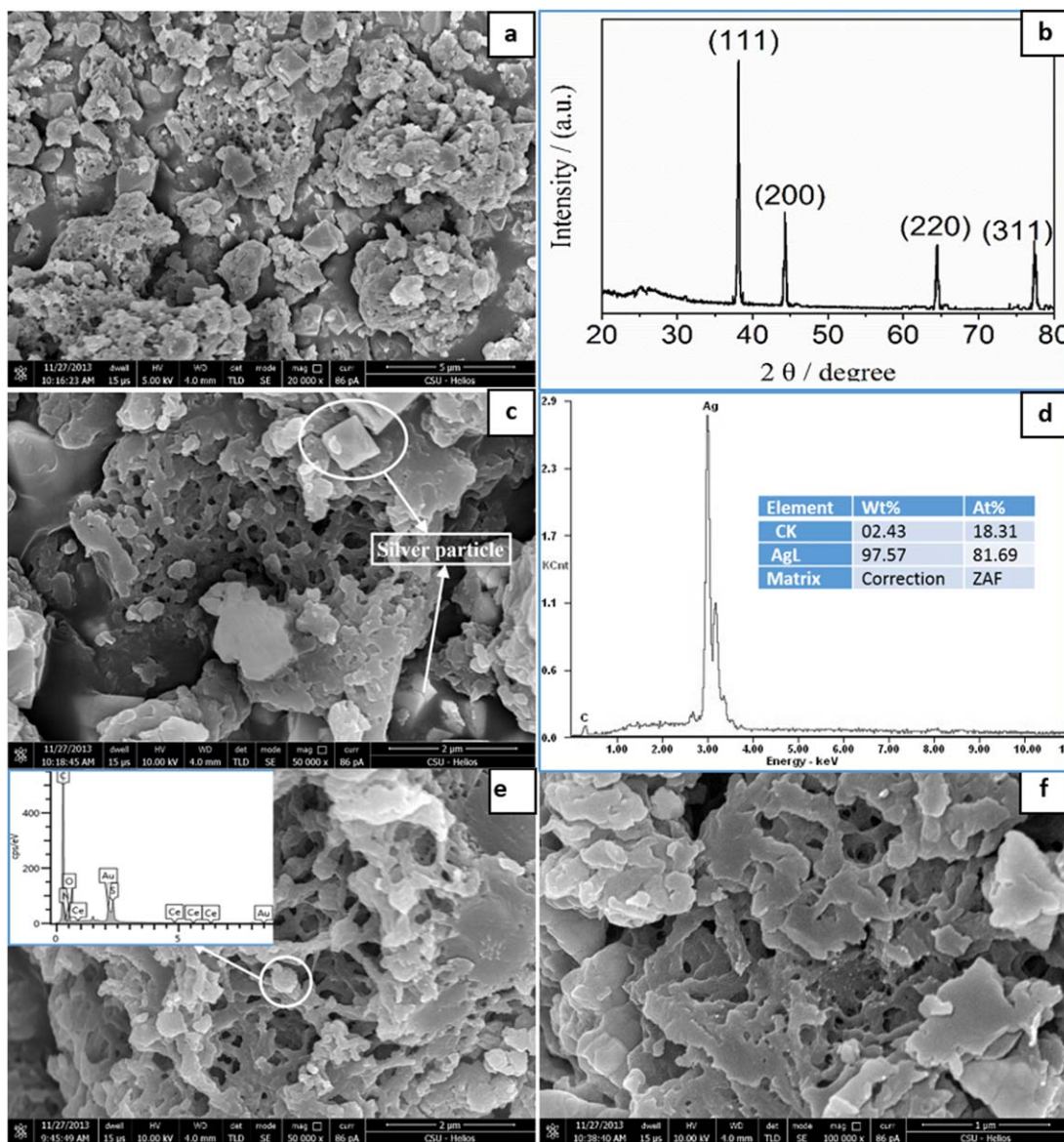
Fourier transform infrared spectroscopy (FT-IR) analysis was performed with a NICOLET 6700 spectrophotometer for wavenumbers ranging from 4000 to 400 cm<sup>-1</sup>. Ultraviolet-visible spectra were obtained in dimethyl sulfoxide using a SHIMADZU UV-2450 spectrophotometer. The concentration of samples was 10 ppm. The morphologies of nanoparticles were observed using scanning electron microscopy (SEM) Helios Nanolab 600i. Brunauer–Emmett–Teller (BET) specific surface area was measured by using N<sub>2</sub> adsorption in Monosorb Autosorb. X-ray (XRD) spectrum of the sample was recorded with Cu Kα radiation ( $\lambda = 1.54 \text{ \AA}$ ) in the diffractometer (model D/Max 2550). Electrochemical behavior of the composites was studied in 0.5 M/L H<sub>2</sub>SO<sub>4</sub> by using Pt as counter electrode, a saturated calomel electrode as reference electrode, and PANI composite as working electrode. PANI or PANI composites, acetylene black, and polytetrafluoroethylene at a composition ratio of 80 : 10 : 10 were pressed on a foam nickel net to form the working electrodes. The impedance spectrum of any sample was recorded under open circuit potential for frequencies ranging from 100 kHz to 5 mHz using 10 mV ac amplitude of sinusoidal voltage. Cyclic voltammograms (CV) were recorded at



