

# Straightforward Synthesis of Carbon-Supported Ag Nanoparticles and Their Application for the Oxygen Reduction Reaction

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Published online: 3 May 2012  
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**Abstract** In this paper we report a simple and environmentally friendly synthesis of silver nanoparticles (AgNps) and their activities towards the oxygen reduction reaction (ORR). Ultraviolet spectroscopy (UV–vis) and transmission electron microscopy confirmed the formation of poly(vinyl pyrrolidone)-protected colloidal AgNps through direct reduction of  $\text{Ag}^+$  by glycerol in alkaline medium at room temperature. For the ORR tests, the AgNps were directly produced onto carbon to yield the Ag/C catalyst. Levich plots revealed the process to occur via 2.7 electrons, suggesting that the carbon support contributes to the ORR. We discuss here possibilities of improving the catalytic properties of the Ag/C for ORR by optimizing the parameters of the synthesis.

**Keywords** Silver nanoparticles · Glycerol · Alkaline medium · Oxygen reduction

## Introduction

Oxygen reduction reaction (ORR) has been extensively studied, in both alkaline and acid solutions, due to its

importance in fuel cells and metal–air batteries [1–3]. Platinum is known to be the best electrocatalyst for ORR in alkaline fuel cell cathodes [4]. However, its high cost and gradual activity decrease in strong alkaline media [5, 6] have catapulted the development of abundant, inexpensive, stable, and efficient electrocatalytic materials for the substitution of Pt-based oxygen cathodes [7]. Fundamental studies have shown that coinage metals (like Au, Ag, Cu) present poorer activity for oxygen reduction than smooth Pt. This is usually attributed to their filled d bands resulting in higher activation barriers than those created by other transition metals with only partially filled d bands, such as Pt. In nanometric range, however, depending on the particle size and shape [8, 9], the catalytic properties of metals can be particularly different compared with those of smooth surfaces. Notoriously, organic molecules and molecular oxygen adsorb on small nanoclusters more easily than on smooth surfaces. The relatively higher reactivity of the small nanoclusters is attributed to the narrow gap between the d-band and the Fermi level of low-coordinated metal atoms, whose fraction at the cluster surface is remarkably larger than that at smooth surface. In this context, silver nanoparticles (AgNps) are good candidates as catalysts for oxygen cathodes in alkaline solutions [10–12] due to their high surface area and promoted catalytic properties. Previous studies of ORR or hydrogen peroxide reduction over Ag-based materials in alkaline media [9, 13] show that the average number of the electrons exchanged per  $\text{O}_2$  molecule is between 2 and 4. Based on that,  $\text{HO}_2^-$  or  $\text{OH}^-$  may be the final reaction products.

A variety of methods, such as polyol and microwave assisted, have been employed in the production of AgNps. The polyol method typically consists in refluxing a mixture

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of a precursor salt (e.g.,  $\text{AgNO}_3$ ), a stabilizing agent [e.g., poly (vinyl pyrrolidone) (PVP)] and a polyalcohol (e.g., ethylene glycol) at  $\sim 160\text{--}240\text{ }^\circ\text{C}$  for 2–12 h, which is tedious, time and energy consuming. The microwave-assisted approach also requires high temperature and has the further inconvenience of demanding a microwave generator. In this work we employed a straightforward nanoparticle production route based on reduction of  $\text{Ag}^+$  by glycerol in alkaline medium at room temperature. The AgNps can be obtained as a colloidal dispersion as well as directly anchored in carbon (AgNps/C), with the latter allowing the direct application for ORR. Furthermore, compared to current reducing agents (e.g.,  $\text{BH}_4^-$ , formamide, and hydrazine), glycerol is a greener option since it is nontoxic and readily biodegradable under aerobic conditions.

## Experimental

### Reactants and Instrumentation

All chemicals used in this work were of analytical grade and used without further purification. UV–vis spectra of the AgNps colloidal suspension were acquired with a Varian/Cary 5G spectrophotometer. For the TEM experiments, copper-coated grids were immersed into the AgNps colloidal and Ag/C suspensions and allowed to dry in a desiccator overnight. The grids were then analyzed using a TEM FEI Tecnai with an accelerating potential of 200 kV. X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer. Energy-dispersive X-ray spectroscopy (EDX) was carried out on a Zeiss-Leica/440 to determine the composition of the Ag/C catalyst. Electrochemical experiments were conducted with an AUTOLAB 30 potentiostat/galvanostat controlled by the GPES software.