**Figure 2.** FT-IR spectra of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** UV-Vis spectra of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Morphology of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composites: (a) SEM image of this composite at low magnification; (b) XRD spectra of this composite; (c) the distribution of particles in composite; (d) the EDX analysis that corresponding to these particles; (e) the sphere structure in composite; (f) the porous structure in composite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

50 mV/s by using a Zahner (IM6ex, Germany) electrochemical station. The electrical conductivity was tested using a PANI or PANI composites pellet that prepared under 15 MPa via the four-probe method.

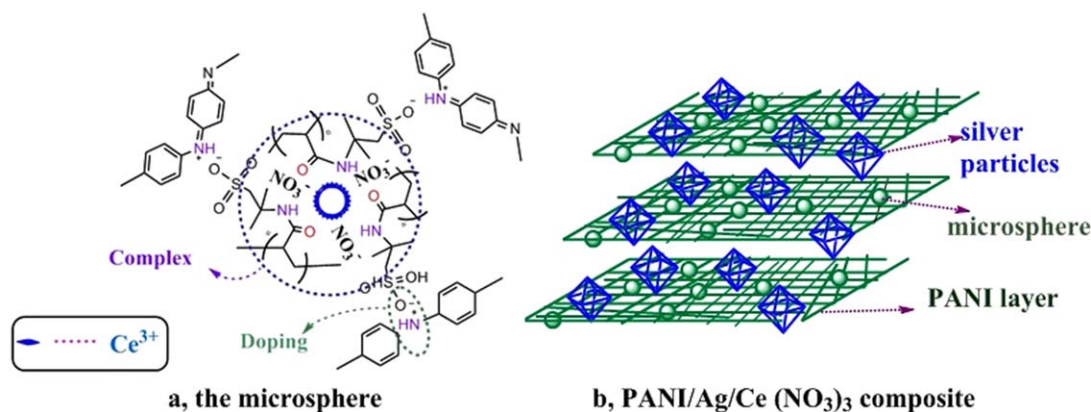
**Table I.** Main Elements of the Composite Sphere

Elements	w %
C	75.19
N	12.02
O	8.00
S	3.99
Ce	0.80

## RESULTS AND DISCUSSION

### Structure and Characterization

Figure 2 shows the spectra of PANI and PANI composites. The peaks at 3427 cm<sup>-1</sup> and 3237 cm<sup>-1</sup> are assigned to the O—H and N—H stretching vibrations, respectively.<sup>30</sup> The peaks near 2922 and 2852 cm<sup>-1</sup> are attributed to the asymmetric and symmetric stretches of CH<sub>2</sub> of PAMPS. The peak at 1645 cm<sup>-1</sup> is attributed to the C=O stretching vibration. The peaks at 1568 and 1493 cm<sup>-1</sup> correspond to the stretching of quinonoid and benzenoid rings of PANI, respectively.<sup>31</sup> The bands near 1388 and 1149 cm<sup>-1</sup> correspond to the antisymmetric and symmetric stretching vibrations of O=S=O.<sup>32</sup> The peaks at 1042 and 619 cm<sup>-1</sup> are assigned to S=O and C—S stretching, respectively. The presence of these peaks demonstrated that PANI was doped by PAMPS. When silver particles



**Figure 5.** Structure of the complex sphere and ternary composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are added to PANI, an obviously red-shifted was observed near the peak of  $1149\text{ cm}^{-1}$ . A probable reason is that a conjugated effect between silver particles with S and O was formed. By comparison with the curves of PANI and PANI/Ag composite, the curve of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> had a weak adsorption at the peaks of  $3427$ ,  $3237$ , and  $619\text{ cm}^{-1}$ , indicating a coordination between Ce ions and N, O of PANI and PAMPS. Besides, nitrate was existed in this ternary composite because of the peaks at  $1293$  and  $701\text{ cm}^{-1}$ , which was assigned to the symmetric stretching and bending vibration of NO<sub>2</sub>, respectively.

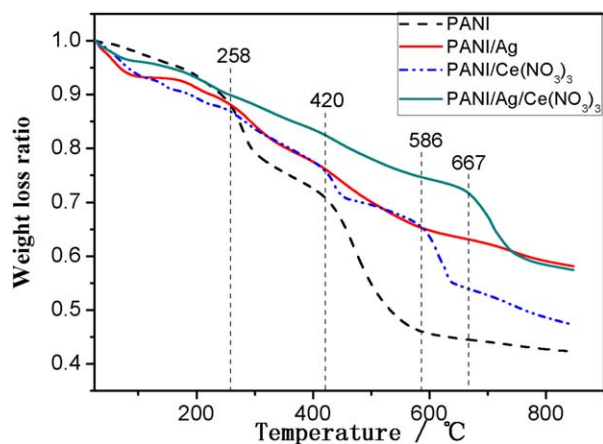
UV-Vis spectra were used to further confirm the structure of PANI composite. As shown in Figure 3, PANI doped by PAMPS has three main peaks. The peak at  $270\text{ nm}$  corresponds to PAMPS which is a conjugated polymer acid. The peaks at  $333$  and  $597\text{ nm}$  correspond to the  $\pi-\pi^*$  transition in the benzenoid ring, and the  $n-\pi^*$  transition in the quinonoid ring, respectively.<sup>33</sup> The peak of benzenoid ring has shifted from  $333\text{ nm}$  to  $365\text{ nm}$  when silver particles are added to PANI. The absorbance of quinonoid ring in PANI/Ag composite also becomes weak. These changes reveal a conjugated structure formed between silver nanoparticles and PANI. When Ce ions were added to PANI/Ag composite, the peaks of PAMPS and benzenoid ring shifted to slightly large wave-

lengths. The intensity of these two peaks also became higher. This indicates Ce ions contribute to an enhanced UV-Vis absorption.

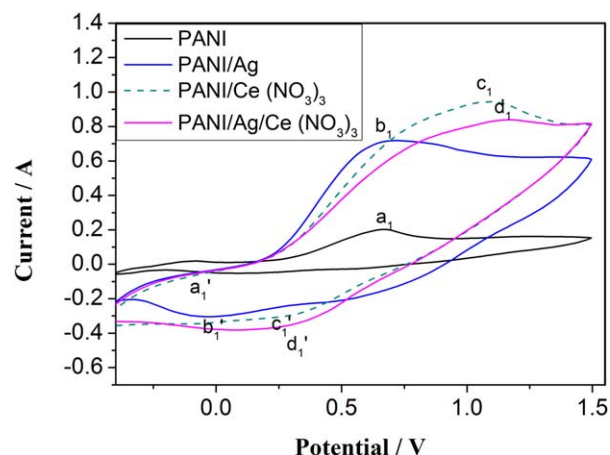
Morphology of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composites had been investigated by SEM. Figure 4(a) shows the overall morphology of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> composites. It is found that some diamond-like particles and massive porous structure were obtained. Figure 4(b) is the XRD analysis of this ternary composite. The four main peaks at  $38.1^\circ$ ,  $44.2^\circ$ ,  $64.4^\circ$ , and  $77.3^\circ$  can be assigned to Bragg's reflections from (111), (200), (220), and