### Synthesis of Colloidal and Carbon-Supported AgNps

In a typical experiment for colloidal AgNps production, known amounts of PVP (Aldrich, MW=10,000) and  $\text{AgNO}_3$  (Aldrich) were dissolved in 5 ml of ultrapure water. In a separate flask, determined quantities of glycerol (Aldrich) and NaOH (Aldrich) were dissolved in 5 ml of ultrapure water. The glycerol–NaOH solution was then added to the  $\text{AgNO}_3$ –PVP solution to yield the following final concentrations: 0.05 mM  $\text{Ag}^+$ , 0.5 M glycerol, 0.1 M NaOH, and  $10\text{ g l}^{-1}$  PVP. The colorless mixture immediately turned into a deep yellow characteristic of colloidal AgNps. The colloidal suspension was then characterized with UV–vis and TEM. For the ORR experiments, the AgNps were produced directly onto Vulcan carbon (Ag/C) without stabilization by PVP. In this way a potential influence of PVP on ORR was eliminated. The synthesis of the Ag/C catalyst consisted in sonicating an appropriate amount

of XC-72 Vulcan (40 mg) carbon in a known volume (50 ml) of ultrapure water and then adding a fixed amount of  $\text{AgNO}_3$  under stirring to promote homogenization. Afterwards, another aqueous solution containing glycerol and NaOH was added to give the following concentrations: 0.82 mM  $\text{AgNO}_3$ , 1 M glycerol, and 0.1 M NaOH. The black suspension was kept during 24 h under stirring at room temperature and then washed, filtered and dried at  $80\text{ }^\circ\text{C}$  for 12 h. The Ag/C electrocatalyst was characterized with EDX to determine the Ag/C load and by XRD to observe the diffraction pattern. The average crystallite size was estimated using Scherrer's equation [14]:

$$D = k\lambda/B \cos\theta \quad (1)$$

where  $D$  is the average crystallite size in angstrom,  $k$  is a coefficient taken here as 0.9,  $\lambda$  the wavelength of the X-rays used ( $1.5406\text{ \AA}$ ),  $B$  the width of the diffraction peak at half height in radians, and  $\theta$  the angle at the position of the peak maximum.

### Electrochemical Measurements

A three-electrode configuration cell was used. A platinum foil, and a Hg/HgO in 1.0 M NaOH were employed as counter, and reference electrodes, respectively. A glassy carbon rotation disk ( $\phi=5\text{ mm}$ , geometric area= $0.196\text{ cm}^2$ ) was used as substrate to prepare active layers of Ag/C. For the preparation of the catalytic layer, 2.0 mg of the Ag/C powder was suspended in a mixture containing 1 ml of isopropyl alcohol and 20  $\mu\text{l}$  of a Nafion solution (5 wt% in low aliphatic alcohol, from DuPont). After ultrasonic homogenization, 20  $\mu\text{l}$  of this ink was deposited onto the glassy carbon electrode and the solvent was then evaporated at room temperature. Rotating disk electrode (RDE) measurements were performed in  $\text{O}_2$ -saturated 1.0 M NaOH solutions prepared with ultrapure water. The overall number of electrons exchanged per oxygen molecule was estimated from the limiting diffusion current density plateaus using the classical Levich's equation:

$$i_d = B\omega^{1/2} \quad (2)$$

where  $i_d$  is the limiting diffusion current and  $B$  is the Levich coefficient.

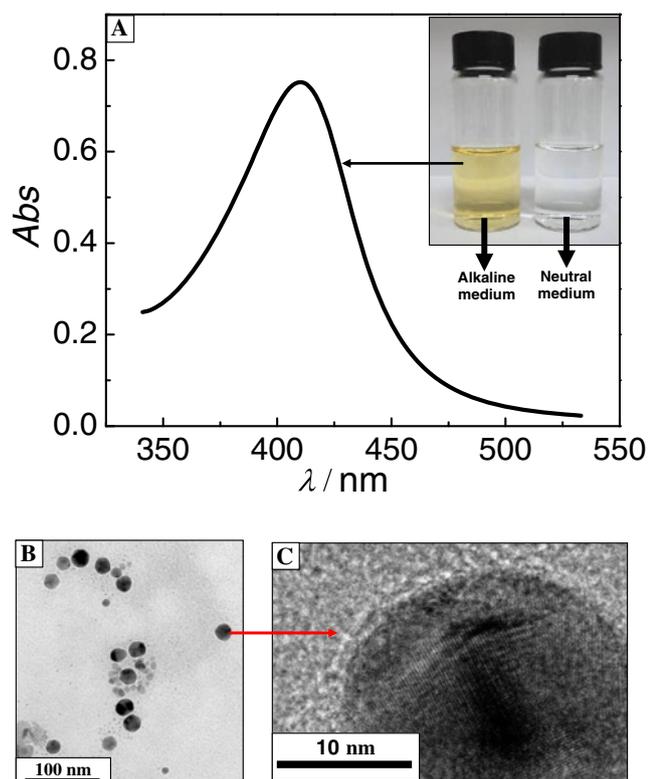
$$B = 0.62nFAD^{2/3}\nu^{-1/6}C^* \quad (3)$$

where  $n$  is the number of electrons involved in the reaction,  $D=1.56\times 10^{-5}\text{ cm}^2\text{ s}^{-1}$  is the oxygen diffusion coefficient [15, 16],  $C^*=8.8\times 10^{-7}\text{ mol cm}^{-3}$  is the oxygen solubility in the solution [12, 13],  $\nu=1.19\times 10^{-2}\text{ cm}^2\text{ s}^{-1}$  is the NaOH solution kinematic viscosity [17], all at  $25\text{ }^\circ\text{C}$ , and  $\omega$  (radian per second) is the RDE revolution speed.

## Results and Discussion

### Chemical and Physical Characterizations of the Colloidal and Carbon-Supported AgNps

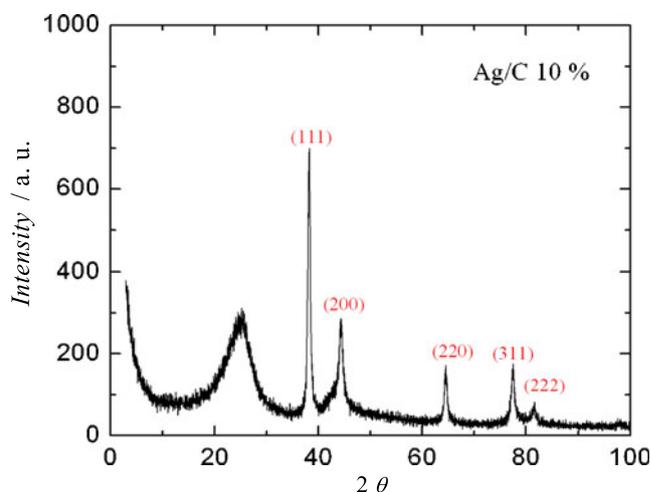
Preliminary results pointed that the use of PVP is imperative to obtain stable colloidal AgNps. In the absence of PVP, silver tended to agglomerate and precipitate in the bottom of the reaction vessel. This means that glycerol itself is not capable of concomitantly functioning as reducing and stabilizing agent. Figure 1a shows the UV–vis spectrum of the colloidal AgNps prepared using glycerol as reducing agent in alkaline medium and PVP as stabilizing agent at room temperature ( $\sim 25^\circ\text{C}$ ). The colloidal AgNps had a maximum absorbance at around 410 nm, a value which agrees very well with data in literature. The yellow color is due to the surface plasmon band (SPB), a broad absorption band in the visible region. The SPB reflects the collective oscillations of the electron gas (electrons of the conduction band) at the surface of nanoparticles. The SPB provides a quick assessment about the size regime of some metal particles (e.g., Ag and Au). The inset of Fig. 1a shows that the yellow-colored solution, which is characteristic of silver in the nanometric regime, is obtained only in alkaline media. Some authors have suggested that polyols dehydrate to aldehydes, which,



**Fig. 1** a UV–vis spectrum of the colloidal AgNps, b TEM image of the colloidal AgNps, and c high-resolution TEM of a single nanoparticle