**Table II.** Electrical Conductivities of PANI Composites

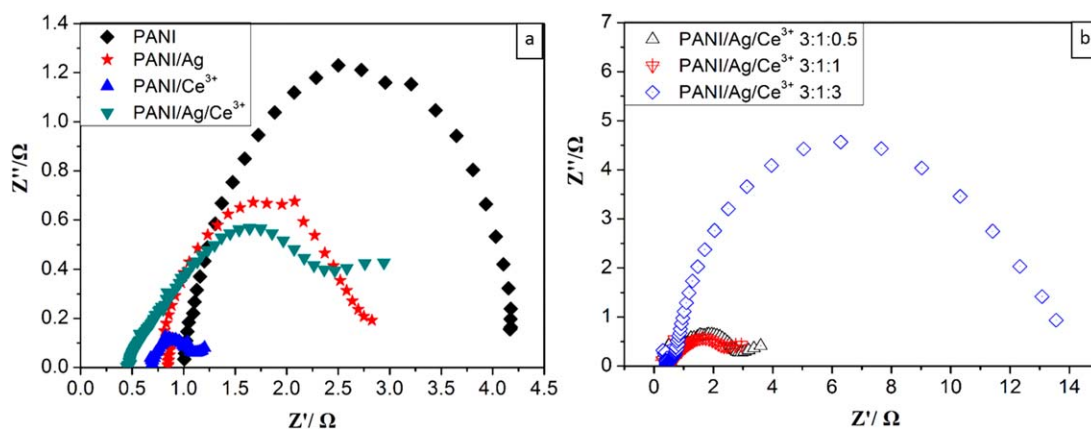
Samples/mole ratio	Electrical conductivity (S/cm)
PANI	1.18
PANI/Ag 3 : 1	2.54
PANI/Ce (NO <sub>3</sub> ) <sub>3</sub> 3 : 1	3.28
PANI/Ag/Ce (NO <sub>3</sub> ) <sub>3</sub> 3 : 1 : 0.5	3.32
PANI/Ag/Ce (NO <sub>3</sub> ) <sub>3</sub> 3 : 1 : 1	3.46
PANI/Ag/Ce (NO <sub>3</sub> ) <sub>3</sub> 3 : 1 : 3	3.49



**Figure 6.** Thermal properties of PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 7.** CV curves of PANI composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 8.** Nyquist plots of PANI composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

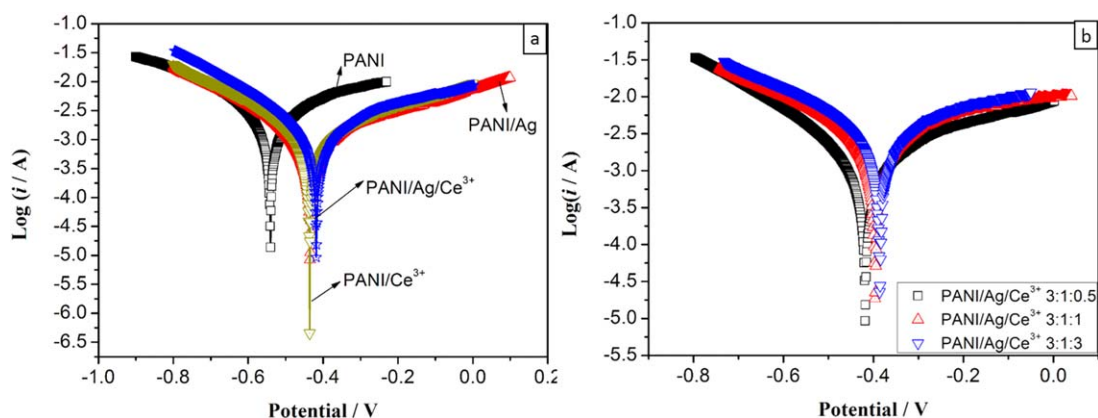
(311) planes of silver, indicating the existence of silver particles in composite. Besides, the peaks at low diffraction angle ( $2\theta = 20^\circ$  and  $25^\circ$ ) can be assigned to PANI.<sup>34,35</sup> Figure 4(c) is a close-up of particles. It is found that these particles take on the shape of the diamond with a diameter of around  $1 \mu\text{m}$ . The EDX result [Figure 4(d)], which corresponding to these particles with diamond shape, confirmed that the main element of them was silver. Figure 4(e) is a magnification of the net-like structure. Interestingly, some small spheres with a diameter of no more than  $1 \mu\text{m}$  are found in this structure. The EDX result (Table I) indicated that these spheres consisted of C, N, O, S, and Ce elements. Combining with the above analyses of structure, a possible structure of these spheres is obtained. As shown in Figure 5(a), the core of sphere is Ce ions that have many unoccupied orbitals for electrons. These Ce ions can form a coordination effect with the N, O of PAMPS and  $\text{NO}_3^-$ ,<sup>36,37</sup> resulting in an inner structure of this sphere. Moreover, the periphery of spheres is mainly PANI layers doped by PAMPS. Figure 4(f) is a magnification of the expanded net-like structure of PANI. It is found that these net-like structures piled up to form a porous structure. The BET surface area of this porous structure achieved  $9.76 \text{ cm}^2/\text{g}$ , which was larger than  $4.46 \text{ cm}^2/\text{g}$  of PANI with an irregular shape. Thus, spheres, PANI with net-like shape and silver particles comprised the PANI/Ag/Ce( $\text{NO}_3$ )<sub>3</sub> ternary composite.