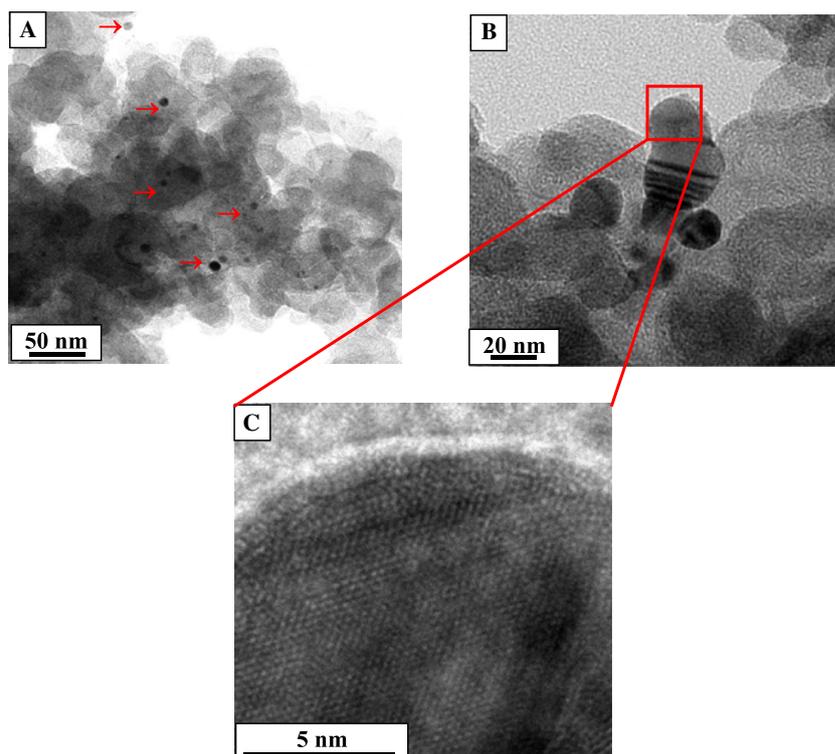
in turn, reduce metallic ions to elemental metal. In our opinion the aldehyde is not responsible for the reduction. We also tried to synthesize AgNps by employing acetaldehyde as reducing agent in neutral medium, and no nanoparticle formation was observed. Therefore the aldehyde is not the responsible for the reduction. At high pH the alcohol is deprotonated and the generated anion may be responsible for the reduction. The complete elucidation of the mechanism is already in course in our laboratory, and the results will soon be presented in a separate paper. Analysis of TEM images of AgNps (Fig. 1b) indicated that most of nanoparticles obtained from the process were spherical in shape around 20 nm in size. High resolution in Fig. 1c shows the polycrystalline structure of the AgNps.

Figure 2 presents the XRD pattern for the AgNps supported in carbon (Ag/C). As discussed in the “Experimental” section, the AgNps for ORR were produced directly on carbon without stabilization by PVP, generating, therefore, the Ag/C catalyst. The goal was to avoid any influence of PVP on ORR, however a complete control of the synthesis is surely expected to be lost. The XRD pattern revealed the typical face-centered cubic (fcc) structure of silver [18] and was further analyzed using Scherrer’s equation [11] in order to estimate the average crystallite size. The mean crystallite size estimated for the Ag/C catalyst resulted in 9.5 and 15.0 nm considering the fcc 200 and 220 diffraction peaks, respectively. Typical TEM images of the Ag/C catalyst are shown in Fig. 3. One realizes a nonhomogenous dispersion of AgNps on the carbon substrate, which is probably due to the absence of PVP in the synthesis (Fig. 3a). Nevertheless, the Ag/C was active towards ORR, as presented in the next section. EDX analyses gave 10 wt% of Ag onto carbon, therefore we conclude that based on the initial  $\text{AgNO}_3$  used in the synthesis, the conversion of silver ions into metal was quantitative. HRTEM images (Fig. 3b, c) revealed some agglomeration and the polycrystalline nature of the sphere-shaped Ag nanoparticles.



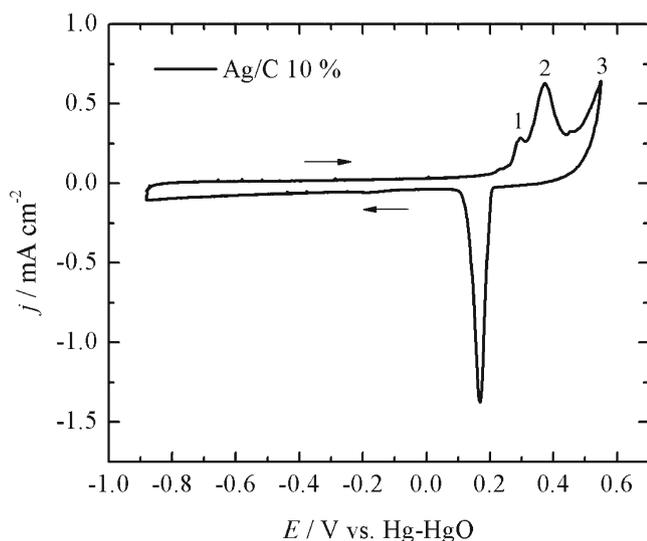
**Fig. 2** XRD pattern of the Ag/C

**Fig. 3** TEM images of the carbon-supported AgNps (Ag/C): **a** the red arrows indicate the Ag nanoparticles, **b** increased magnification showing some coalesced particles, and **c** high-resolution TEM image



#### Electrochemical Characterization of the Ag/C Catalysts and Application on ORR

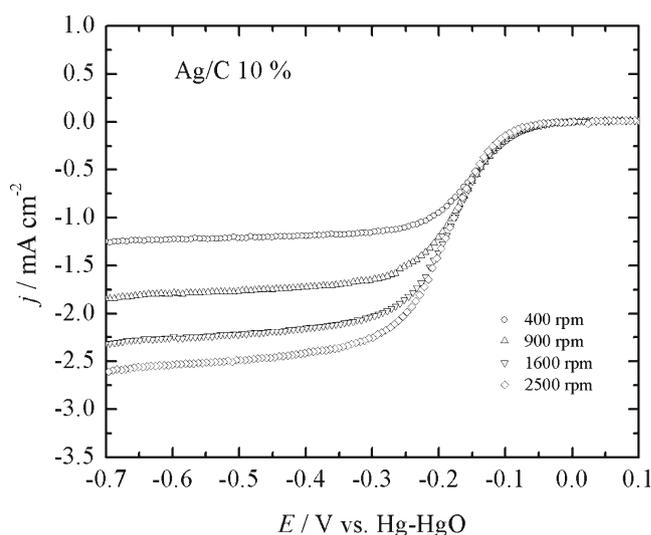
The electrocatalytic activity of the Ag/C catalyst towards oxygen reduction was then studied by cyclic voltammetry. Figure 4 shows the cyclic voltammogram (CV) profile of the Ag/C in O<sub>2</sub>-free 1.0 M NaOH at a scan rate of 5 mV s<sup>-1</sup>. In the potential range between -0.9 and 0.6 V (vs. Hg/HgO), the CV presents well-defined peaks characteristic of Ag [19–21]. The small peak (1) is attributed to the formation



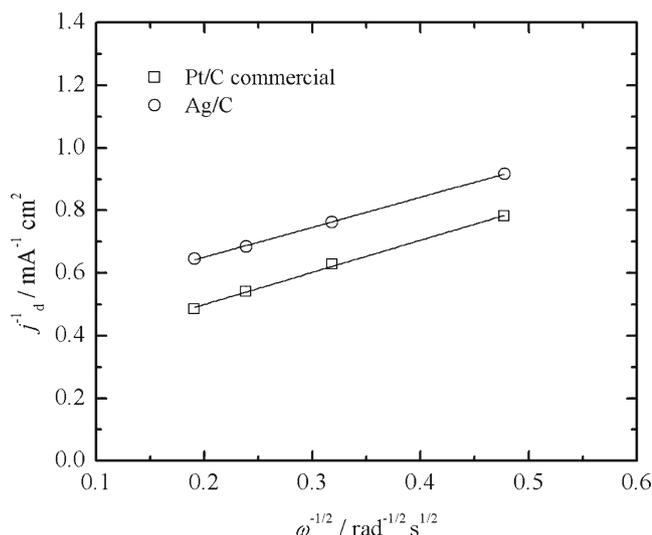
**Fig. 4** Cyclic voltammogram for the Ag/C catalyst in O<sub>2</sub>-free 1.0 mol l<sup>-1</sup> NaOH electrolyte at 5.0 mV s<sup>-1</sup>

of a few monolayers of AgOH and Ag(I) species. Peaks (2) and (3) were assigned to the formation of inner hydrous oxide layer and more compact outer oxide layer, respectively. In the back scan, the cathodic current peak at 0.22 V was ascribed to the electroreduction of the silver oxides formed during the positive-going scan.