**Table III.** Electrochemical Impedance Parameters for PANI Composites in  $0.5 \text{ M H}_2\text{SO}_4$

Samples	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
PANI	1.02	1.25
PANI/Ag (3 : 1)	0.76	0.69
PANI/Ce( $\text{NO}_3$ ) <sub>3</sub> (3 : 1)	0.67	0.14
PANI/Ag/Ce( $\text{NO}_3$ ) <sub>3</sub> (3 : 1 : 0.5)	0.48	0.65
PANI/Ag/Ce( $\text{NO}_3$ ) <sub>3</sub> (3 : 1 : 1)	0.46	0.57
PANI/Ag/Ce( $\text{NO}_3$ ) <sub>3</sub> (3 : 1 : 3)	0.34	4.56

### Thermal Stability

Thermal stabilities of PANI and PANI composites are shown in Figure 6. A typical three-step weight-loss behavior, including the loss of water, the disappearance of dopant and the degradation of PANI chains,<sup>38</sup> can be seen from the curves of PANI and PANI composites. It is also found that the poor thermal properties of PANI can be distinctly improved when silver particles or Ce ions were added to PANI. The initial temperature of an extensive thermal degradation of PANI chains increased from  $420^\circ\text{C}$  of PANI to  $586^\circ\text{C}$ , evenly up to  $667^\circ\text{C}$  for PANI/Ag/Ce( $\text{NO}_3$ )<sub>3</sub> ternary composite. The thermal stability of composites had been improved significantly.



**Figure 9.** Polarization curves of PANI composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** The Anticorrosion Properties of PANI Composites

Samples	$E_{\text{corr}}$ (mV vs SCE)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	Inhibition efficiency (%)
PANI	-535	29.04	-
PANI/Ag (3 : 1)	-435	8.41	71.04
PANI/Ce(NO <sub>3</sub> ) <sub>3</sub> (3 : 1)	-437	0.45	98.45
PANI/Ag/Ce(NO <sub>3</sub> ) <sub>3</sub> (3 : 1 : 0.5)	-418	9.27	68.08
PANI/Ag/Ce(NO <sub>3</sub> ) <sub>3</sub> (3 : 1 : 1)	-397	18.54	36.16
PANI/Ag/Ce(NO <sub>3</sub> ) <sub>3</sub> (3 : 1 : 3)	-386	22.91	21.11

### Electrical Conductivity

The influence of Ce ions on the electrical conductivities of PANI composites was investigated. As shown in Table II, the conductivity of PANI/Ce (NO<sub>3</sub>)<sub>3</sub> binary composite achieved 3.28 S/cm, which was higher than both 1.18 S/cm of PANI and 2.54 S/cm of PANI/Ag at the same mole ratio. The conductivity can increase further when Ce ions and silver nanoparticles are added to PANI together. The maximum value (3.49 S/cm) was gained when the mole ratio was 3 : 1 : 3. These test results reflect an enhanced conductivity of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> composite. V. V. Abalyaeva *et al.*<sup>24</sup> thought that release of rare earth ions in PANI occurred several times faster than that of protons in PANI. Based on this viewpoint, the charge transport in PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> composite is much faster and efficient compared with PANI or PANI/Ag composite. In addition, the charge transport will be much easier when silver particles were added into PANI material. This is the probable reason that PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite had the best conductivity among these PANI composites.