Steady-state polarization curves of ORR for the Ag/C catalyst recorded in oxygen-saturated 1.0 M NaOH at different rotation rates are shown in Fig. 5. The expected increase of the limiting diffusion current density in the disk



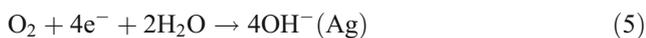
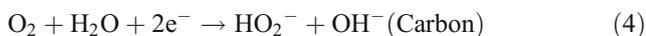
**Fig. 5** Steady-state polarization curves for the ORR on Ag/C catalyst in O<sub>2</sub>-saturated 1.0 mol l<sup>-1</sup> NaOH at 25 °C



**Fig. 6** Levich plots for the ORR on the Ag/C catalyst compared to commercial 20 % Pt/C in 1.0 mol l<sup>-1</sup> NaOH

is observed as a function of the rotation rate. According to the Levich theory, the value of the limiting diffusion current for an electrocatalyst that follows four-electron mechanism is 3.28 mA cm<sup>-2</sup> at 1,600 rpm in alkaline medium. For Ag/C in 1.0 M NaOH, the determined value was 2.3 mA cm<sup>-2</sup>. The discrepancy between the theoretical and experimental values is explained by the fact that the electrocatalytic layer might not have homogeneously covered the entire glassy carbon surface. Furthermore, the carbon support contributes with only two electrons, as explained later. The polarization curves at different rotation rates were used to construct Levich curves and estimate the number of electrons ( $n$ ) involved in the ORR [19], as shown in Fig. 6. For the commercial 20 % Pt/C catalyst, the calculations were made taking the Levich plot in the same alkaline medium and assuming  $n=4$ . For the Ag/C synthesized by glycerol method, the determined number of electrons exchanged by O<sub>2</sub> molecule was 2.7.

Previous works [22, 23] have shown that the ORR occurs mainly through the four-electron mechanism in Ag bulk and the two-electron process in carbon in alkaline solutions. Hence, the oxygen reduction may occur in parallel at the Ag sites (following a four-electron pathway) and at the carbon sites (following a two-electron mechanism):



As a balance, the number of electrons of 2.7, obtained from Levich plots, indicates that the Ag sites catalyze 35 % of the total process. Therefore we conclude that the Ag/C electrocatalyst reduces oxygen predominantly via peroxide

formation (Eq. 4). The discrepancy between the catalytic responses of Ag/C (prepared by the method of glycerol) and commercial Pt/C towards the ORR can be associated with differences in: (1) the mean crystallite size, which is 3 nm for the commercial Pt/C while it is about 10 nm for Ag/C; (2) metal loadings (20 % Pt vs. 10 % Ag); and (3) the reaction mechanisms on the distinct catalysts. We should emphasize that the effectiveness of the ORR can be enhanced by increasing the Ag loading and/or decreasing the particle size through optimization of the synthesis, an aspect we did not pursue in this paper. Herein we aimed in showing a simple, inexpensive, and environmentally friendly method to produce active AgNps towards ORR.

## Conclusions

Colloidal and carbon-supported AgNps were successfully generated using glycerol as reducing chemical in alkaline conditions. A maximum in the UV–vis spectrum suggested the nanosized nature of the silver particles, which was then confirmed by TEM images. AgNps directly produced onto carbon (Ag/C) were capable of reducing oxygen exchanging 2.7 electrons per O<sub>2</sub>, implying some contribution of the carbon support. The efficacy of the process can be improved through optimization of the synthesis. In our opinion the glycerol method should be carefully regarded as a routine way of producing Ag nanoparticles since it is simple, inexpensive, and environmentally friendly.

**Acknowledgments** The authors thank CNPq and FAPESP for the overall support of this research. We would also like to thank Cleiton Pires for the assistance in the UV–vis experiments.

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