### Electrochemical Properties

To study the electro-activation of PANI composites, CV curves were recorded from -0.5 to 1.5 V at 10 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

As shown in Figure 7, the main peaks ( $a_1$ - $a_1'$ ,  $b_1$ - $b_1'$ ,  $c_1$ - $c_1'$ , and  $d_1$ - $d_1'$ ), which are attributed to the redox conversion of emeraldine/permanganine,<sup>39</sup> are shown in CV curves. By comparison with each pair peak, it is found that the addition of silver particles and Ce ions caused a high response current and resulted in a large area of CV curve. This effect was more obvious especially for PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite, indicating a high electrochemical activity and a large capacitance of this ternary composite. Besides, a high reversibility of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> electrodes also was found due to the addition of Ce ions.

Typical results of Nyquist plots for PANI and PANI composite in 0.5 M H<sub>2</sub>SO<sub>4</sub> are shown in Figure 8. It is found that the addition of silver particles or Ce ions in PANI had a significantly effect on the electrochemical impedance. As shows in Table III, Ce ions caused a considerable low  $R_s$  (solution resistance), which reduced from 1.02  $\Omega$  of PANI to 0.67  $\Omega$  of PANI/Ce (NO<sub>3</sub>)<sub>3</sub>. This value of  $R_s$  can further decreased when silver particles and Ce ions were added to PANI together. The minimum of  $R_s$  was 0.34  $\Omega$  when the mole ratio is 3 : 1 : 3. A great

improvement had been made by comparison with PANI binary composite. Besides, the  $R_{ct}$  (charge transfer resistance) was also under the influence of silver particles or Ce ions. The diameter of a semi-circle in high frequency region decreased significantly when a certain of amount of silver particles or Ce ions were added to PANI, indicating a low  $R_{ct}$  of PANI composite. However, this value increased if excess Ce ions were added to PANI. This could be assigned to the electric layer that formed in an aqueous solution by excess Ce ion diffusion from bulk to interfaces between electrodes and aqueous solution.

Figure 9 shows the polarization curves of PANI composites. The important corrosion kinetic parameters viz. corrosion potential ( $E_{\text{corr}}$ ), the corrosion current density ( $i_{\text{corr}}$ ), and inhibition efficiency ( $IE\%$ ) were calculated and showed in Table IV. It is found that the corrosion potential increased effectively by adding silver particles or Ce ions to PANI. The value of PANI binary composites reached -437 mV, which was higher than -535 mV of PANI. Meanwhile,  $i_{\text{corr}}$  decreased obviously. When the mole ratio kept unchanged, the inhibition efficiency ( $IE\%$ ) achieved 98.45% for PANI/Ce (NO<sub>3</sub>)<sub>3</sub>, revealing a high corrosion resistance of Ce ions. By comparison with that of PANI binary composites, the corrosion potential of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> can further increase with the amount of Ce (NO<sub>3</sub>)<sub>3</sub> increasing. When the mole ratio was 3 : 1 : 3, the corrosion potential of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> achieved a maximum value (-386 mV), which was much higher than the ones of PANI binary composites. However, the corrosion current density of PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> at this mole ratio kept increasing as the amount of Ce (NO<sub>3</sub>)<sub>3</sub> increasing. Consequently,  $IE\%$  decreased from 68.08 to 21.11%. A probably reason is that the fast release of massive Ce ions in PANI composite resulted in a large corrosion current, although a considerable high corrosion potential of this ternary composite were achieved.

### CONCLUSION

In summary, we had successfully prepared PANI/Ag/Ce (NO<sub>3</sub>)<sub>3</sub> ternary composite in a PAMPS aqueous solution. The detailed analyses indicated that this kind of material consisted of silver particles, porous PANI and some complex spheres. By comparison with PANI and PANI binary composites, this ternary composite exhibited a good thermal stability, a high electrical conductivity, a large capacitance and an enhanced corrosion inhibition because of the fast release ability of Ce ions and the high charge-transferring ability of silver particles. Therefore, this ternary composite has promising applications in capacitor, anticorrosion coatings, and other related fields.

### ACKNOWLEDGMENTS

The authors are grateful for the financial support by the Open-End Fund for the Valuable and Precision Instruments of Central South University (CSUZC2014009).

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